ON THE MECHANISM OF ELECTRON TRIBOEMISSION FROM CERAMICS

Gustavo MOLINA1, Michael FUREY2, Czeslaw KAJDAS3, Nils STEIKA2

1 School of Technology, Georgia Southern University, Statesboro, USA, gmolina@georgiasouthern.edu.
2 Department of Mechanical Engineering, Virginia Tech, Blacksburg, USA, mfurey@vt.edu.
3 Central Petroleum Institute, Warsaw, Poland, ckajdas@zto.pw.plock.pl.

ABSTRACT

The authors have carried out extensive characterizations of negatively-charged triboemission from scratching of ceramics and of semiconductors in high vacuum. This experimental work explores if the measured triboemission-output evolution may relate to worn surface features. Delays on the start of the triboemission outputs from an alumina-ball sliding on alumina-disk with respect to those from the diamond scratching of alumina are consistent with the observed surface modifications. Electron triboemission features are discussed, and it is concluded that new findings on the reduction of electron work function during dry sliding can help understanding electron triboemission and its origin.

KEYWORDS: triboemission, exoemission, ceramics, electron work function.

1. INTRODUCTION

Triboelectrons are produced when an insulator or semiconductor are disturbed by sliding contact, and they pertain to the more general phenomena of triboemission, which also includes emission of ions, neutral particles, photons, and radiation during tribological damage. The possible action of triboemitted charged-particles, in particular of low-energy electrons, on tribochemical processes is reviewed by Molina et al. [1].

Early triboemission research was carried out by Nakayama et al. [2] on detecting bursts of electric current from diamond scratching on metals and insulators. Dickinson et al. [3] investigated photon and electron triboemission and measured electron-energy from diamond scratching of MgO. The work of Molina et al. [1, 4-6] characterized burst-type negatively-charged triboemission under high vacuum for constant load and speed scratching of the insulators alumina, sapphire and silicon nitride and the semiconductors Si and Ge [7, 8], and from an alumina-ball sliding on alumina. They also reported the absence of semiconductor triboemission after the contact ceased when compared to significant post-contact triboemission from all tested insulators [7, 8].

The measured triboemission levels cannot be explained by emission from surface oxides alone, as shown in studies by Molina et al. [4, 6]. They also detected much lower level of positively-charged emission from insulators [4, 6]. Diamond scratching of metals does not produce significant triboemission [1, 2, 4-6].

The related phenomena of fractoemission (e.g., particle emission during bending fracture) were extensively investigated by Dickinson et al. for insulators (including surface metal-oxides) [9, 10] and by Kaalund et al. for semiconductors [11]. In fractoemission experiments the onset of plastic deformation is found simultaneous with bursts of electron, ion and acoustic emissions.

Energy measurements for both fracto-emission and triboemission show that important fractions of the electron outputs are emitted for energy lower than the electron work function (WF) of the bulk materials. The WF is usually defined as the minimum energy to remove one electron from the solid surface to the outside vacuum. Molina et al. detected large fractions of low-energy triboelectrons (1 to 5eV) for alumina and sapphire scratching in retarded-energy measurements, and spectra extending beyond the largest measured potential (48eV) [4, 6]. Nakayama et al. [12] recently measured electron energy from low values to above 900eV during alumina scratching at a speed (7cm/s) two orders of magnitude higher than those of Molina et al, and an energy spectrum for n-type Si scratching from low-energy to about 50eV; it is possible that surface tribocharging accelerated the low-energy triboemitted electrons.

It is believed that the mechanisms for electron triboemission and fractoemission phenomena, which show typical long-decay outputs are closely related, and that they are fundamentally different than those of thermionic and field stimulated electron emission.
A “conceptual” fractoemission mechanism was postulated by Dickinson et al. [13] based on charge separation and comprising three primary steps: (i) charge separation due to fracture and building of an electric field on charged nascent surfaces, (ii) desorption of gases in the crack tip, and (iii) gas breakdown producing local electron-discharge and photon emission; experimental evidence of these processes was presented by Dickinson et al. [14].

