

SOME RESULTS OF THE OXIDATION INVESTIGATION OF COPPER AND SILVER SAMPLES FLOWN ON LDEF

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INTRODUCTION

The LDEF mission provides a unique opportunity to study the long term effects of the space environment on materials. The LDEF has been deployed in orbit on 7 April 1984 by the shuttle Challenger in an almost circular orbit with a mean altitude of 477 km and an inclination of 28.5°. It was retrieved from its decayed orbit of 335 km by the shuttle Columbia on 12 January 1990 after almost 6 years in space.

The LDEF is a 12-sided, 4.267 m diameter and 9.144 m long structure. The experiments, placed on trays, are attached to the twelve sides and the two ends of the spacecraft. The LDEF was passively stabilized with one end of the spacecraft always pointing towards the earth centre and one of the sides (row 9) always facing the flight direction.

The materials investigated in this paper originate from the Ultra-Heavy Cosmic Ray Experiment (UHCRE). The main objective of this experiment is a detailed study of the charge spectra of ultraheavy cosmic-ray nuclei from zinc to uranium and beyond using solid-state track detectors. Besides the aluminium alloy used for the experiment, UHCRE comprises several other materials. The results of space exposure for two of them, the copper grounding strips and the thermal covers (FEP Teflon/Ag/Inconel) painted black on the inner side (Chemglaze Z306), will be presented here.

The three samples of thermal covers were taken from tray 10 (E10) and were examined using the SEM. Line profiling was performed to investigate the distribution of oxygen and fluor over the sample. Size measurements were performed on the silver as well on the FEP (coated with gold for conductivity reasons) using the scanning electron microscope. The five grounding strips originating from trays 1, 2, 6, 7 and 10 were examined. Originally these copper strips were used as grounding strips on the experiment trays. The strips came from different trays and as such had different atomic oxygen levels. A part of the strips, fixed under the experiment trays, was not exposed to atomic oxygen. The copper strips were examined using a Cambridge S360 scanning electron microscope equipped with a Link X-ray analyser, an LaB₆ electron gun, a windowless detector and a four-element solid state back-scatter detector. The thickness of the oxide layer was determined using the TFOS (Thin Film On Substrates) programme supplied with the LINK X-ray analyser (ref 1). Auger-XPS profiling was performed using a VG SCIENTIFIC ESCALAB MKII Spectrometer fitted with an LEG200 electron gun and an AG21 Ar⁺ ion gun.

RESULTS and DISCUSSION

Three pieces of thermal blanket were examined originating from different locations and each showing a penetration by presumably a micro-meteoroid. Those locations were selected having different penetration hole sizes. The samples were cut out and the top FEP layer was mechanically separated from the underlying metal layers. The layout of the UHCRE thermal blanket is illustrated in figure 1.

The first noticeable observation on the silver layer that can already be done by the naked eye is the presence of black concentric rings around the hole in the silver layer. All three samples exhibit these attributes to the extent that the bigger the hole in the silver layer the more pronounced the presence of these concentric rings. Closer observation always reveals the same pattern. Around the hole a dark region is found, surrounded by a light ring. Further away the dark rings are recognised. These rings are found in clusters of three to four rings. An example of these clusters of rings is given in figure 2. This exposure is achieved using the electron backscatter technique in the atomic number contrast mode. In this mode the brightness of the features on the photo is related to the atomic number: the higher the atomic number, the brighter the feature. Silver-oxide would appear dark and silver would appear as white, because the average atomic number of silver-oxide is lower than of silver itself.

These types of rings are often seen on outer surfaces that are bombarded with hyper-velocity particles and originate from the impact shock wave and vapourised matter from the target and source material. However, in the case of the thermal blanket the silver layer is not the outer layer, but is found under the FEP top layer.

