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September 10, 1965

Representative
National Aeronautics and Space Administration
Post Office Box 5700
Bethesda, Maryland

Dear Sir:

Subject: Contract NASw-1203, "A Study of the Blistering of Metal Surfaces by Solar System Ions"

In accordance with the terms of the subject contract, enclosed are two copies and one reproducible master of the first quarterly progress report for the period ending July 14, 1965.

Very truly yours,

Michael I. Gamble, Manager
Environmental Physics Programs

MIG:nvm

Enclosures (3)

[redacted]

August, 1965

First Quarterly Progress Report
For Period Ending July 14, 1965
Contract NASw-1203

AVCO/Tulsa Document TR 65-363-1

"A Study of the Blistering of Metal Surfaces
by Solar System Ions"

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AVCO CORPORATION
TULSA DIVISION

Contract NASw-1203

ABSTRACT

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Single crystal samples of pure aluminum were irradiated in vacuum with 30, 50 and 70 Kev protons at different total fluxes. The objective was to define optimum parameters for oxide film removal with no residual blistering of the surface. Results were not consistent, thus indicating probable variation of oxide layer thickness. Two pure polycrystalline gold samples were irradiated, one with 15 Kev protons and one with 100 Kev protons. No surface blistering was noted on these samples.

I. INTRODUCTION

Several single crystal samples grown from 99.999 percent pure aluminum ingot were irradiated with protons in an energy range of 30 Kev to 70 Kev and at different total fluxes. These tests were run in an effort to define optimum values of irradiation parameters for removal of surface oxide layers. The tests were in concurrence with Step A-1 of the proposed surface film studies as described in Section II of this report.

The results of these tests were not consistent with those from the previous year's work in which oxide removal occurred consistently for samples irradiated with 50 Kev protons. The most probable conclusion is that the thickness of the oxide layer on the present samples differs from that of the previous ones and is not even consistent between samples.

Two samples of 99.999 percent pure polycrystalline gold were irradiated, one with 15 Kev protons and one with 100 Kev protons. The surfaces of these samples were prepared by electropolishing and were badly etched. Surface changes occurred on both samples which were visible to the naked eye. Microscopic examination showed the surface of the sample irradiated at 15 Kev to be sputtered and darkened, whereas the change at the higher energy appeared only as a darkening of the surface. The only result of high temperature annealing of these samples was elimination of the darkening.

Monthly conferences have been scheduled alternately at AVCO/Tulsa and at the University of Oklahoma to improve communication on this project.

II. PROPOSED SURFACE FILM STUDIES

The role (or roles) of surface films appears to be of basic importance to the study. Initial efforts in the continued study were therefore to be aimed at defining the effects of this parameter according to the following schedule:

A. Aluminum Samples

Studies were to be continued initially with 99.999 percent pure aluminum. All irradiations would, as always, be conducted with the sample in ultra-high vacuum, and samples would be water cooled as in previous tests.

1. Two samples were to be irradiated with 50 Kev protons, one with a total flux of 10^{16} p/cm^2 and the other with a total flux of 10^{17} p/cm^2. This latter condition had previously produced surface cleaning. The samples were to be removed and analyzed for completeness of oxide film removal, spontaneous blistering, or blistering during high temperature annealing. This step was to be repeated at different total fluxes and proton energies to determine optimum values of these parameters for oxide film removal without blister production. Sample preparation techniques were to be held constant throughout this and subsequent tests and measurements by interference techniques were to be made at the boundary of the cleaned areas to determine uniformity of film thickness.

2. A pair of samples were to be placed in the chamber. The surface of one of these would be cleaned as determined in Step 1. Both samples would then be irradiated with 10^{17} p/cm^2 using 100 Kev protons. The samples would then be removed and investigated for blister appearance during air annealing. Blistering should occur on the uncleaned sample as indicated by our previous studies. Failure of the cleaned sample to blister, or greatly reduced blistering, would indicate a proton energy effect in that depth of penetration of the protons is sufficiently great to reduce deformation of the surface. Prolonged heating or annealing at higher temperatures might produce some blistering under these conditions. If blistering occurred readily on the pre-cleaned surface, even though different in appearance than for the uncleaned sample, this might indicate that proton

penetration is not too great a factor, at least within limits, but the surface film may still be necessary to blistering; e.g., blistering may occur only in the surface film.

3. To check the latter possibility, another pair of samples were to be installed in the chamber and the irradiations conducted as in Step 2. These samples would be annealed in situ to minimize reforming of an oxide layer after the initial cleaning. The samples would then be removed for analysis. Failure of blistering to occur on the clean sample under these conditions would indicate that it is the surface film that usually blisters, or that proton penetration has been too deep into the aluminum. Blistering might indicate that the oxide film is not necessary to the phenomenon except, perhaps, in limiting proton penetration.

4. To eliminate the factor of proton penetration, Steps 2 and 3 were to be repeated with the exception that, after cleaning, the one sample would be irradiated with protons of reduced energy such that penetration into the clean aluminum would be essentially the same as for 100 Kev protons after passing through the oxide layer. The uncleaned sample would be irradiated with 100 Kev protons as a control test. If blistering of the cleaned sample readily occurred during air annealing and did not in Step 2, then proton penetration into the aluminum must be an important factor. If blistering occurred during air anneal but not when annealing was conducted in situ, this strongly suggests that only the surface films are blistering.

