

PHOTOEXOEMISSION OF METALS AS AN OXIDE-FILM-CONTROLLED PHENOMENON

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Abstract. In an attempt to elucidate plausible mechanism(s) of the photostimulated exoemission of metals, we investigated the spectral distributions of photoemission and time evolution of photocurrents from cold-worked (milled, abraded, deformed) or chemically cleaned samples of Al, Fe, and Cu. The experiments were made in the gas environment as well as in a vacuum of 5×10^{-10} mbar. After the above treatments all tested samples exhibited photostimulated exoemission (PSEE) – a considerable increase in the photoelectric yield in the visible and near-ultraviolet region. After treatment PSEE relaxed to lower intensities (decays) in the gas environment, but arose further if stored in a vacuum after *in situ* abrasion of the surfaces. The obtained results support the concept of mechanoinduced PSEE from metals which considers the uprise of PSEE as a result of mechanical removal of the natural oxide film from the surface and attributes its decay to the recovery of the oxide, which attenuates the photoelectron flux from the metal substrate.

Key words: photostimulated exoemission, metals, cold work, oxide growth, aluminium, copper, iron.

1. INTRODUCTION

It was known long ago (see, e.g. [1]) that preliminary mechanical treatment, such as abrading, scratching or deformation, changes the photoelectric response of metals. The threshold wavelength of the photoelectron emission is red-shifted, whereas the overall photoemission yield is enhanced. However, this is a temporary change: after the treatment it relaxes, decays towards the initial, unperturbed values. To distinguish this additional part of the photoemission current, it is traditionally called *photostimulated exoelectron emission* or briefly – *photostimulated exoemission* (PSEE). The terms *exoelectron emission* and *exoelectrons* were introduced by a German physicist Johannes Kramer who made the first systematic investigations of this kind of phenomena. He supposed that the extra emission from mechanically treated metals was induced by exothermic recovery

processes in objects. Hence the prefix *exo-*. Though subsequent investigations revealed that the dominating part of the observations could not be interpreted in this way, the terms retained. Now *exoemission* is used as an umbrella term to denominate the nonstationary electron emission phenomena appearing only from emitters (metallic as well as nonmetallic) after some prior treatment (irradiation, deformation, etc.) and accompanying the relaxation of the perturbed state. Phenomenologically they closely resemble the afterglow (phosphorescence), and thermo- or photostimulated luminescence in the realm of photon emission phenomena. Analogously, the terms afteremission, thermo-, and photostimulated exoemission (TSEE and PSEE) are used. A most comprehensive survey on EE was published by Glaefeke [2], some peculiar topics were considered also in a recent review by Greber [3]. For more details consult the surveys [4,5].

Several attempts have been made to use the PSEE from metals and semiconductors for nondestructive testing of machine parts and devices, and mapping their surface defect topography [5,6-8]. Thus, the problem of proper interpreting of PSEE mechanisms has also considerable practical significance. In view of technological applications, it seems especially important to test common polycrystalline materials under natural atmospheric conditions, because the practically usable routine PSEE testing methods should be favourably simple and convenient to use.

We encountered the mechanoinduced PSEE in connection with a problem from the practical metrology. Namely, after even the slightest frictions (at switchings, contactings, etc.) in the input contactors of the high-sensitivity electrometers (attoammeters) relaxing spurious currents appeared, limiting the reliability and sensitivity of the devices [9]. Partially these noises can be generated by exoemission, in particular by PSEE. We dealt with this problem in another work [10], where we established that the intensity and decay rate of PSEE from different metals and alloys differs by several orders of magnitude. The inspection of the existing literature on PSEE revealed rather contradictory views on the nature of PSEE from cold-worked metals. Some authors have interpreted it as a vacancy-diffusion-governed emission, whereas others attribute it to the electron traps in the surface oxide layer (see, e.g. [2,4,5]). Some authors have suggested a model of the mechanoinduced PSEE, ascribing its uprise to the mechanical removal of the native oxide film from the emitter surface and its decay to the recovery of the surface oxide layer under appropriate conditions [5,11,12].

