N93-28272

SURFACE CHARACTERIZATION OF SELECTED LDEF TRAY CLAMPS

T.F. Cromer, H.L. Grammer and J. P. Wightman
Virginia Polytechnic Institute and State University
Department of Chemistry
Blacksburg, VA 24061
Phone: 703/231-5854 Fax: 703/231-3971

P.R. Young and W.S. Slemp
NASA Langley Research Center
Hampton, VA 23665-5225
Phone: 804/864-4265 Fax: 804/864-8312

SUMMARY

The surface characterization of chromic acid anodized 6061-T6 aluminum alloy tray clamps has shown differences in surface chemistry depending upon the position on the LDEF. Water contact angle results showed no changes in wettability of the tray clamps. The overall surface topography of the control, trailing edge(E3) and leading edge(D9) samples was similar. The thickness of the aluminum oxide layer for all samples determined by Auger depth profiling was less than one micron. XPS analysis of the tray clamps showed significant differences in the surface composition. Carbon and silicon containing compounds were the primary contaminants detected.

INTRODUCTION

One of the tasks of the MSIG (Materials Special Investigation Group) is the detailed analysis of the chromic acid anodized 6061-T6 aluminum alloy tray clamps. These tray clamps were located at regular intervals over the entire LDEF frame and were exposed to varying amounts of atomic oxygen and vacuum ultraviolet radiation.

A detailed study of the relatively small but statistically significant changes in the optical properties of 228 anodized clamps has been reported [1]. However, there has been no systematic study reported of the effect of low-earth orbit (LEO) environment on the surface chemistry of these clamps.

The objective of this work was to document changes in the surface chemistry of tray clamps taken from different locations on LDEF. Surface characterization of the anodized aluminum clamps using contact angle measurements, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Auger electron spectroscopy (AES), and x-ray photoelectron spectroscopy (XPS) is reported.

EXPERIMENTAL

The surface analytical techniques used in the characterization of the surface of the seven anodized aluminum tray clamps (control and six flight) are described below. Tray clamps were cut manually to prevent heating of the sample as well as possible contamination of the surface when cutting. Typical sample sizes were 13mm x 13mm. Surface characterization techniques were used in the following order due to the nondestructive/destructive aspects of the analyses: XPS, SEM/EDS and AES. Water contact angle measurements were made to evaluate the wettability of the aluminum surface using a Rame-Hart 100-00115 NRL goniometer equipped with a video monitor. Different samples were used for the contact angle measurements.

Surface topography was examined by scanning electron microscopy using an ISI-SX-40 microscope operating at 20kV beam voltage. Near surface/bulk (1-5mm) elemental analysis was performed using a Tracor Northern energy dispersive spectrometer. Auger electron spectroscopy-depth profiling was performed on a Perkin-Elmer PHI-610 spectrometer operating at an electron beam voltage/current of 3kv/0.05mA and an argon ion beam voltage/current of 4kV/20mA. X-ray photoelectron spectroscopy was performed utilizing a Perkin-Elmer PHI 5400 spectrometer equipped with a Mg Ka X-ray source (1253.6eV), operating at 15kV/120mA.

The flight samples were located at the following positions on the LDEF: E3 (trailing edge), B4 (near trailing edge), D7 (near leading edge), D9 (leading edge), H9 (space end), and G2 (earth end).

RESULTS/DISCUSSION

Contact Angle

Water contact angle measurements were used to evaluate the wettability of the clamp surface. The results are listed in Table I. An average water contact angle of 62° was calculated for the seven samples independent of location. The high water contact angles on the clamps are indicative of low energy surfaces such as polymers [2]. A near zero contact angle would be expected for a clean anodized aluminum surface [3]. As shown by the results, no changes in wettability of the clamps were observed due to exposure to the low-earth orbit environment.

Scanning Electron Microscopy/Energy Dispersive Spectroscopy

SEM photomicrographs of the control, leading (D9) and trailing (E3) edge samples are shown in Figure 1. The overall surface topography of the three samples is similar. No significant change in the surface topography was evident for the leading compared to the trailing edge samples.

Energy dispersive spectroscopy(EDS) is a near surface/bulk elemental analysis technique. The EDS results for the tray clamps are listed in Table II. An average composition of fifty-two weight percent aluminum and forty-eight weight percent oxygen was determined for the three samples. These results are consistent with the calculated weight percent of aluminum(53%) and oxygen(47%) for Al_2O_3. Aluminum and oxygen were the only elements detected by EDS in the sampling depth of 1-5mm.