UHCRE THERMAL BLANKET Sheldahl G401500 with black paint

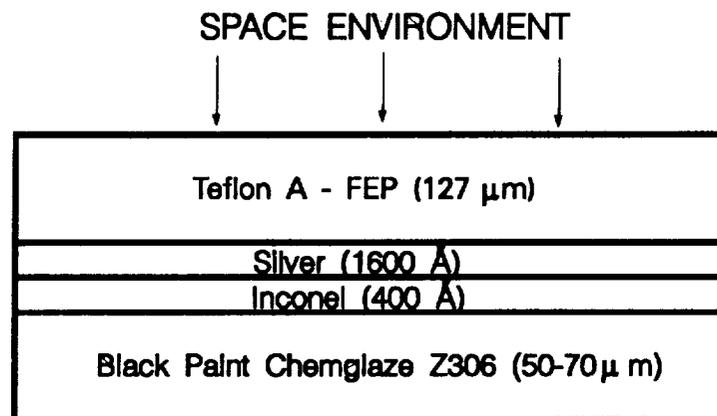


Figure 1. Layout of UHCRE thermal blanket



Figure 2. SEM backscatter image of oxidised rings found on the silver layer under the FEP top layer of the UHCRE thermal blanket. Magn. X20

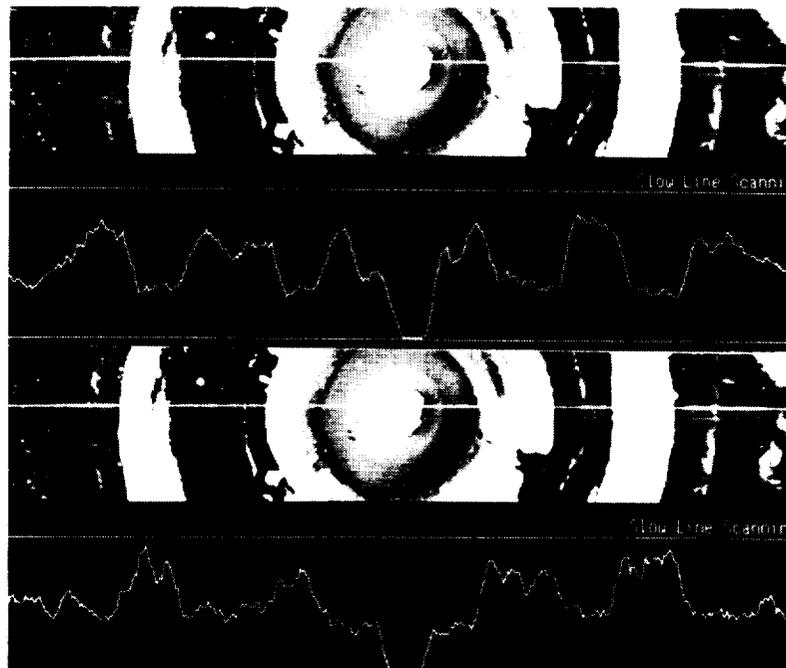


Figure 3. Oxygen linescan (top) and Fluor linescan across the rings.

Obviously these dark rings are oxidised silver. Oxidised silver frequently occurs when silver is exposed to atomic oxygen found in low earth orbit. X-ray analysis indeed confirms the presence of silver-oxide in these black regions. The X-ray spectrum of the light rings shows the presence of fluor, which was absent on the dark rings. Indeed, a linescan across the sample, on oxygen and fluor, reveals an alternating pattern of oxygen and fluor with oxygen in the dark areas and fluor in the light areas. Carbon is found everywhere on these rings. A linescan across one of the samples is found in figure 3.

The circular patterns on the silver layer result from the ejection of fluor/carbon atoms caused by the impact produced shock waves and local vaporizing of the FEP. Due to this impact the silver layer locally debonded from the FEP. Through the hole in the FEP, the silver was oxidised by the atomic oxygen. On the circular locations, where a thin fluor/carbon layer was formed by the vaporizing of the FEP and the shock wave, no attack of the silver was possible. Usually these thin layers are not very protective, but the incoming atomic oxygen has only its highest energy at the centre of the hole. Further away from the centre, the silver is attacked by reflected atomic oxygen that has a much lower energy and these oxygen atoms are unable to remove the protective fluor/carbon layers.

The sizes of the impact holes were measured in the FEP layer as well as in the silver/inconel layer and at the rear side of the silver/inconel where the black paint is present. The hole size increases with the journey of the micro-meteoroid through the sample. The smallest hole size is found at the FEP side. At the exposed FEP side the surface shows clearly signs of atomic oxygen attack. A substantial increase in hole dimensions is measured going from the FEP to the silver/inconel layer.

