General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

EXOELECTRON EMISSION FROM A CLEAN, ANNEALED MAGNESIUM SINGLE CRYSTAL DURING OXYGEN ADSORPTION

by John Ferrante
Lewis Research Center
Cleveland, Ohio 44135

Exoelectron Emission From a Clean, Annealed
Magnesium Single Crystal During Oxygen Adsorption

by

John Ferrante
NASA-Lewis Research Center
Cleveland, Ohio

Exoelectron emission has been observed from a clean, annealed Mg
(0001) surface during oxygen and chlorine adsorption at pressures of
6.5×10^{-5} N/m^2 and lower. The studies were performed in an ultrahigh vacuum
system. The crystals were cleaned by argon ion bombardment and annealed at
300° C. Auger electron spectroscopy was used to verify surface cleanliness,
and low energy electron diffraction was used to verify that the surface
was annealed. The emission was found to be oxygen arrival rate dependent.
Two peaks were observed in the electron emission with exposure. Evidence
is presented that the formation of the second peak corresponds to oxidation
of the Mg surface. No emission was observed from clean aluminum during
adsorption. The results verify that electron emission occurs from a strain
free surface simply upon adsorption of oxygen. A qualitative explanation
for the mechanisms of emission in terms of chemical effects is presented.

INTRODUCTION

The term exoelectron emission has been applied to many different properties ranging from emission after abrasion of materials, emission following chemisorption to enhanced photoemission. A review by Brotzen (1) summarizes the exoelectron emission from metals for the period up to 1967, and Larikov and Baklanova (2) summarize work performed on metal surfaces for the period extending to 1974. Baxter (3) reports studies which will be referred to in this paper as enhanced photoemission. In enhanced photoemission, areas of surface strain aré observed by shining light on a metal surface and noting differences in photoyield in areas where surface deformation has occurred. In this study we will concentrate on exoelectron emission from metal surfaces which occurs in the absence of photo stimulation. Although many of exoelectron emission studies have been performed, few have been performed in the well-controlled environments of ultrahigh vacuum systems. Gesell, Arakawa, and Calicott (4) have observed electron emission from abraded films and evaporated films of magnesium resulting from adsorption of oxygen and water vapor under controlled conditions. Kasemo (5) has observed photon emission (emission of light) from magnesium and aluminum single crystals upon adsorption of oxygen which will be related to exoemission later in this report.

Moucharatieh and Olmsted (6) and Uebbing and James (7) have observed electron emission from vapor deposited cesium films during exposure to oxygen. Uebbing and James have verified that the emission is electrons and not negative ions by use of magnetic fields.

The principal objective of this investigation will be to evaluate the importance of surface strain on exoemission since this is the quantity

2

of principal importance to tribologists. This objective will be accomplished by examining exoemission from annealed and unannealed single crystals upon admission of gases into an ultrahigh vacuum system. The significance of strain to the emission of electrons will be discussed, and a qualitative model will be proposed for chemically induced exoemission. In this study we will examine exoelectron emission from magnesium and aluminum resulting from the adsorption of oxygen and chlorine in an ultrahigh vacuum system. LEED (low energy electron diffraction) (8) will be used to establish surface crystalline structure and provide evidence that the magnesium single crystal surface (0001) is strain free. Magnesium will be ion bombardment cleaned and annealed. AES (Auger emission spectroscopy) (8) will be used to demonstrate surface cleanliness and examine the chemical effects of adsorption.

EXPERIMENTAL

The equipment used in this study is a standard four-grid LEED-AES retarding potential analyzer shown schematically in Fig. 1. Experiments were performed in a bakeable stainless steel ultrahigh vacuum system. The system is sorption, sublimation and ion pumped and attains pressures in the 1×10^{-8} N/m^2 (10^{-10} torr) range with filaments hot.