The goal of the present work was to obtain reliable experimental criteria to make a choice between these alternatives. We attempted to do this on some selected objects by (1) trying different oxide removal procedures, including mechanical as well as chemical ones, and (2) observing the temporal evolution of PSEE in different environments (gas, vacuum). Besides, it turned out that most experiments on PSEE have been performed with polychromatic illumination, neglecting the most informative spectral characteristics of PSEE. Thus, differently from the other authors, we used monochromatic illumination

and recorded PSEE spectral distributions and their time variance during the decay process.

2. EXPERIMENTAL

The metallic samples were prepared in the form of 7×7 mm² platelets cut from 0.5 to 2.0 mm thick sheets. Before use the samples were degreased by acetone rinsing and dried at 60°C. The elemental composition of the samples was determined by the X-ray quantitative microanalysis with a JEOL-produced analyser JXA-50A. Some trace amounts of Fe (0.06 wt %) and Mg (0.1 wt %) were established in the Al specimens, and Fe (0.07 wt %) in the Cu specimens; Fe contained 0.6 wt % Cu, 0.2 wt % Mn, 0.1 wt % Si, and 0.02 wt % Cr.

In the experiments made in the gas ambience, the samples were mechanically pretreated ("excited") by one of the following means:

- (i) scraping (milling) with a rotating steel edge; the specimens were pressed against the edge with a fixed force by a spring;
- (ii) polishing (abrading) with an abrasive paste containing chromium oxide;
- (iii) bending once by 90° and restraightening (deformation treatment).

For the sake of comparison, some specimens were also subjected to chemical surface-cleaning treatments: etching in a 10% NaOH solution, or electropolishing in the mixture of H₂SO₄ (36 vol %), H₂O (14 vol %), and glycerine (50 vol %). The abrasion and chemical/electrochemical treatments were followed by water and acetone rinsing and drying.

After pretreatment the samples were transferred into a demountable flow counter (90% Ar + 10% CH₄ mixture as counting gas) and illuminated with condensed light of a 150 W incandescent bulb in order to check the presence of PSEE. The counter had a point anode, a quartz window for the sample illumination, and its functioning was periodically checked with a superweak Ra irradiator.

For spectral investigations a DMR-4 quartz double monochromator (made in FSU) with a 1 kW xenon lamp was used. The spectra were recorded at quantum intensities (quanta/cm²·s) equalized for all test points. The intensity monitoring was carried out according to readings of a FEU-62 photomultiplier (FSU production), calibrated using a Vth-1 (Carl Zeiss, Jena) vacuum thermolement.

Ultra-high vacuum experiments were accomplished with a baked vacuum equipment pumped down to a 5×10^{-10} mbar base pressure using turbomolecular and titanium sputtering pumps. The vacuum chamber was equipped with quartz windows for illumination and observing; electron emission was registered with a FSU-produced secondary-electron multiplier VEU-OT-8M operated in the electron counting mode. A bellows-manipulated steel brush was mounted into the vacuum chamber for the mechanical abrading of the probe surfaces *in situ*. The spectral distributions of the photoemission yield in a vacuum were recorded with the above-mentioned optical devices.

3. RESULTS AND DISCUSSION

The incandescent bulb illumination did not induce any discernible photoemission from the as-received samples of all tested metals, but stimulated a well-pronounced (thousands counts/s) PSEE after mechanical pretreatment, e.g. milling.