The same mechanism would proceed for secondary events by (iv) electron bombardment of newly created surfaces producing electron-hole pairs, (v) electron-hole recombination yielding an emitted electron or a photon, and (vi) electrons striking positive charges, emitting them as either positively-charged or neutral particles. Statistical models analyzing fractoemission and triboemission outputs in frequency-domain are reviewed by Molina et al. [15], and they suggest that secondary events occur following primary emissions.

Nakayama et al. [16, 17] extended the charge separation mechanism to the ion emission from dry-ceramic sliding contact to include ionization of surrounding gases. They suggest, however, that the same number of negative charges than that of positive charges would be produced but that the higher mobility and drift velocity of the former, because of their lower mass, would allow them easier reaching of the detector [16]. It is possible, however, that Nakayama et al. measured both triboemitted and surface charges, the latter being characteristically developed as patches of positive or negative-charge. Further development of the model may also explain measured minimum and maximum charge intensities in the range of atmospheres of 10⁵ Pa to 10⁷ Pa [17].

This idea of tribological contact interacting with surrounding gases as the source of varied emission was earlier introduced by Thiessen as the tribomicroplasma concept [18]. The Nakayama’s model may explain the lower emission from ceramics lubricated with hydrocarbon liquids, for larger mass and lower drift velocity. They observed, however, that emission increased for gas pressure below 1Pa: in high-vacuum the occurrence of gas discharge and ionized components are unlikely, and in the works of Molina et al [1, 4-6] and Dickinson et al [3] triboemission should be of mainly electrons.

The reviewed mechanisms do not explain how electron triboemission occurs for energy values lower than the electron work-function (WF) of the bulk material. Dickinson et al early suggested that strained surface would grow surface defects which might locally reduce the WF [9]. Relating tribological surface modification to WF change can help understanding triboemission. Zharin et al. [19] used a non-contacting probe (i.e., the Kelvin probe) to measure variation of the WF during tribological damage. Kasai et al. [20] employed the technique to monitor damage accumulation during continued sliding of selected metals, and Bhushan et al. [21] observed changes of Kelvin-probe potential to detect wear precursors at ultra-low loads for Au, Al, Si and alumina. The technique proved useful to measure WF change for metals and semiconductors, but for the insulator alumina the isolated surface charges and polarization dominated the surface potential; measurement of WF is difficult for dielectrics. Li et al. [22] have recently correlated elastic deformation during sliding to decreasing WF for Cu, Al and steel, and reported a stable WF value from the onset of plasticity, which was measured 0.3 to 0.4eV lower than those of Cu unworn surfaces. They also presented a model by which increases in dislocation density and surface roughness led to lower WF for Cu [23]. This paper discusses these new findings on the reduction of WF during dry sliding to help understanding some electron triboemission features.

2. EXPERIMENTAL

The triboemission instrument developed by Molina et al. [4, 6] was used for negative-charge intensity measurements from diamond-cone sliding on rotating alumina-disk, and alumina-ball on alumina-disk in a vacuum of 10⁻⁵ Pascal or better. A channel electron multiplier (CEM) detector in the pulse-counting mode was operated at 2750V and a +200V input bias. Individual charged-particles reaching the CEM are detected as individual counts in windows as short as 10 msec. Instrument features are presented by Molina et al. [4, 6]. The contact geometries consisted of rotating 25.4mm-diameter-disks of amorphous alumina (99.5% isostatically-pressed alumina) that were scratched by fixed pins: a 90 degree-angle-cone diamond-pin or a 0.125-inch (3.175mm) diameter alumina-ball (99.5% alumina, grade 25). Constant rotational speeds (10rpm for a linear speed of 0.48 cm/s at the circular wear track) and loads (2N and 10N for respectively diamond-cone and alumina-ball sliding) are applied. For each measurement, an initial background-reference is taken for 15 to 30 seconds; background- noise was less than 0.1count/sec. The contact is then applied for a total run of typically 320 seconds.