The experimental apparatus for performing the exoemission experiments is also shown schematically in Fig. 1. The current leaving the sample is measured by a Keithley 417 electrometer. The samples used are single crystals of high purity magnesium ((0001) plane) and aluminum ((001) plane). The samples were discs 2.5 cm in diameter and .2 cm thick. The procedure used in obtaining the data was first to clean the samples by argon ion bombardment at a 1000 eV beam energy and a current density of 2 micro amp/cm^2.

The Mg was then annealed at 300° C. Following annealing the sample was examined by AES in order to establish surface cleanliness. The Mg was then examined by LEED in order to establish that the surface is annealed and strain free. In the case of aluminum, the sample was not annealed and, therefore, was not examined for surface strain. Following examination with LEED and with the sample cooled to room temperature, the exoemission experiment is performed by admitting oxygen or chlorine into the vacuum system through a leak valve to a pressure of typically 6.5×10^{-5} N/m^2 (5×10^{-7} torr). The pressure and the current emitted by the sample were then recorded on a two-pen strip chart recorder. The sample was then examined by AES in order to establish that oxygen had been adsorbed.

All gases used in the study are research grade. Temperatures were measured with a chromel-alumel thermocouple spot welded to the back face of the crystals. All viewing ports were covered during the exoemission experiment in order to guarantee that no external light influenced the results. The experiments were performed with the ionization gauge on and off in order to guarantee that light from the ionization gauge had no effect on the results. Also, the ion pump was turned off in order to verify that the current didn't result from the pump. In addition, once the process was complete, readmission of the gas produced a null result. The exposure was stopped and restarted at various points during the exposure in order to establish whether surface condition determined the nature of the exo-emission curves. Also, the pressure dependence of the exoemission curves was observed.

RESULTS

Fig. 2 shows the AES spectrum for magnesium a.ter annealing and after exposure to oxygen for Auger energies ranging from 80 to 600 eV. We can see

4

that the oxygen AES peak is present after exposure, confirming that oxygen has been adsorbed by the surface. In addition, we can see a large change in background slope indicating a difference in secondary electron yield from the clean and oxygen-exposed surfaces. There are other features present in the clean and oxygenated spectra which do not have the characteristics of Auger peaks and may be due to diffraction effects in the solid (9).

Fig. 3 shows the LEED pattern for magnesium following annealing at 300° C. We can see the characteristic hexagonal symmetry for the (0001) surface. The presence of the undistorted LEED pattern gives evidence of the success of annealing the surface damage done in polishing and by ion bombardment. The annealing was also checked by comparing X-ray diffraction Laue patterns (not shown) before placement of the sample in the vacuum system and after removal from the system. Before annealing in vacuum, the Laue patterns showed considerable strain with some double spots. After annealing, the Laue pattern showed sharp well-defined diffraction spots indicating that bulk strain in the very soft magnesium had been annealed from the specimen.

Figures 4 and 5 show the exoemission curves for magnesium exposed to oxygen (actual strip chart data). There are a number of interesting features in the Mg exoemission curves. First, there are two peaks in the emission curves (Fig. 4), and we can see that the emission immediately follows the rise in oxygen pressure to approximately 8×10^{-5} N/m^2 (6×10^{-7} torr). Finally, when the pressure is cut off we see a drop in the emitted current. In Fig. 5 the pressure is cut off after the first peak starts to decline. In this case the maximum pressure is approximately 1.3×10^{-5} N/m^2 (1×10^{-7} torr), a factor of four smaller. We see that after cutting off the oxygen pressure, the emission ceases. When we reintroduce oxygen into the system, the emission proceeds from the point where it had ceased. The latter effect

5

occurred regardless of where the oxygen supply was cut off. A final feature of this curve is that the emission follows the arrival rate of oxygen atoms in that at lower pressure the exoemission peak heights are smaller but the distribution of electrons is spread out; i.e., the rate of electron emission (current) is proportional oxygen arrival rate. The exoelectron current persists for long times even at the higher pressure; i.e., the decay of the second peak is very slow at the pressure used. Chlorine adsorption on Mg gave similar results to oxygen on Mg but the emission curves were less repeatable. Adsorption on aluminum under similar conditions produced a null result; i.e., no electron current was observed to within the sensitivity of the present detection scheme.

