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J. T. Dickinson
Washington State University

P. Braunlich
Washington State University

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Comments
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TRIBOSTIMULATED EMISSION OF ELECTRONS AND NEUTRAL PARTICLES FROM ANODIZED ALUMINUM

J.T. Dickinson and P. Braunlich
Physics Department
Washington State University
Pullman, WA 99164

ABSTRACT

The physical and chemical properties of anodic oxide layers on metals such as Al play important roles in a number of applications such as adhesive bonding and corrosion resistance. An overall test of an oxide layer sensitive to a number of oxide properties is difficult to find. We have been studying the tribostimulated emission of charged particles, neutral particles, and photons during tensile deformation of anodically oxidized Al alloys. The characteristic emission curve (emission rate vs. strain of the Al substrate during constant strain rate) is found to depend strongly on the anodization parameters. A comparison of neutral particle emission with electron emission will be presented. Correlations between acoustic emission from oxide cracking and electron emission will also be discussed.

INTRODUCTION

Exoelectron emission is generally due to the release of highly localized energy at the surface of a solid in a relatively short time period. Many competing processes can dissipate this energy, particle emission being one of the least likely and phonon production being the most likely. The emission we observe in these experiments can be directly correlated with the propagation of cracks in the oxide coating. The manner in which an oxide coating responds is uniform to training of the aluminum substrate and the resulting emission of particles is strongly dependent on the mechanical and chemical nature of the oxide coating.

Experimental details of our experiments may be found in references 1-3. The electron emission is measured in 10^-9 torr vacuum with a channeltron electron multiplier. A typical characteristic emission curve for a dense barrier-type oxide on Al 2024 clad is shown in Fig. 1. The shape of the large peak at 5% strain agrees well with optical microscopy measurements of rate of crack growth. The small peak at 14% strain coincides with the necking of the sample prior to rupture. Any phenomena which disrupts the oxide layer and initiates crack growth leads to the emission of electrons.

DEPENDENCE ON ANODIZATION PARAMETERS

Certain porous duplex oxides grown in H3PO4 are known to facilitate adhesive bonding of Al. The samples prepared by a laboratory "baseline" procedure provided by the Boeing Commercial Aircraft Co. are referred to as Boeing Baseline samples. Figures 2 and 3 show characteristic exo-emission curves (CECs) for a Boeing Baseline sample and two samples with oxides formed under slightly anodization conditions. One sees that the CECs change for these different conditions.

We have carried out a systematic variation of a number of anodization parameters around the Boeing Baseline procedures. One simple effect to show is the change in the total number of electrons counted as a function of this single parameter. Fig. 4 illustrates the manner in which total emission changes with oxide thickness (varied by varying the anodization voltage). The observed increase with film thickness is seen to be exponential above 2500 A. Fig. 5 shows the effect of changing the electrolyte concentration and Fig. 6 is the total emission as a function of electrolyte temperature. Qualitatively, the behavior observed in these last three figures can be explained on the basis of the assumption that the more bonds that are broken the greater the electron emission. Examination of the samples under the SEM shows variations in both thickness and porosity. Both these features will alter the number of bonds ruptured in the cracking process.

NEUTRAL PARTICLE EMISSION

We have also observed neutral particle emission during tensile deformation of anodized Al. It also takes on a characteristic shape and intensity which depends on the nature of the oxide. Fig. 7 shows the neutral emission observed during the elongation of a sample with a dense oxide (ammonium tartrate-3000 A). For comparison, the electron emission curve for an identical sample is also shown. With a quadrupole mass spectrometer, the neutral species were determined to be O2 and CO2 for the dense oxide. For porous H3PO4 oxides, we only observed O2. We are fairly sure these molecules are associated with trapped impurities because they are the same species released when the samples are heated to a few hundred degrees C. One notices the much slower decay of the neutral emission relative to the electron emission in Fig. 7. This occurred on all samples studied. If one stops pulling the sample while it is emitting one finds that the neutral emission decays away with time constants of 6 sec for the CO2 and 10 sec for O2. This implies a very slow process which we feel is the diffusion of atoms/molecules to the crack wall before desorption. The conduction of the cracks is much to large to account for these large time delays. We have modeled the release of neutral molecules following crack propagation and can fit the experimental data quite well. Fig. 8. shows the dependence of neutral emission on oxide thickness for dense oxide layers.

CORRELATION OF ELECTRON EMISSION WITH ACOUSTIC EMISSION

By attaching an acoustic emission (AE) transducer to the back of the sample, we can detect the bursts of acoustic energy associated with oxide cracking. Tests with no oxide present, various lengths of oxide on the sample gauge, and correlations with optical microscopy measurements show that
the acoustic emission observed is associated with oxide cracking. For this work we have been using Al 1350 (99.5% Al) annealed at 270 C which yields negligible substrate AE. The AE and exoelectron emission (EE) can be obtained simultaneously. With a 5 mm² patch of 5000 A thick oxide (densenitro ammonium tartrate) on the side of the sample facing the electron multiplier, healthy quantities of AE and EE are observed.

Fig. 9 shows AE EE count rate vs. strain curves for the above oxide. The two curves are seen to be intimately related. We thus conclude that a necessary condition for tribostimulated EE is the occurrence of oxide cracking.

Fig. 10 shows AE and EE curves taken at a slower strain rate such that the absolute rates of detected emission were carefully determined throughout the experiment. This allows us to take an accurate ratio of EE to AE indicating what the probability of EE is relative to AE. The EE/AE ratio is seen to be near unity and depends on strain. The ratio climbs as the AE curve is seen to drop off faster than the EE curve. We believe this is due to chemiemission as we will comment later.