Consider first Al, a favoured object of exoemission investigators (Figs. 1–4). Figure 1 displays the spectral distributions of photoemission from Al samples. The curves have been obtained after different treatments in air and registered with the gas counter. Comparing curve 5 (left lower frame), registered using an untreated sample, and curves 1, measured immediately after different mechanical

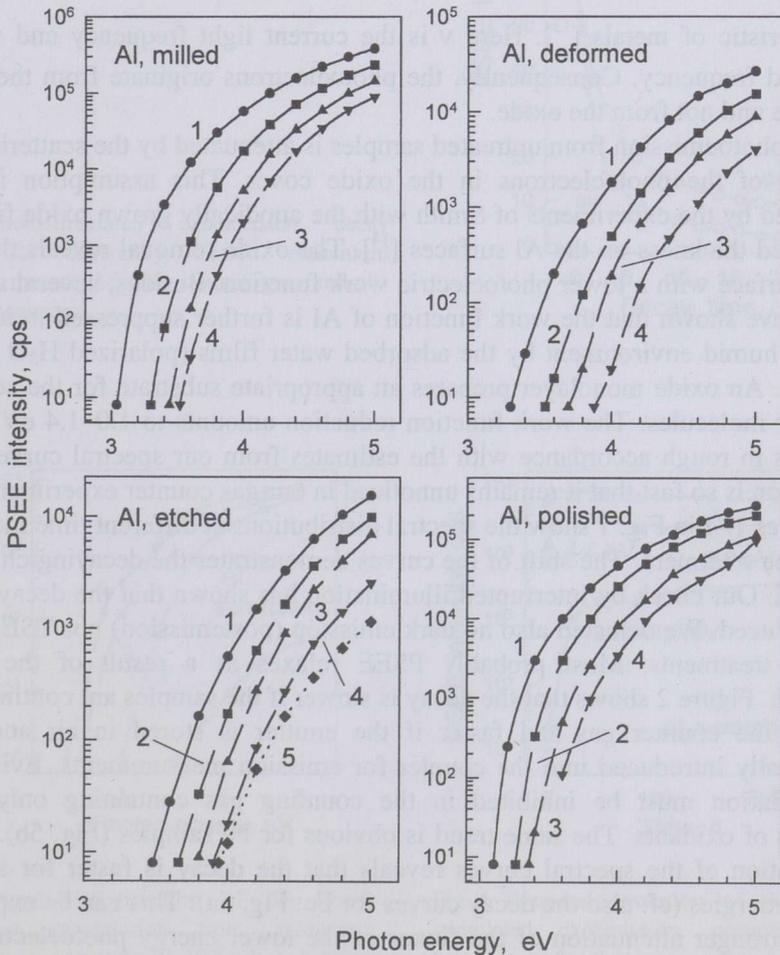


Fig. 1. Gas-counter-registered spectral distributions of the photostimulated exoemission from the milled, bending-deformed, etched, and grinding-polished aluminium samples at successive decay stages: 1, $t = 0$; 2, $t = 48$ h; 3, $t = 100$ h; 4, $t = 200$ h; 5, an untreated sample.

treatments, one sees that mechanical treatment induces a considerable increase in the photoemission yield in the whole spectral region covered, as well as a red shift of the photoemission threshold. This is a typical occurrence of PSEE.

It is remarkable that also the chemical removal of the natural oxide film from the surface, etching, gives a similar result. Thus, it is plausible that the mechanoinduced PSEE is also caused by the mechanical destruction and partial removal of the oxide layer. (In the case of bending deformation the bare metal surface is opened in the cracks of the surface layer.) The spectral distributions for as-treated samples can be satisfactorily approximated with a parabolic expression

$$J(\nu) \sim (\nu - \nu_0)^2,$$

characteristic of metals [13]. Here ν is the current light frequency and ν_0 the threshold frequency. Consequently, the photoelectrons originate from the metal substrate and not from the oxide.

The photoemission from untreated samples is attenuated by the scattering and trapping of the photoelectrons in the oxide cover. This assumption is well supported by the experiments of Smith with the anodically grown oxide films of controlled thickness on the Al surfaces [14]. The oxide removal reveals the bare metal surface with a lower photoelectric work function. Besides, several authors [15-18] have shown that the work function of Al is further suppressed in an even slightly humid environment by the adsorbed water films (polarized H₂O or OH dipoles). An oxide monolayer prepares an appropriate substrate for the sorption of water molecules. The work function reduction amounts to 1.0-1.4 eV [15,18], which is in rough accordance with the estimates from our spectral curves. The adsorption is so fast that it remains unnoticed in our gas counter experiments.