B. Gold Samples

Gold samples of 99.999 percent purity were to be irradiated with 100 Kev and 10 Kev protons using total fluxes of 10^{16}, 10^{17}, and 10^{18} protons/cm^2 at each energy. The samples would subsequently be examined for spontaneous blister formation and for blister formation during annealing. The results of these studies were to be correlated with those for the aluminum samples.

III. SUMMARY OF SAMPLE TREATMENTS

A. Aluminum Samples

Eight samples of pure single crystal aluminum were irradiated with protons in an effort to define optimum values of energy and flux for oxide film removal as described under Section II, A-1. Irradiation parameters are tabulated below. Sample numbers are sequential with the previous year's work to eliminate confusion.

Sample No.	Proton Energy	Flux Rate ($p/cm^2/sec \times 10^{12}$)	Total Flux ($p/cm^2 \times 10^{17}$)	Sample Temp. °C
26	50	2.0	0.1	15
27	50	11.0	1.0	15
28	50	11.0	2.0	15
29	50	11.0	0.5	15
30	50	11.0	1.0	15
31	50	5.5	1.0	15
32	30	11.0	1.0	15
33	70	11.0	1.0	15

Sample No. 26 exhibited no change prior to heat treatment. After five minutes at 250° C a slight difference in reflectance could be observed in the irradiated area under high illumination with the naked eye.

Sample No. 27 exhibited a darkening of the irradiated area before heat treatment. After five minutes at 250° C the area became darker and some oxide removal appeared to have occurred in very small scattered areas. An additional five minutes of annealing produced no further changes.

After irradiation, and prior to annealing, Sample No. 28 exhibited two lines along the length of the irradiated area at the edges. These lines appeared to be due to oxide removal resulting in a lowering of the surface level with respect to the surrounding area. No free microscopic oxide particles were on the surface, thus indicating that removal may have occurred due to sputtering. After five and ten minute intervals at 250° C, no change occurred.

Prior to annealing, Sample No. 29 exhibited complete oxide removal along one-third of the irradiated diameter nearest one edge of the sample with many microscopic pieces of oxide lying in the vicinity. Nothing was observed on the remainder of the sample. After annealing for five and ten minute intervals at 250° C, no changes occurred.

Nothing was observed on Sample No. 30 prior to heat treatment, nor after five minutes at 250° C. After five minutes at 300° C, a fine blistering occurred in the irradiated area.

The results for Sample No. 31 were identical with those for Sample No. 30, which was irradiated at the same 50 Kev energy but at twice the rate.

Observation of Sample No. 32 prior to annealing revealed relatively large irregular areas on the irradiated diameter where the oxide was cracking along various planes of its crystal structure and was lifting off the surface of the substrate. This appeared to be the first stage of the oxide removal for which we were looking and which had previously occurred for 50 Kev protons. No change had occurred in the surface following a five minute air anneal at 250° C. Further annealing for five minutes at 300° C produced a darkening of the irradiated area and some blisters similar in size and form to those on Samples No. 30 and 31 and previous samples.

Sample No. 33 exhibited a darkening of the irradiated area, as viewed under the microscope, prior to annealing. No change occurred during a five minute anneal at 250° C. An additional five minute anneal at 300° C produced a fine blistering in the irradiated area.

B. Gold Samples

Two samples of 99.999 percent pure polycrystalline gold were prepared by electropolishing the surfaces. This resulted in rather deep etching of the surface. The samples were irradiated with protons according to the following schedule:

Sample No.	Proton Energy	Flux Rate ($p/cm^2/sec \times 10^{12}$)	Total Flux ($p/cm^2 \times 10^{17}$)	Sample Temp. °C
34	15	11	1.0	15
35	100	11	1.0	15

Examination of the irradiated area of Sample No. 34 with a microscope prior to annealing revealed that the area had been sputtered as evidenced by a lowering of the surface level. In addition, there was some darkening of the irradiated area. The only change produced by air annealing of the sample was that the area no longer appeared darkened.

Sample No. 35 exhibited no noticeable change other than a darkening of the surface in the irradiated area prior to annealing. Again, the only change which occurred during annealing was to eliminate the darkening.

IV. DISCUSSION OF OBSERVATIONS

The tests on the aluminum samples failed to produce results in agreement with the previous tests where irradiation with 50 Kev protons produced oxide removal. In addition, differences occurred between samples irradiated under virtually the same conditions. The conclusion from this was that the thickness and perhaps other characteristics of the oxide layers differed from one sample to the next. It was decided to postpone further tests with the aluminum pending establishment of a method for determining oxide layer thickness prior to the irradiation of the samples.

The tests with the gold samples were somewhat inconclusive. The badly etched condition of the sample surfaces made examination of the surfaces difficult. However, no indication of blistering of the surface was noted either before or after annealing.

V. PLANS FOR SECOND QUARTER

Tests will continue on gold samples, including solid polycrystalline samples and samples of evaporated layers of gold on aluminum. Initial tests with the solid gold samples will be with machined finishes to eliminate the etching problem associated with electropolishing. Consideration will be given to purchasing single crystal samples of gold for future tests.

The feasibility of measuring oxide layer thicknesses on aluminum samples prior to irradiation by use of interference or ellipsometric techniques will be studied. This should provide a means of selecting samples with consistent and uniform oxide layers with which to continue the tests.

Design and fabrication of a vacuum furnace by AVCO/Tulsa for crystal growing will be completed in the second quarter. This should minimize the possibility of impurity contribution by the furnace, which we suspect with current equipment.