Figure 1 shows a typical measurement of electron triboemission from diamond cone-on-alumina, while figure 2 presents electron tribo-emission from alumina-ball sliding on alumina-disk for the same sliding velocity.
Figures 1 and 2 show that the measured negatively-charged triboemission outputs are clearly associated with sliding contact. While in figure 1 emission from diamond-cone on alumina starts at a relatively constant level upon application of sliding contact, figure 2 for an alumina-ball on alumina-disk suggests that a considerable delay occurs until the appearance of large bursts of triboemission. These delays were consistently observed for the ball-on-flat geometry when compared to scratching by a diamond-cone.

This experimental work investigates if the observed delays on burst-emission reflect the different evolution of surface modification and wear for the two compared systems. A study of the wear-track surface (e.g., of optical microscopy and profilometry) was carried out for alumina-disks specimens after scratching by diamond-cone or by alumina-ball for a discrete sequence of number of passes (e.g., for one, five, ten, twenty and forty disk turns) on same circular wear-track. The pin-on-disk setup of the triboemission instrument was used for wearing these specimens at constant speed (10rpm for 0.48cm/s) and two loads (2N or 10N for respectively diamond-cone and alumina-ball sliding). Figures 3 and 4 show optical microscopy of the alumina-disk for each of the two contact geometries after five passes on the same wear track.
Optical microscopy observations, as that of figure 3, showed that the wear track for diamond-cone scratching was clearly defined from the first pass. Figure 3 shows the well-defined wear track for five repeated passes. For the case of alumina-ball, however, no wear was visible for first pass, while the wear track was barely outlined for five passes as seen in figure 4, and it was not fully defined for ten passes. Therefore, for alumina-ball the wear-track depth or width measurements were possible for only twenty and forty passes samples. Measurements of wear-track depth and width were carried out for four positions along each wear-track on the alumina-disks. Optical microscopy of the diamond-cone pins showed no visible wear, while no wear measurement was carried out for the alumina-balls. Figure 5 is a plot of the measured averages for alumina-disk wear-track depth and width for the used sequence of passes.

Figure 5 shows that for diamond-cone scratching important disk wear occurs on the first pass; wear-track depth and width then progresses for about five passes, to slightly grow for larger number of passes; this wear evolution is consistent to plowing by harder-cone geometry. However, for alumina-ball no significant track width or height can be measured until twenty passes.

3. DISCUSSION

The presented triboemission measurements show electron-emission bursts clearly associated with sliding contact. Decreasing emission is observed when the same wear track is scratched in repeated passes; this trend relates to decreasing wear: figure 5 shows that large fractions of disk-wear occur for the diamond-cone scratching from start of contact to five passes, after which wear rate seems to diminish. Ten or twenty passes are needed for measurable wear by alumina-ball sliding: over ten repeated passes are need for alumina-ball contact for the used load and speed.

Triboemission from alumina-ball sliding on alumina-disk also shows a considerable delay until the appearance of large bursts of triboemission, by comparison to the relatively constant-level emission observed upon scratching starts for diamond-cone on alumina disks. This delay for the alumina-ball-geometry triboemission is consistent with the delays on producing a measurable alumina-disk wear-track.

Figure 6 compares for alumina-ball sliding the typical evolution of the triboemission output (during continuous sliding only from figure 2) and the average wear-track depth and width of figure 5. The same horizontal scale of number of disk turns (e.g., of passes on same wear track) is used for the two sets of data.

In figure 6 the low-level triboemission from start of contact to about 14 passes is in coincidence with the observed non-measurable-wear, and also with the optical-microscopy in figure 4, for which the wear track barely outlines in isolated patches. The authors believe that for the used load, speed and contact geometry, the main surface change in this period consists of isolated plastic deformation around contact asperities, and by some wear debris production by asperity crushing and fracture. After such initial period (e.g., at about 14 passes for the specimens, loads and speeds shown in figure 6) the wear-track becomes fully defined and high-level burst-type triboemission starts; high peaks also are observed seemingly associated with each disk-turn for about eight passes.