Curves 1-4 in Fig. 1 show the spectral distributions at different time moments t after the treatment. The shift of the curves demonstrates the decaying character of PSEE. Our check by interrupted illumination has shown that the decay is not light-induced. We detected also no dark emission (postemission) nor TSEE after applied treatments. Most probably PSEE relaxes as a result of the oxide regrowth. Figure 2 shows that the decay is slower if the samples are continuously kept in the counter gas and faster if the emitter is stored in air and only periodically introduced into the counter for emission measurements. Evidently, the oxidation must be inhibited in the counting gas containing only trace amounts of oxidants. The same trend is obvious for Fe samples (Fig. 5b). Close examination of the spectral curves reveals that the decay is faster for smaller photon energies (cf. also the decay curves for Fe; Fig. 5a). This can be explained by the stronger attenuation of the fluxes of the lower energy photoelectrons at penetration of the oxide. A similar dependence of the electron attenuation length on the photon energy was distinctively established in [19] for different dielectric films (LiF, NaI, Al₂O₃, n-C₃₆H₇₄, etc.), evaporated onto CsI or CuI photocathodes.

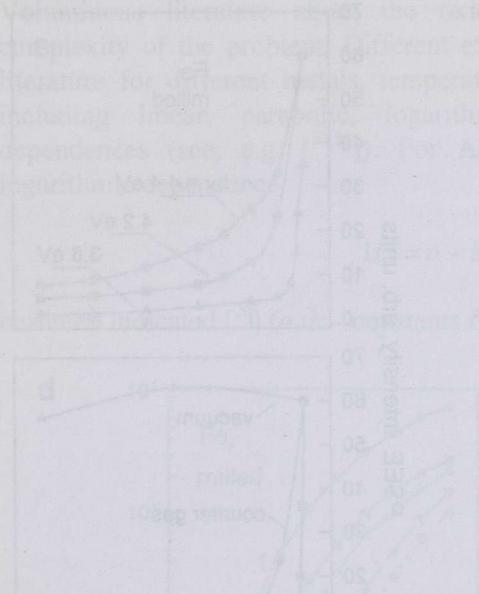


Fig. 2. Photostimulated exoemission decay curves for differently treated aluminium samples, measured for the counter-gas- and air-stored specimens.

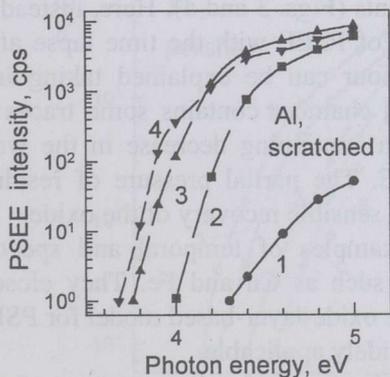
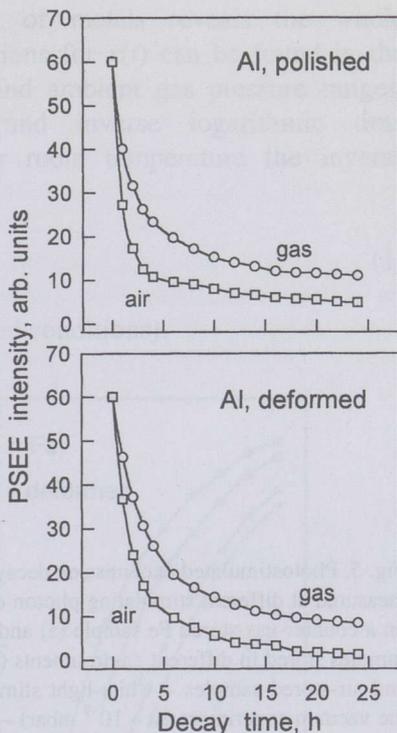


Fig. 3. Spectral distribution of the photostimulated exoemission from aluminium, measured in a vacuum of 10^{-9} mbar. 1, before the treatment; 2, immediately after scratching *in situ* with a steel brush; 3, 23 h later; 4, after storing in a vacuum for 240 h.