Fig. 6 shows the low energy AES spectrum (25 eV to 50 eV) for (a) clean magnesium, (b) the spectrum following the development of the first exoemission peak, (c) the spectrum following the development of the second exoemission peak, and (d) the spectrum following a long exposure to oxygen. We can see that following the first peak there is no change in the AES spectrum whereas following the second peak the spectrum changes substantially.

DISCUSSION

The present results demonstrate several points. It is possible to obtain exoemission from a clean annealed single crystal. This rate of emission is dependent on the arrival rate of oxygen atoms at the surface. The current can be obtained when there is no light present to stimulate emission. There is a structure to the emission curves (two peaks) indicating that more than one process may be occurring. Emission occurred from a strain free surface (magnesium) but did not occur from an ion-bombardment damaged surface (aluminum).

Similar results have been observed by Gesell, et. al. (4) although not for a strain free surface. Gesell exposed both abraded and evaporated films of magnesium and aluminum to oxygen. Gesell also observed two peaks and the arrival rate dependence for electron emission on magnesium and also obtained a negative result with aluminum. Kasemo (5) exposed clean aluminum and magnesium to oxygen but looked at the emitted light rather than the emitted electrons. He observed photon emission from both aluminum and magnesium and also observed the oxygen arrival rate dependence of the photon emission. In addition, he observed that light emission occurred at two photon energies for each element upon dispersive analysis.

The primary purpose of this study was to demonstrate exoelectron emission from a clean annealed single crystal of magnesium with modern surface research tools that enable characterization of the surface. The specific emphasis was to determine whether electron emission would occur from a strain free surface in order to determine the relevance of exoemission to tribology. It was found that electron emission could be entirely chemically induced with no surface strain needed. It is of interest, therefore, to discuss these results in terms of possible physical mechanisms for the emission and to point out necessary experiments that should be performed in order to clarify these mechanisms. The present results will be discussed in terms of previously proposed models and other possible mechanisms. The primary result of this paper, exoemission with no strain or photon stimulation, suggests a chemical interpretation for the process. This proposal was suggested as an explanation for exoemission in References 1, 2, 4-7. The basis for this mechanism is that if the heat of formation of the compound, e.g., MgO is greater than the work function of the metal, sufficient energy is available from the reaction to eject an electron from the metal upon adsorption. Another possibility for

7

the emission involves the heat of chemisorption as distinct from the heat
of reaction being transferred to an electron in the conduction band of
the metal. In fact, the process could involve an interaction similar to
an Auger process (10). If the binding state of the adsorbed atom is
sufficiently lower in energy than the top of the conduction band of the
metal, a direct transfer of an electron from the metal to the binding state
of the atom may occur. The excess energy may then be absorbed by another
electron in the conduction band of the metal and result in the emission of
that electron. The electron transfer also may result in the complementary
process, the direct emission of a photon (fluorescence yield) (10). The
latter process could be an explanation for Kasemo's results (5).

If we examine the present results in terms of the heat of reaction of
the compounds involved, we find that MgO has a heat of formation of
6.2 eV/atom of oxygen, Al_2O_3 has a heat of formation of 5.77 eV/atom of
oxygen and $MgCl_2$ has a heat of formation of 3.33 eV/atom of chlorine (11).
The work functions of polycrystalline Mg and Al are 3.66 eV and 4.19 eV (12),
respectively. These results would suggest that exoemission is energetically
possible for Al and Mg exposed to oxygen but not for Mg exposed to chlorine.
The experimental observations are that Mg exposed to oxygen or chlorine
produces exoelectrons whereas Al exposed to oxygen does not. The oxygen
on Mg and Al observations agrees with those of Gesell (4). Kasemo (5)
observed photon emission from both Mg and Al upon oxygen adsorption,
however, photon emission doesn't suffer from the same work function
restriction as electron emission and could explain the difference. If
we consider Mg reacting with chlorine, the molecular form of the compound
is $MgCl_2$. Therefore, if the chlorine interacts directly as two atoms,
6.66 eV of energy are available--which is sufficient to remove an electron
from the solid.