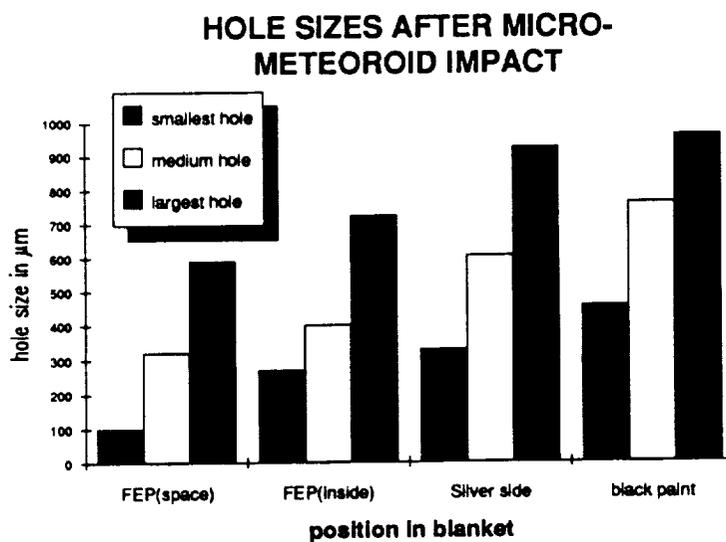


Figure 4a. Holes sizes measured in UHCRE Thermal blanket after micro-meteoroid impact

The sizes of the impact holes of the three examined samples are given in figure 4a. The first position is the space side of the FEP. The second position is the under side of the FEP that was in contact with the silver layer. The third position is the entrance hole in the silver layer, while the fourth position is the rear side of the blanket, i.e. the black paint Chemglaze Z306. A specific row of holes is illustrated in figs. 4b–e.