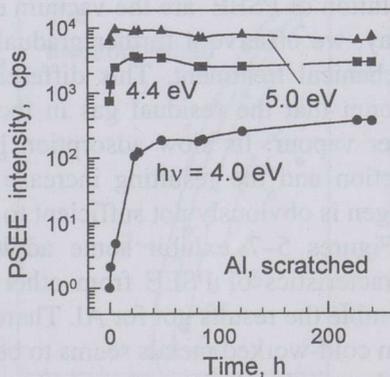


Fig. 4. Temporal evolution of the photostimulated exoemission, occurring after brushing of aluminium samples in a 10^{-9} mbar vacuum under illumination at the indicated quantum energies.

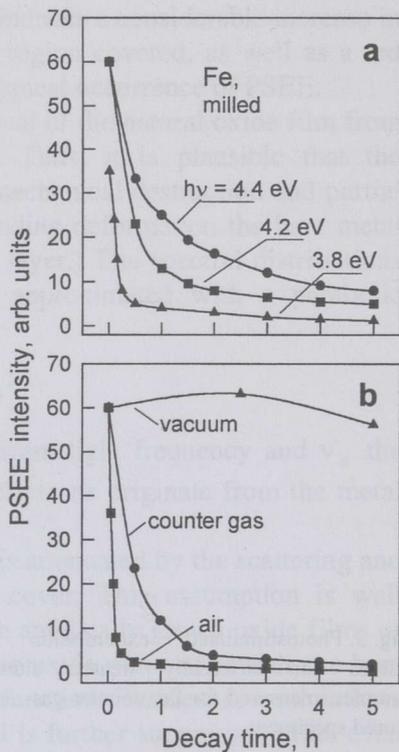


Fig. 5. Photostimulated exoemission decay curves measured at different stimulating photon energies on a counter-gas-stored Fe sample (a) and for the samples stored in different environments (b); gas- and air-stored samples – white-light stimulation, the vacuum experiment (at $\sim 10^{-9}$ mbar) – 4.4 eV stimulation after a steel brush scratch.

Especially illustrative to the effect of the environment upon the time evolution of PSEE are the vacuum experiments (Figs. 3 and 4). Here, instead of decay, we observe a further gradual growth of PSEE with the time lapse after mechanical treatment. This different behaviour can be explained taking into account that the residual gas in the vacuum chamber contains some traces of water vapour. Its slow adsorption leads to a continuing decrease in the work function and the resulting increase in PSEE. The partial pressure of residual oxygen is obviously not sufficient to induce a sensible recovery of the oxide.

Figures 5–7 exhibit some additional examples of temporal and spectral characteristics of PSEE from other metals, such as Cu and Fe. They closely resemble the results got for Al. Therefore, the oxide-layer-based model for PSEE from cold-worked metals seems to be more widely applicable.

Hence, the decisive factor, determining the form of a decay curve of the PSEE, should be the dependence of the oxide thickness x on its growth time t : $x = x(t)$. The most straightforward control of the presented concept should be parallel registration of PSEE decay and oxide thickness (e.g. by the ellipsometric technique as in [14]). Unfortunately, this is a rather complicated task for mechanically treated rough surfaces. Besides, the measurements can be complicated by a nonuniform oxide growth on highly perturbed metal faces.

Voluminous literature about the oxidation of metals reveals the whole complexity of the problem. Different expressions for $x(t)$ can be found in the literature for different metals, temperature, and ambient gas pressure ranges, including linear, parabolic, logarithmic, and inverse logarithmic time dependences (see, e.g. [20,21]). For Al near room temperature the inverse logarithmic dependence

$$1/x = a - b \ln t \quad (1)$$

has been indicated [20] (a, b – constants for fixed conditions).