Auger Electron Spectroscopy

Auger depth profiling was used to determine the thickness of the oxide layer on five of the clamps. The depth profile of the space end (H9) sample is shown in Figure 2 which is representative of the other samples. The thickness of the aluminum oxide layer was calculated at the time when the oxygen and aluminum signals cross. Aluminum with an oxide layer of known thickness was used as a standard to determine the sputtering rate. Aluminum oxide thickness values are listed in Table III. The average thickness of 0.82 mm is consistent with the results of Plagemann [1] who concluded from SEM measurements that the oxide thickness was <1mm. The range in oxide thickness from 0.6 to 1.0 mm for the trailing edge (E3) and space end (H9) samples respectively can not be attributed to the LEO environment but in fact may be a result of variation in the anodization conditions.

X-Ray Photoelectron Spectroscopy

The XPS results shown in Table IV for the LDEF tray clamps are reported as binding energy (B.E.) in eV and atomic concentration (A.C.) in %. All photopeaks were referenced to the C 1s photopeak taken at 285.0 eV. The largest amount (53%) of carbon-containing organic contamination was detected on the control sample. However, significant quantities of this same contamination were found on all the LDEF tray clamps. There is no discernible correlation of the surface atomic concentration of carbon with clamp position. This carbon contamination as determined by XPS is indicative of a hydrophobic surface and is consistent with the high water contact angles determined on the same surfaces (see Table I). If the control surface were clean, the expected atomic concentration of aluminum and oxygen for a 1mm aluminum oxide (Al_2O_3) surface layer would be 40% and 60% respectively; and, the O/Al atomic concentration ratio would be 1.5. The fact that the atomic concentration of aluminum is only 11% is prima facie evidence that an ultra-thin layer of carbon-containing organic contamination covers the aluminum oxide surface. The thickness of these contamination layers cannot be more than 5 nm otherwise no aluminum signal would have been detected. The fact that the O/Al ratio is nearly 3 also suggests that this contamination layer contains oxygen in addition to carbon. It is recognized that some of the excess oxygen is probably associated with the silicon which was also detected on the control sample. The sources of the small quantities of nitrogen, sulfur and sodium detected on the control sample were not identified.

It is noteworthy that the silicon content of all flight samples exceeded that of the control sample form 4 to 16 times. Thus, these XPS results further support the case for extensive silicon contamination of the LDEF clamps [4]. Again, there was no discernible correlation of the surface atomic concentration of silicon with clamp position. On the other hand, there was definitive shift in the binding energy of silicon on the clamps (D7, D9, H9,G2) which received a higher atomic oxygen fluence compared to those clamps (E3, B4, control) receiving a lower atomic oxygen fluence. This definitive shift in binding energy of $1.1_8 \pm 0.1_7$ correlates to a change in the state of silicon contamination. The organo-silicon (lower B.E.) material contained in the contamination on the clamps subjected to a higher atomic oxygen fluence was converted to an inorganic-silicon (higher B.E.) or silicate type material. Such an effect of atomic oxygen on organo-silicon material has been noted previously [5].

The fluorine contamination detected on all the flight samples is in the form of inorganic fluorine (fluoride) with a binding energy of 686 eV. In contrast, the binding energy of fluorine in a fluoropolymer is approximately 689 eV. The fluorine contamination present in the ion

form may be a result of the degradation effects of vacuum ultraviolet radiation on the carbon-fluorine bonds of fluoropolymers such as fluoroethylene propylene copolymer (FEP) on the backside of the satellite.

Trace amounts of sulfur, nitrogen and sodium contamination were present on the majority of the flight samples as well as the control. The source of the contamination may be a result of preflight or post flight handling.

ACKNOWLEDGEMENTS

The authors (T.F.C., H.L.G. and J.P.W.) acknowledge the support of this research under NASA Grant NAG-1-1186.

REFERENCES

[1] Walter L. Plagemann: *Space Environmental Effects on the Integrity of Chromic Acid Anodized Coatings.* LDEF 69 Months in Space First Post-Retrieval Symposium, NASA CP-3134, Part 2, p. 1023-1040, Jan. 1992.

[2] M. Yekta-Fard and A.B. Ponter, *J. Adhesion Sci. Technol.*, 6, 253 (1992).