8

We should emphasize that the interaction of aluminum with oxygen demonstrates an energy argument by itself is insufficient to predict exoemission. It was pointed out earlier that the current emitted depended upon the arrival rate of oxygen atoms at the surface. Therefore, the sticking coefficient of atoms to the surface determines the rate of inter- action with an incident gas for a given pressure. Fluggel, et. al. (13) found that it takes an exposure six times greater for Al than for Mg to form a monalayer film which they define as the point at which the uptake of oxygen dropped to approximately zero. We can conclude from these results that the oxygen sticking coefficient to Al is substantially lower than to Mg and thus a higher pressure is needed for aluminum in order to obtain comparable emission current. Unfortunately, in the present study interaction of oxygen with the ionization gauge and with the ion pump produce currents which obscure the exoemission currents in the 10^{-4} N/m^2 (10^{-6} torr) pressure range. In addition, the present detection scheme which was similar to Gesell's (4) was limited in sensitivity because of signal to noise problems to about 1×10^{-13} amps. Other experimenters (1, 2) used electron multipliers for detection. However, in the event that the emission from aluminum is present but below detection sensitivity, it is necessary to explain why on the basis of a chemical model why emission from aluminum is so much lower than emission from magnesium.

A second and probably additional consideration of importance with aluminum is the work function change with adsorption relative to magnesium. Agarwala and Fort (14) observe maximum work function decreases of approximately -.5 eV upon adsorption of oxygen on aluminum using a vibrating capacitor method. Gesell and Arakawa (15) obtained a work function change of -1.8 ev for oxygen

9

adsorbed on Mg using photoemission. It is possible that if all of the energy from . .ats of reaction is not available that the lower work function of Mg would permit emission whereas the higher work function of Al would not. Finally, with regard to the chemical binding upon chemisorption mechanism, Lang and Williams (16) report that the oxygen aluminum binding state exists at -5.4 eV--a level not sufficiently low for the Auger emission of an electron upon binding. Unfortunately, a comparable calculation doesn't exist for Mg but the trend should be towards tighter binding which, coupled with the lower work function, should give higher emission. Therefore, there are a number of plausible reasons for the lack of emission from aluminum. It is likely that a combination of these effects is responsible for the lack of emission. Exoemission from aluminum has been observed under conditions where surfaces have been strained (1). It is conceivable that the work function change could be reduced by strain resulting in the emission of electrons. Therefore, exoemission may yet be of importance in tribology experiments regarding strain and is certainly of importance regardir chemical interactions with lubricants.

The results for Mg exoemission could result from either adsorption or chemical reaction or both as pointed out. The emission curves have some interesting features. First, that the emission could be stopped and restarted by pumping out, then reintroducing oxygen into the vacuum system with emission continuing from the point where it was stopped. This result indicates that a stable change has occurred on the surface solely from adsorption which affects subsequent emission. The second feature of interest is the existence of two peaks in the emission curves. Gesell (4), who observed the same features, explained them in terms of two work function minima which occurred during oxygen exposure (14). In the present study the

10

oxygen exposure was stopped after the establishment of the first peak and
a low energy AES spectrum taken then oxygen was reintroduced and an AES
trace taken after the formation of the second peak, and finally an AES
spectrum after a long oxygen exposure was taken. This data is shown in
Fig. 6. It is known that upon oxidation the low energy magnesium peak
shifts its position from 45 eV to 34 eV (17). We can see that after the
first exoemission peak no change from the clean AES spectrum occurs; after
the second, a considerable change occurs showing a growth of the oxidized
magnesium peak and a decrease of the clean magnesium peak. The results for
a long oxygen exposure are included for comparison. This result suggests
that the first peak may be a result of pure chemisorption, and the second
may represent nucleation of the oxide. This result is not necessarily in
conflict with Gesell's observations (15). In addition, Kasemo (5) observes
photons of two distinct energies being emitted which suggests two different
energetic processes occurring.