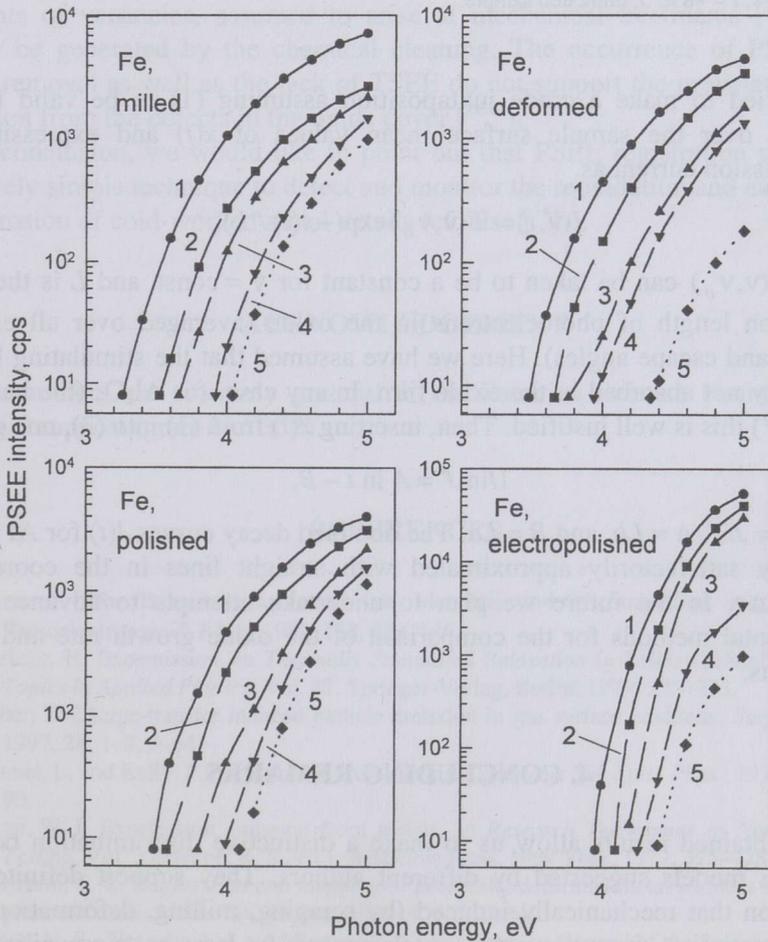


Fig. 6. Gas-counter-registered spectral distributions of the photostimulated exoemission from variously treated iron samples at different time intervals after treatment: 1, $t = 0$; 2, $t = 15$ min; 3, $t = 1$ h; 4, $t = 24$ h (10 h for the case of electropolish); 5, $t = 100$ h.

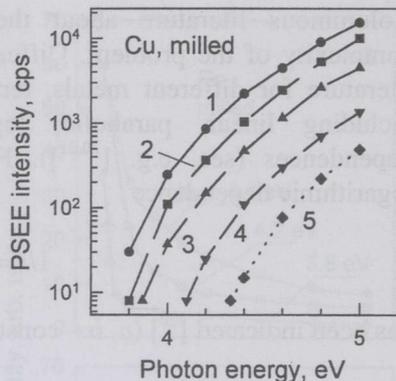


Fig. 7. Gas-counter-registered spectral distributions of the photostimulated exoemission for milled copper at different time lapses: 1, $t = 0$; 2, $t = 5$ h; 3, $t = 10$ h; 4, $t = 48$ h; 5, untreated sample.