[3] William C. Wake, *Adhesion and the Formulation of Adhesives* (Applied Science Publishers, NY 1982) p. 52.

[4] E.R. Crutcher and K.J. Warner: *Molecular Films Associated with LDEF.* LDEF 69 Months in Space First Post-Retrieval Symposium, NASA CP-3134, Part 1, p. 155-177, Jan. 1992.

[5] B.A. Bank, Joyce A. Dever, Linda Gebauer and Carol M. Hill: *Atomic Oxygen Interactions with FEP Teflon and Silicones on LDEF.* LDEF 69 Months in Space First Post-Retrieval Symposium, NASA CP-3134, Part 2, p. 801-816, Jan. 1992.

TABLE I

WATER CONTACT ANGLES ON LDEF TRAY CLAMPS

SAMPLE LOCATION	θw
Control	61°
E3	64°
B4	66°
D7	63°
D9	66°
H9	63°
G2	54°

TABLE II

ENERGY DISPERSIVE ANALYSIS OF LDEF TRAY CLAMPS

SAMPLE	ALUMINUM (wt%)	OXYGEN (wt%)
Control	54.	46.
E3	53.	46.
D9	49.	50.

TABLE III

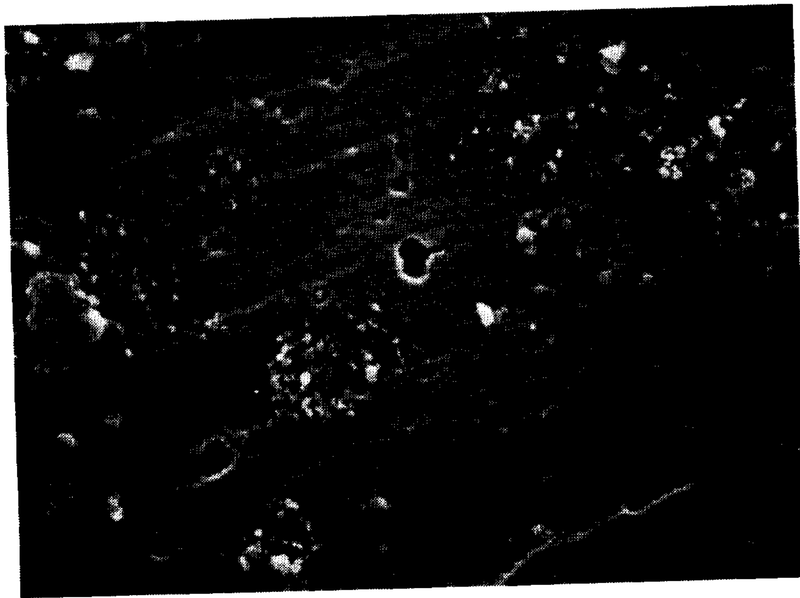
THICKNESS OF OXIDE LAYER ON LDEF TRAY CLAMPS