This study points out the difficulties involved in performing an
exoemission study and arriving at a complete quantitative model for the
phenomenon. The studies must be performed in vacuum systems where surface
conditions can be controlled. It is necessary to have the proper analytical
tools to establish the state of the surface. It will be necessary to know
the variation in work function of both the emitting and collecting surfac.s
as a function of coverage. The sticking coefficient as a function of
coverage must also be determined. The energy distributions of emitted
electrons must be known in order to establish what processes are occurring.
The conditions will then have to be folded into an analytical model. Finally,
the effects of varying gases and materials must be known. These studies

will be pursued in the future. Exoelectron emission has the potential of providing important information about surface chemistry and reactions and should be an active area for research both in lubrication and in understanding surface chemical reactions.

CONCLUDING REMARKS

Exoelectron emission has been observed on a clean well-annealed Mg single crystal upon exposure of the surface to both oxygen and chlorine. This result establishes that the emission is of chemical origin and not from surface strain. The dependence of the emission on oxygen arrival rate and surface state has also been demonstrated. No emission from aluminum has been observed and an explanation for this lack of emission based on sticking coefficient, work function change and adsorption binding states has been offered. Some mechanisms for exoelectron emission in terms of heats of formation of compounds and Auger processes involving chemical binding states have been offered.

REFERENCES

1. F. R. Brotzen, "Emission of Exoelectrons from Metallic Materials",
    Phys. Stat. Sol. 17, 9-30 (1967).

2. L. N. Larikov and L. M. Baklanova, "Exoelectronic Emission from Metal
    Surfaces/Review/", Metallotizka 50, 3-23 (1974).

3. W. J. Baxter and S. R. Rouze, "Photoemission Electron Microscopy of
    Oxide Fracture at Slip Steps on Metals", J. Appl. Phys. 46, 2429-2432
    (1975).

4. T. F. Gesell, E. T. Arakawa and T. A. Callcott, "Exoelectron Emission
    During Oxygen and Water Vapor Chemisorption on Fresh Magnesium Surfaces",
    Surf. Sci. 20, 174-178 (1970).

5. B. Kasemo, "Photon Emission During Chemisorption of Oxygen on Al and Mg
    Surfaces", Phys. Rev. Lett. 32, 1114-1117 (1974).

6. N. Moucharatieh and J. Olmsted III, "Chemiemission from the Cesium-Oxygen
    Surface Reaction", J. Phys. Chem. 75, 1928-1936 (1971).

7. J. J. Uebbing and L. W. James, "Behaviour of Cesium Oxide as a Low Work
    Function Coating", J. Appl. Phys. 41, 4505-4516 (1970).

8. J. Ferrante, D. H. Buckley, S. V. Pepper and W. A. Brainard, "Use of LEED,
    Auger Emission Spectroscopy and Field Ion Microscopy in Microstructural
    Studies", Published in "Microstructural Analysis: Tools and Techniques",
    Eds. J. L. McCall and W. M. Mueller, Plenum Press, (1973) pp. 241-279.

9. F. G. McRae, "Diffraction Effects in Low-Energy Electron Emission",
    Surf. Sci. 44, 321-336 (1974).

10. E. S. Burhop, "The Auger Effect", Cambridge University Press, (1974)
    pp. 1-22.

11. A. Glassner, "Thermochemical Properties of the Oxides, Flourides and Chlorides to 2500° R", Argonne National Laboratories Publication ANL-5750, (1957).

12. N. D. Lang and W. Kohn, "Theory of Metal Surfaces: Work Functions", Phys. Rev. B. $\underline{3}$, 1215-1223 (1971).

13. J. C. Fluggel, L. M. Watson, D. J. Fabian and S. Affrossman, "X-Ray Photoelectron Studies of the Reaction of Clean Metals (Mg, Al, Cr, Mn) with Oxygen and Water Vapor", Surf. Sci. $\underline{49}$, 61-76 (1975).