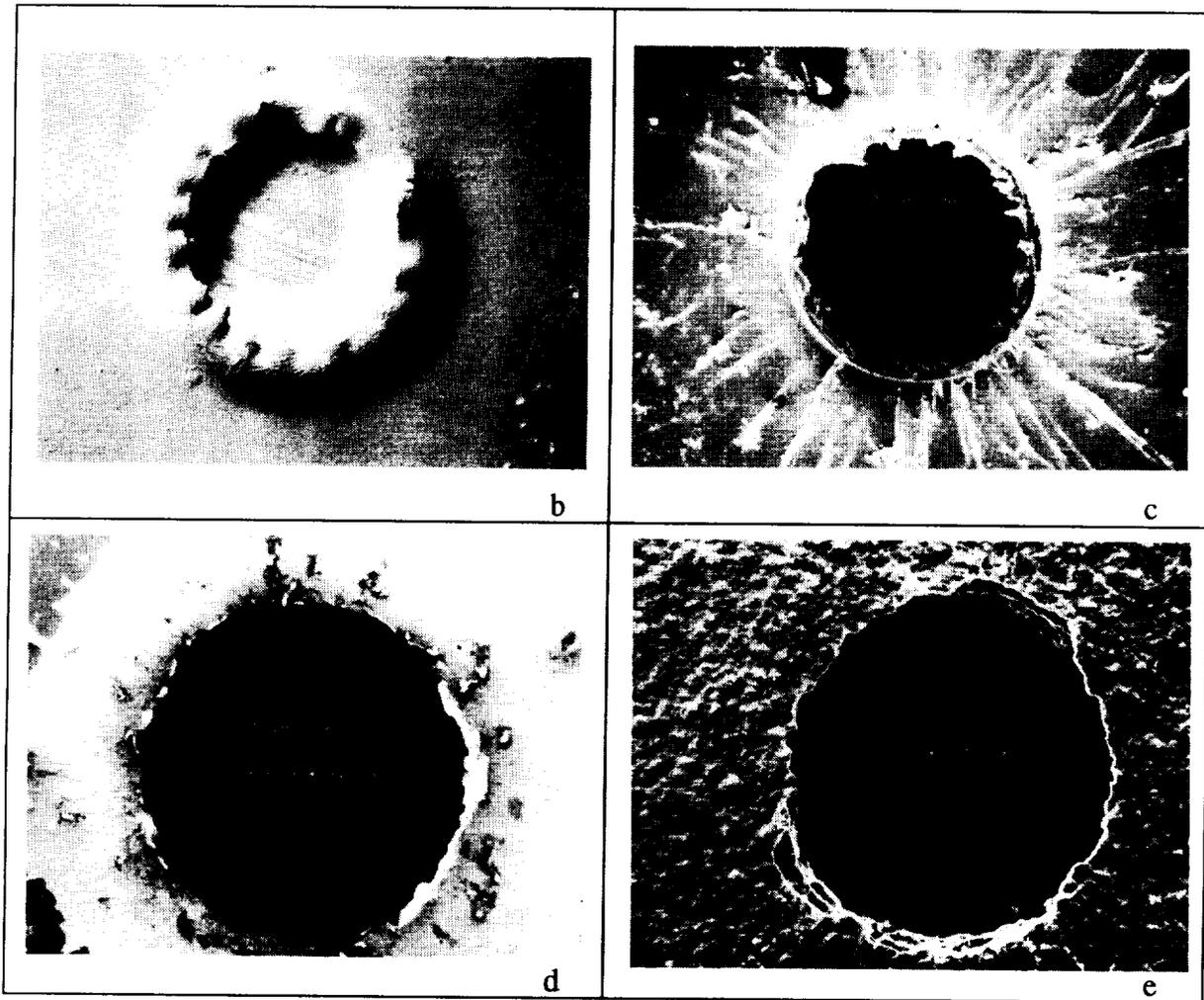


Figure 4b. SEM view on the space exposed side of the FEP layer showing the smallest hole with deformed edges and atomic oxygen erosion (size 590 μm).

Figure 4c. SEM view on the silver contacted side of the FEP layer showing an already larger hole than seen in figure 5a and radial marks of re-solidified FEP (size 710-735 μm).

Figure 4d. SEM view on the layer of silver/inconel. The hole size is approximately 1.5 times as large as found in figure 5b (size 909-940 μm).

Figure 4e. SEM view on the black paint on the rear side of the thermal blanket (size 917-1010 μm).

Five copper grounding strips were examined. These five strips came from different experimental trays. The atomic oxygen fluences experienced by the grounding strips are related to the position of the experimental tray, and for the five grounding strips the fluences following reference 2 are given as:

Table I. Atomic Oxygen Fluence Experienced By The Examined Copper Grounding Strips

Strip nr.	Fluence at/cm ²
D01	1.22 .10 ¹⁷
E02	1.37 .10 ⁰⁹
C06	4.93 .10 ¹⁹
D07	3.16 .10 ²¹
E10	7.78 .10 ²¹

The fluence values given in table I are maximum values because the grounding strips are generally not in plane with the experimental tray. Only close to the fixation point have the grounding strips seen these fluences.

The visual result of the exposure to atomic oxygen on copper is a discolouration of the surface to levels corresponding to the oxygen fluences. The oxide type on copper is usually Cu₂O and has a ruby red appearance. From these colours the oxide thickness can be estimated. Several authors have found a relationship between the oxide thickness and the colour of the oxide layer (see reference 3).

Before measuring the thickness of the tarnish film, the type of oxide film is established. The chemical shift effect in X-ray photoelectron spectroscopy (XPS) provides us with the information about the chemical structure and the oxidation state of the surface compound. The XPS spectra from Cu₂O (Cu¹⁺) and CuO (Cu²⁺) exhibit different binding energies while also the Cu²⁺ spectrum shows 'shake-up' satellite peaks, as illustrated in figure 5.

The identification of CuO on the oxidised samples is performed by positions of the Cu(2p_{3/2})-XPS spectrum, by Cu(L₃M_{4,5}M_{4,5})-Auger spectra and the O(1s) line positions. These three spectra enable us to distinguish between Cu, Cu₂O, CuO and Cu(OH)₂. Especially the difference between CuO and Cu(OH)₂, both Cu²⁺, can be determined with high confidence in the O(1s)-XPS energy region.

It was noted that during the Auger-XPS depth profiling measurements the CuO powder was reduced to Cu₂O. The reduction of CuO to Cu₂O has been reported in literature under intense beam fluxes (see reference 4). Several measurements on the CuO powder were performed to gain insight into this phenomenon. These experiments demonstrate that the reduction of CuO to Cu₂O was caused by the ion etching necessary for depth profiling and not by the electron beam. Ion etching changes the sample composition by selective removal of atoms in the topmost one or two atom layers and by cascade mixing over a depth of about 1-20 nm depending on the sample and sputtering conditions.

