Exo-Electron Emission from Corroded Metal Surfaces

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Abraded and etched titanium, aluminium and copper surfaces and oxidized and irradiated beryllium bronze surfaces were investigated by means of exo-electron emission. The glow curves of the emission for abraded and etched metal surfaces were almost the same independently of metals and etching reagents. As the glow curves were essentially identical with that for emery powder, it was concluded that the exo-electron emission from the abraded metal mainly resulted from emery powder embedded in the metal surface. The surface of beryllium bronze oxidized in air at 520–550°C and irradiated with γ-ray gave a glow curve identical with BeO. It was confirmed that the protective film on beryllium bronze consists of BeO. The characteristic emission at 230°C from BeO was weak for the specimens oxidized at lower temperature and unknown stronger emission was observed at 100–150°C. It was implied that some other substance was formed on the surface prior to the protective film of BeO.

1. Introduction
Exo-electron emission (Kramer effect) is an interesting phenomenon on solid surface. After the first work by Kramer,1) many workers have studied the phenomena from various points of view. Kimura2) observed the emission from iron, nickel, aluminium, and brass cathodes of Geiger-Müller counters when they were heated. Grunberg, et al.,3) have found that abraded aluminium surface acquires a high activity of emission when an outermost dead layer has been removed by etching. Ohashi, et al.,4) reported that abraded iron surface, when etched slightly by dilute nitric acid solution, gave the exo-electron glow curve having an emission peak at about 140°C.

In this study, exo-electron emission from the abraded and etched metal surface and emission from the oxidized and irradiated metal surface were investigated in connection with corrosion.

2. Experimental
The exo-electron emission from the corroded metal surfaces was detected by a windowless gas-flow Geiger Müller counter and measured with a scaler and a rate meter. Commercial Q-gas (99% helium, 1% isobutane) used as the counting gas was maintained at a constant flow rate of about 120 bubbles per minute nearly equal 25 cc/min during the experiment.

The specimens used were cut from sheet stocks to a disk of 14 mm diameter. They were annealed in a vacuum at 500°C, polished with emery paper (#3/0) and then subjected to various corrosion treatments. Immediately after the treatment, the specimen was inserted into the gas-flow counter and heated to 450°C at the rate of 40°C/min to measure the glow curve of the exo-electron emission.

3. Results and Discussion
3.1. Emission from Abraded and Etched Metal Surface
Titanium specimens polished with emery paper and etched by hydrochloric acid (1:1) solution at room temperature gave the results shown in Figure 1. When the specimen was as polished, exo-electron emission was weak. As etching time increased, emission became stronger. When the abraded surfaces of titanium were etched by nitric acid (1:1) solution at room temperature, the same results as hydrochloric and sulfuric acid etching were observed. The typical glow curves of exo-electron emission from the titanium surface etched about 1 μ in thickness by hydrochloric and sulfuric acid solutions are shown in Figures 2 and 3, respectively. It was found that the abraded titanium surface, when etched by these solutions, shows the identical exo-electron glow curve having a higher emission peak at 140 to 150°C and two lower peaks at 310 to 320°C and 390 to 410°C.

As shown in Figure 4, etching of abraded titanium specimens by nitric acid (1:1) solution gave the same results as hydrochloric and sulfuric acid etching except that in the case of room temperature etching, the emission peak at 140°
to 150°C was as tall as the other peaks and that the peak disappeared in boiling temperature etching. The decrease of the emission peak can be elucidated by fading during the etching, because the etching temperature was only 40 to 50°C lower than that of the emission peak. It was interesting to note that the effect of nitric acid solution in which titanium was passive was similar to that of corrosive hydrochloric and sulfuric acid solutions.

Figure 5 shows the results of titanium etched by the mixed solution of 2% HF and 1.5% HNO₃ in which titanium is very corrosive. In this case, emission decreased with etching time, though the pattern of the glow curve was similar to those described above. It was found that deep etching deprived abraded titanium of the activity of exo-electron emission.

Aluminium and copper specimens were also examined. The results are shown in Figures 6 and...
7, respectively. The glow curves were found to be similar to those for titanium. It is clearly indicated in Figure 6 that the abraded surface of aluminum is deprived of the exo-electron activity by deep etching.

Since exo-electron glow curves of abraded metal surface were independent of metals and etching reagents, emery powder was suspected as the emission source. The results obtained in copper abraded with a steel file are compared in Figure 7 with those obtained in copper abraded with emery paper. No exo-electron emission was observed on the copper surface abraded with a steel file, while the surface abraded with emery paper acquired a high activity of the emission by the same etching treatment.

Emery powder was extracted by nitric acid etching from the copper dust produced by polishing copper with emery paper. The exo-electron glow curve for the emery powder is shown in Figure 8. The same glow curves were obtained in emery powder extracted by etching the same copper dust with H\textsubscript{2}SO\textsubscript{4}+H\textsubscript{2}O\textsubscript{2} solution and the powder produced by rubbing two emery papers together. It was demonstrated that the glow curve for emery did not differ from that of abraded and slightly etched metal surfaces except in the relative intensities of the three emission peaks. From the results described above, it was concluded that exo-electron emission from abraded metal mainly resulted from emery powder embedded in abraded metal surface. This fact should be considered in the study of friction, abrasion, and corrosion of metal surface polished with emery paper.

3.2. Emission from Oxidized and Irradiated Surface of Beryllium Bronze

Mechanically finished specimens of beryllium bronze (1.9\% Be, 0.26\% Co) were oxidized in air at 300, 400, and 520 to 550°C for 10 minutes and irradiated with \(\gamma\)-ray from cobalt-60 to excite the oxide film. The surface of the specimens thus prepared gave the exo-electron glow curves shown in Figures 9 and 10. The specimen oxidized at 520 to 550°C showed a glow curve identical to that for beryllium oxide BeO reported by Kramer. The protective film on beryllium bronze consists of BeO. In this study...
this was confirmed by means of exo-electron emission.

The glow curves for the specimens oxidized at 300 and 400°C, however, were quite different from that for BeO except for the emission above 360°C. For the specimen oxidized at 400°C, the characteristic emission at 230°C from irradiated BeO was appreciable and unknown stronger emission was observed at 100 to 150°C. Since pure copper oxidized and irradiated in the same manner emitted no exo-electron, cuprite Cu₂O and tenorite CuO were not responsible for the emission. The emission could not be attributed to emery, because the specimen was not polished with emery paper. It was implied that some other substance was formed prior to the protective film of BeO.

The specimen of beryllium bronze etched with nitric acid (1:1) solution for 1 minute prior to oxidation was also oxidized in air at 520 to 550°C for 10 minutes and irradiated with γ-ray in the same manner. This specimen did not show any exo-electron emission. This indicates that beryllium dissolved preferentially from the surface of beryllium bronze during the etching.

Two examples of the application of the Kramer effect (exo-electron emission) were described in this study. It was demonstrated that the measurement of exo-electron emission is a useful and effective means for the study of metallic corrosion.

(Received December 19, 1973)

References