Another basic question is the time relation between AE and EE. If one pulls the sample very slowly, the bursts of AE and EE can be displayed as single events by means of suitable pulse shaping and the use of two synchronized strip chart recorders (We refer to this as our two graduate student coincidence experiment). Manually, the observer can detect "coincidence" between the two emissions to perhaps within 0.1 sec. Fig. 11 shows the two sets of bursts over approximately 4 minute intervals: a) near the peak of exoelectron burst and b) out on the tail of exoelectron burst with the pulling stopped and the sample held at constant strain. The bursts labeled o are out of "coincidence" and those labeled i are in "coincidence". Near the peak one sees that nearly all of the electron bursts are in "coincidence" with an AE burst. Those EE bursts out of coincidence can easily be accounted for by background which is two to three counts per minute. This implies that EE occurs within 0.1 sec of the propagation of a crack in the oxide. Fig. 11-a also shows that a number of AE bursts occur without an accompanying electron burst. From our ratio determination in Fig. 10, this implies that many electron bursts consist of more than one electron.

In Fig. 11-b, one sees a few electron bursts in coincidence (those marked i) but a much larger number that are out of coincidence (o). It is this random component that we feel is due to chemiemission due to the reaction of gaseous species with the freshly exposed Al upon cracking of the oxide. The source of the gas could be the oxide itself or it could be from the 10-5 torr background in which the experiments were performed. We are planning to repeat these experiments in UHV to determine the source of gas. With Al, O₂ is a likely candidate.

Finally, we have been attempting to measure more precisely the time interval distribution between the AE burst and the emitted electrons.

It is very difficult to determine the t=0 point of the AE burst. To within an uncertainty of about 20 ysec, the two events appear simultaneous.

Fig. 12 shows the distribution of time between AE and EE determined by a time-of-flight like experiment, where we mention again our t=0 mark is still uncertain. However, a very sharp distribution is observed, suggesting that the electrons are released very rapidly after the crack propagates and do not continue to emit for times on the order of a few microseconds. This is consistent with a mechanism wherein the energy available for emission is rapidly dissipated. We are nearly in the position to reduce the t=0 uncertainty by at least a factor of 10. We can then approach a model for EE with more confidence.

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REFERENCES

FIG. 1. Typical data obtained from a strong exoemitter (Al 2024 clad, covered with 3000 A thick dense oxide grown in ammonium tartrate). The upper curve represents the recorded display of the multichannel analyzer. The lower curve is a strip chart recording of the rate-meter output obtained with a 5 second response time. The small peak preceding rupture occurs when the sample is necking down which severely disrupts the surface of the aluminum. This leads to additional oxide cracking and exoemission.
FIG. 2(a). The characteristic exoemission curve from a Boeing Baseline sample anodized in a 10% by weight H₃PO₄ solution. The substrate was Al2O3 clad. Although the emission was weak, it was very reproducible from sample to sample.

FIG. 2(b). Another CEC from a porous oxide with deviations from the Boeing Baseline procedure (a lower anodization voltage, lower anodization bath temperature and acid concentration). This produced a slightly thinner and smoother (less porous) oxide. Note the comparison with the Baseline CEC.
A third variation on the Boeing anodization procedure. A substantially higher anodization voltage, a slightly lower temperature, and a lower acid concentration were used for this sample. This produced a thicker oxide than the baseline sample. It is interesting that the CEC from thicker porous oxides resemble the CECs from dense oxides, suggesting similar cracking mechanisms.

Figure 4. Total exoemission (total counts accumulated during the pull) vs. thickness for a voltage-varied porous oxide (H₃PO₄). All the anodization parameters other than voltage are the same as Boeing baseline.

Figure 5. Total exoemission vs. electrolyte concentration for two porous oxides. The upper curve was grown at 30V, the lower curve at 10V. This results in a considerably thicker oxide for the 30V samples. The dominant effect in the concentration range studied here is an increase in the porosity of the oxide with concentration. This leads to less oxide material actually cracking and therefore a decrease in emission.
Figure 6. Emmission vs anodization temperature for a H₃PO₄ porous oxide. Both oxide thickness and porosity change with temperature.

Figure 7. Total neutral emission as measured by a Bayart-Alpert gauge vs strain for a dense ammonium tartrate oxide (3000 Å) on Al 2024 clad. Also shown is an electron emission curve for an identical sample. The circles are the calculated points for a model of neutral emission. The cracking of the oxide is clearly the initial step. Gases observed for the dense oxide were O₂ and CO₂. Note the peak at rupture.

Figure 8. A summary of the total amount of neutral and O₂ emission from dense oxides on bare 2024 Al. This differs from exoemission in that in this thickness range, it grows exponentially. Note the the O₂ emission actually begins to decrease at higher thicknesses.

Figure 9. Correlation of acoustic emission from cracking oxide and exo-electron emission. The curves are very similar. This helps substantiate that the mechanism for electron emission is indeed the propagation of cracks in the oxide. Data is output of two count rate meters.
Figure 10. The AE and EE from anodized Al 1350. Care was taken to obtain the absolute intensities of the two emissions for the entire pull. This allows us to take the ratio of EE/AE, which is the dotted curve. "New" cracks emit electrons better. The rise in the ratio during the tails of the emission curves is believed to be due to chemi-emission.

Figure 11. The correlation of EE and AE in time for relatively slow times. The spikes shown correspond to the occurrence of bursts of AE and EE.

Figure 12. Distribution of time between occurrence of acoustic emission and electron emission.

The distribution of the time interval between the occurrence of AE and EE. A multichannel analyzer with a time-of-flight module was employed to detect electrons correlated in time with an acoustic burst. At the moment we can not say with certainty where \( t = 0 \) is relative to this distribution. This is due to the nature of the AE burst. In spite of about a 20 usec uncertainty, we can say that within these few microseconds, all of the electron emission is over.