14. V. K. Agarwala and T. Fort, "Effect of Pressure and Temperature on Changes in the Work Function of Aluminum During Interaction with Oxygen", Surf. Sci. $\underline{48}$, 527-536 (1975).

15. T. F. Gesell and T. Arakawa, "Work Function Changes During Oxygen Chemisorption on Fresh Magnesium Surfaces", Surf. Sci. $\underline{33}$, 414-421 (1972).

16. N. D. Lang and A. R. Williams, "Self-Consistent Theory of the Chemisorption of H, Li and O on a Metal Surface", Phys. Rev. Lett. $\underline{34}$, 531-534 (1975).

17. M. Suleman and E. B. Pattinson, "Changes in Auger Spectra of Mg and Fe Due to Oxidation", Surf. Sci. $\underline{35}$, 75-81 (1973).

FIGURE TITLES

1. Schematic Diagram of LEED-AES Apparatus with Inset Showing Exoemission Electrical Schematic

2. AES Spectrum of Magnesium Surface (a) Following Cleaning and Annealing at 300° C (b) Following Exposure of the Surface to Oxygen 6.5×10^{-3} N-sec/m^2 (50 Langmuir)

3. LEED Pattern of the Magnesium Surface Following Cleaning and then Annealing at 300° C (Beam Energy = 91 eV)

4. Exoemission from Magnesium During Exposure to Oxygen at 8×10^{-5} N/m^2 (6×10^{-7} torr)

5. Exoemission from Magnesium During Exposure to Oxygen at 1.3×10^{-5} N/m^2 (1×10^{-7} torr). Exposure was stopped after 15 sec. and reinitiated at 80 sec.

6. Low Energy AES Spectrum of Magnesium (a) Cleaned and Annealed (b) After Formation of the First Exoelectron Peak (c) After Formation of the Second Exoelectron Peak (d) After Long Oxygen Exposure

Fig. 1

E-8599

Fig. 2

Fig. 3

Fig. 4

Fig. 5

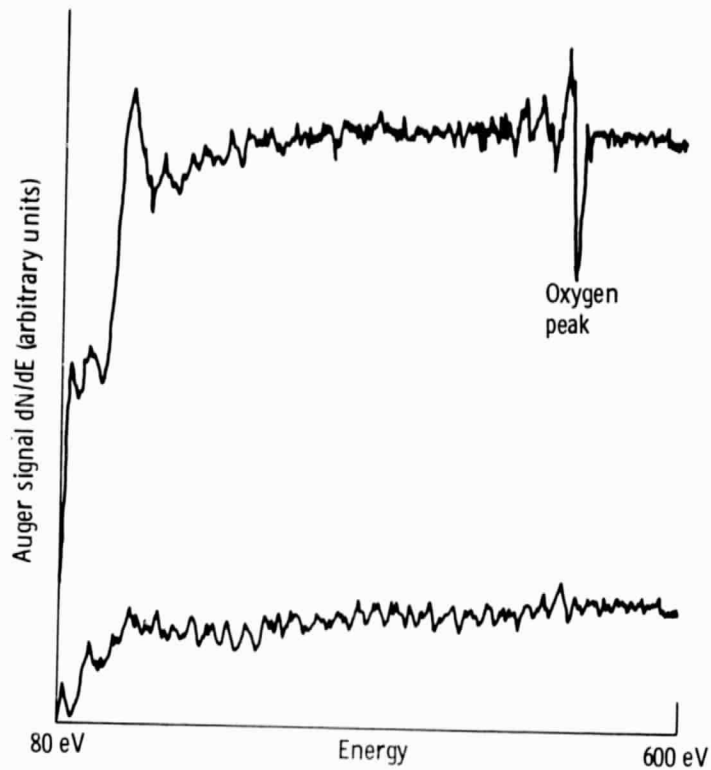Fig. 6