SAMPLE	τ(nm)
Control	785
E3	1005
D9	865
H9	765
G2	665

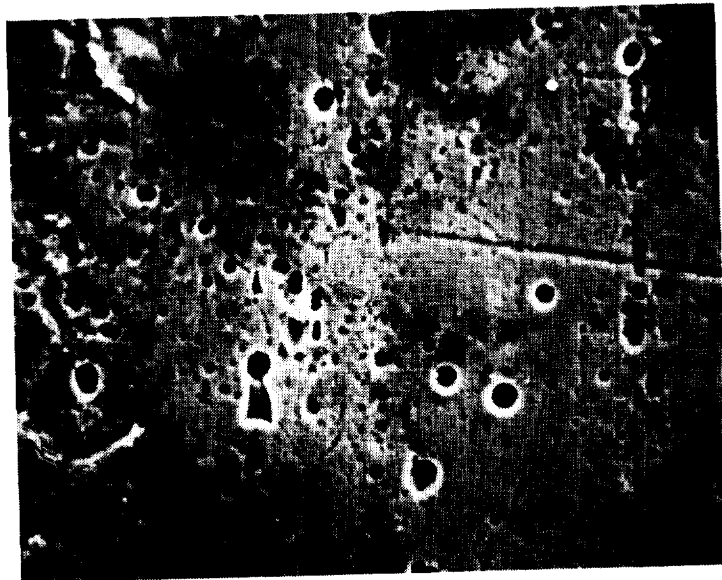
TABLE IV

XPS ANALYSIS OF LDEF TRAY CLAMPS

	SAMPLES						
PHOTOPEAKS	Control	E3	B4	D7	D9	H9	G2
C1s A.C. (%)	53.2	27.8	28.0	16.5	20.7	16.6	30.0
B.E. (eV)	285.0	285.0	285.0	285.0	285.0	285.0	285.0
Al2p	11.4	17.6	15.8	17.0	4.9	15.8	8.2
	74.6	74.7	74.6	74.6	74.8	74.6	74.7
O1s	31.0	46.8	47.2	53.4	51.1	52.4	43.5
	532.2	532.3	533.1	532.4	533.0	532.5	532.6
Si2p	1.4	6.0	6.1	10.5	22.6	11.0	13.1
	102.2	102.1	102.2	103.2	103.6	103.3	103.4
N1s	1.8	0.6	1.3	0.3	--	0.3	1.4
	399.9	400.2	400.2	400.6		400.1	400.4
S2p	0.6	0.3	0.4	0.3	--	0.9	--
	169.0	169.5	169.6	169.6		169.5	
Na1s	0.7	0.6	0.7	0.7	--	1.4	1.5
	1072.2	1072.8	1073.0	1072.8		1072.9	1072.7
F1s	--	0.3	0.5	1.5	0.7	1.5	2.4
		686.3	686.4	686.1	686.5	686.5	686.6



CONTROL 0.5 KX



E3 0.5 KX

FIGURE 1: SEM PHOTOMICROGRAPHS OF LDEF TRAY CLAMPS.

D9 0.5 KX

FIGURE 1: CONCLUDED.

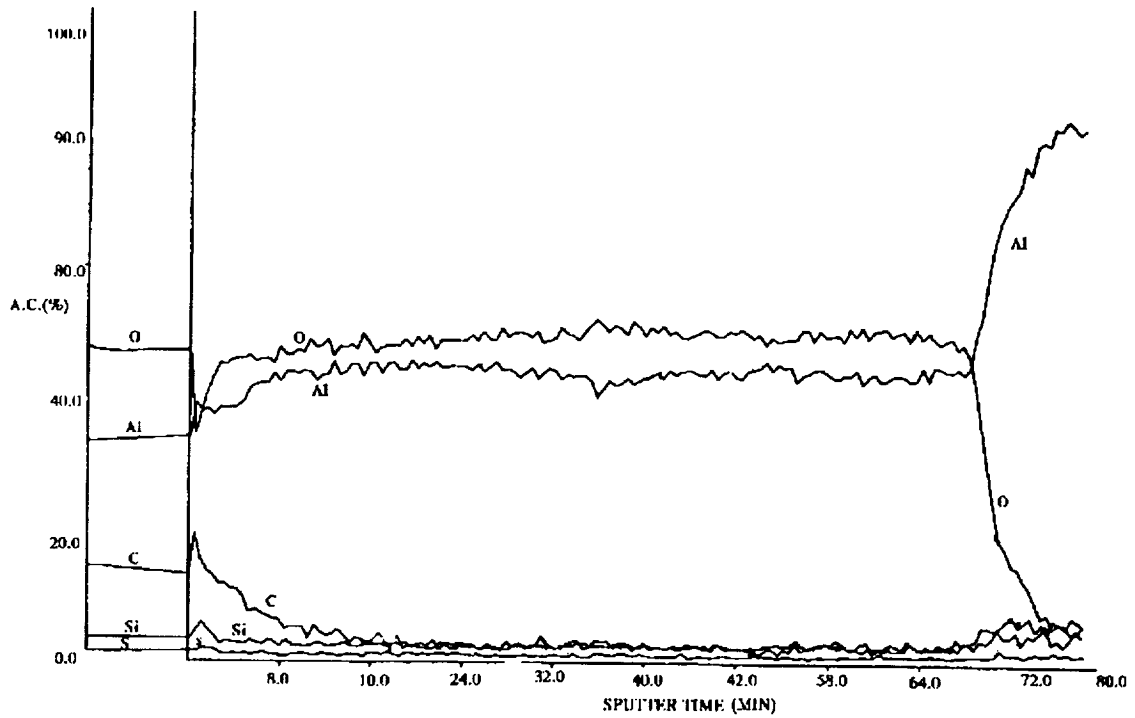


FIGURE 2: AUGER DEPTH PROFILE OF LDEF TRAY CLAMPS.