We tried to make a crude juxtaposition assuming (1) to be valid for the averaged over the sample surface mean values of $x(t)$ and expressing the photoemission current as

$$J(v, t) = F(v, v_o) \exp(-x(t) / L), \quad (2)$$

where $F(v, v_o)$ can be taken to be a constant for $v = \text{const}$ and L is the mean attenuation length of photoelectrons in the oxide (averaged over all electron energies and escape angles). Here we have assumed that the stimulating light is practically not absorbed in the oxide film. In any case, for Al_2O_3 (the band gap $E_g = 7$ eV) this is well justified. Then, inserting $x(t)$ from (1) into (2), one gets

$$1/\ln J' = A \ln t - B, \quad (3)$$

where $J' = J/F$, $A = Lb$, and $B = La$. The obtained decay curves $J(t)$ for Al and Fe are really satisfactorily approximated with straight lines in the coordinates $1/\ln J' \sim \ln t$. In the future we plan to undertake attempts to advance direct experimental methods for the comparison of the oxide growth rate and PSEE decay runs.

4. CONCLUDING REMARKS

The obtained results allow us to make a distinctive discrimination between the PSEE models suggested by different authors. They support definitely the assumption that mechanically induced (by scraping, milling, deformation, etc.) photoexoemission from the tested metals appears (at least in its prevailing part) as a result of the mechanical removal of the natural oxide film from the surface of the metal substrate and the following adsorption-assisted reduction of the work function. The subsequent decay of the intensity of the emission in an open atmosphere is due to the recovery of the oxide layer. The growing oxide

attenuates gradually the photoelectron flux escaping from the substrate metal. Note that Allen and Gobeli [22] interpreted exactly in the same way their results about photoemission from oxide-coated and Ar-ion-sputtered Si surfaces. The interpretation given by Buzulutskov et al. [19] to their measurements of the attenuation of the photoemission in dielectric protective coating films on the surfaces of CsI and CuI photocathodes also follows quite the same lines. These results lend some co-argument to our conclusion.

The analysis of previous publications has revealed that our observations, at least in some significant details, do not support the other alternative mechanisms of mechanoinduced PSEE, such as the vacancy-diffusion-governed emission [23-26] or emission from the electron traps in the oxide layer [27,28]. Indeed, large amounts of vacancies, assumed to arise at mechanical treatments [23-26], can hardly be generated by the chemical cleaning. The occurrence of PSEE after oxide removal as well as the lack of TSEE do not support the prevalence of the emission from the defects in the oxide cover [27,28].

In conclusion, we would like to point out that PSEE registration provides a relatively simple technique to detect and monitor the reoxidation and early stages of corrosion of cold-worked metal details (cf. also [14]).

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METALLIDE FOTOEKSOEMISSION KUI OKSIIDIKELME KAUDU OHJATUD NÄHTUS

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Üritades selgitada metallide fotostimuleeritud eksoemissiooni tekke-
mehhanismi, on uuritud fotoemissiooni spektraaljaotumusi ja fotovoolude ajalast
kulgu mehaaniliselt töödeldud (freesitud, kriimustatud, deformeeritud) või

võrdluseks ka keemiliselt oksiidist vabastatud Al, Fe ja Cu katsenditel. Mõõtmisi tehti nii gaasloenduriga kui ka elektronkordistiga 5×10^{-10} millibaarilises vaakumis. Testitud katsendid annavad ülalloeletud töötluste järel fotostimuleeritud eksoemissiooni (FSEE): ilmneb fotoelektrilise saagise tunduv kasv nähtavas ja lähilultravioletti piirkonnas. Pärast töötlust FSEE gaasikeskkonnas aja jooksul vaibub, kuid vaakumis töödeldud ja hoitud katsenditel kasvab edasi teatava tasakaaluväärtuseni. Tulemused kinnitavad käsitust, mille kohaselt mehaanoindutseeritud FSEE tekib metallidelt pinna oksiidikile mehaanilise kõrvaldamise tagajärjel ja vaibub aja jooksul tingimustes, mille puhul oksiid taastub, sest oksiidikiht nõrgendab metallist väljuvate fotoelektronide voogu.