Fig. 3. Optical microscopy of alumina-disk wear track for five passes of diamond-cone.

Fig. 4. Optical microscopy of alumina-disk wear track for five passes of alumina-ball.
Fig. 5. Averages of alumina-disk wear-track depth and width for diamond-cone and alumina-ball scratching after repeated passes on same wear-track.

Fig. 6. Triboemission measurement from alumina-ball-sliding and disk average wear-track depth and width for same number of passes on wear track.
Figure 7 presents the triboemission output from alumina-ball on alumina-disk of figure 2 between the consecutive 13 to 23 passes.

Figure 7 suggests that triboemission large-bursts start in coincidence with ball pass on the same region of the circular wear-track. It is possible that significant particle detachment started on such region at about pass 14, then extend through the whole circular track in the shown consecutive passes.

There is extensive data that triboemitted electrons are of low energy (e.g., 1 to 5 eV) [4, 6, 12] and it suggests that a reduction of surface workfunction (WF) due to strain and deformation is needed for triboemission to occur. Experimental [22, 23] and theoretical [23, 24] evidences are available that plastic deformation and increased dislocation density during sliding reduce WF, and that a stable lower WF value is measurable from the onset of plasticity in metal wear. The authors believe that this reduction of WF and the surface charging are essential to electron triboemission from insulators. Microfracture during sliding could lead to charge separation according to the Dickinson et al.’s mechanism [13], and charged nascent surfaces and their weak electric field in patches would be able to produce tribo-electrons for the lowered values of surface WF.

The evolution of the presented electron triboemission outputs from alumina-ball sliding corresponds to the sequence of (i) WF reduction and low-rate emission during elastic and mainly plastic deformation and for a corresponding increase in dislocation density, which are followed by (ii) emission of electrons for lowered WF from the onset of wear and during the continuous sliding and contact, these electrons may be eventually accelerated by surface charging patches.

The triboemission outputs from diamond-cone scratching of alumina disk as in figure 1, which show no delay on the occurrence of triboemission outputs, are consistent with fast reaching the second stage of this sequence (e.g., the onset of wear would occur upon sliding), because the diamond-cone plowing makes negligible any initial elastic-plastic asperity deformation period. Therefore, triboemission large-bursts from diamond-cone scratching proceed upon sliding starts.

The proposed mechanism also is consistent with the triboemission measurements of Molina et al. for after-contact triboemission: they measured significant electron triboemission from insulators under vacuum (e.g., from alumina, sapphire and Si3N4 ) for minutes after the contact ceased, while no after-contact triboemission was detected from the semiconductors Si and Ge [1, 4-8]. When sliding and contact end the electron emission can continue from the insulators due to the tribocharging on surface patches. In this, Dickinson et al. [3] and Bhushan et al. [21] measured important surface electrostatics-charge under vacuum for insulators, including alumina, during sliding and after sliding ceased. But for semiconductors only negligible surface charge exists under vacuum [25] and therefore no post-contact triboemission is produced.
4. CONCLUSIONS

The experimental work of this paper measured consistent delays for large-burst electron triboemission occurrence from alumina-ball sliding on alumina disk when compared to large-bursts upon sliding starts from diamond-cone scratching. The observed surface modifications and wear for the two compared systems are consistent with the different evolutions of the triboemission outputs. After large bursts around the onset of wear decreasing triboemission is observed when the same wear track is scratched in repeated passes; this decrease relates to diminishing wear.

A conceptual mechanism is postulated to explain the delays in the occurrence of electron triboemission outputs, that is based on recent findings about electron work-function reduction from the plastic deformation and increased dislocation density which occur during sliding. This two-stage mechanism is consistent with wear data for alumina sliding. This two-stage mechanism is also found consistent with the triboemission data during both contact and after-contact emission from insulators and semiconductors, and with the triboelectron-energy measurements. The used ball-on-disk contact proves to be a geometry more sensitive than the diamond-cone-on-disk for the determination of the onset of wear, which is found related to the initiation of large-bursts of triboemission.

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