The Auger-XPS spectra are measured at the surface of the sample E10 and after repeated etching with the Argon ion gun. At the surface the presence of a thin CuO layer is determined. After two sputtering events the CuO signal disappears and a Cu₂O signal is measured. As discussed, the measurement of a Cu₂O signal after a CuO signal does not necessarily mean that Cu₂O is really present. A part of the oxide layer of sample E10 was removed using a new scalpel blade while the specimen was positioned on the Auger specimen table. Immediately after the partial removal of the oxide layer the sample was returned into the airlock to avoid any re-oxidation. Auger-XPS spectrum of this area shows the presence of Cu₂O instead of CuO. This sequence of oxide layers is consistent with observations on copper oxidised in air at low temperature as depicted in figure 6.

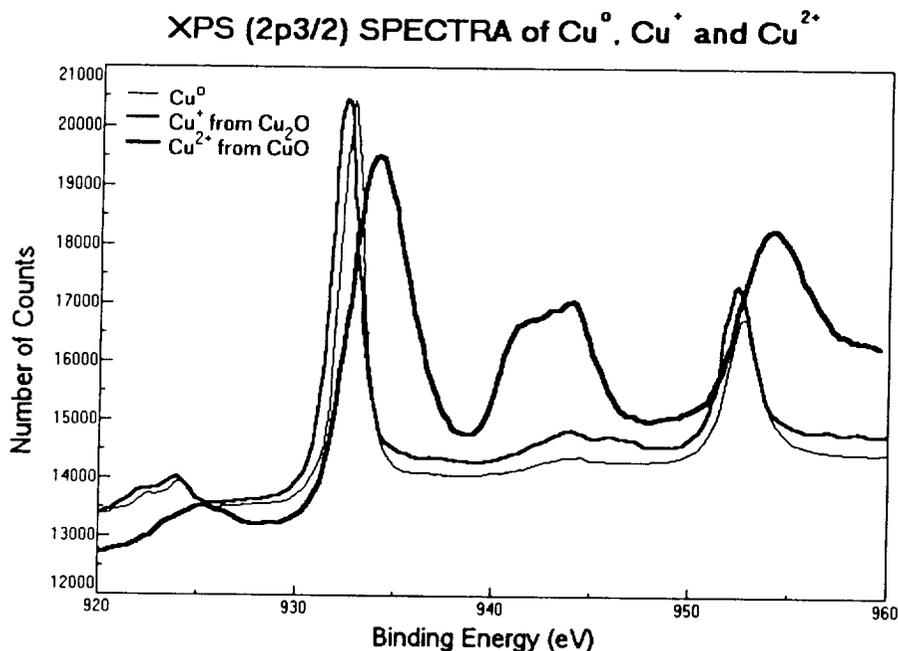


Figure 5. Copper 2p spectra of Cu⁰, Cu¹⁺ and Cu²⁺ showing the chemical shifts due to the oxidation state. The 2p spectrum of Cu²⁺ shows the two strong 'shake up' satellites.

At low oxygen pressures, the only oxide found on copper is Cu_2O as illustrated in figure 7. It is reasonable to assume that this is also true for copper exposed under low earth orbit conditions. The presence of a CuO layer on top of the Cu_2O layer as found on the LDEF samples should then be questioned. It can be argued that this CuO layer is formed on ground during the time of storage after retrieval of LDEF.

Although fundamentally significant for understanding the corrosion mechanism of copper under low earth orbit conditions, the presence of a very thin CuO layer on top of a Cu_2O layer is of minor importance for oxide thickness determinations.

Several authors have applied spectrophotometric techniques to the determination of the thickness of oxide films on copper. Several tables exist that give the relation between the observed colour of the oxide and the oxide thickness. The colour of the oxide layer on sample E10 is red brown. This colour leads to a thickness estimation between 400 and 500 Å.

X-ray analysis of surface layers measures partly the layer and partly the underlying base metal if the thickness of the layer is smaller than the X-ray generation depth. The X-ray generation depth depends on the material properties (atomic mass, density), X-ray line measured and the acceleration voltage. Using the TFOS programme supplied with the Link AN10000 X-ray analyser the thickness of the oxide layer on sample E10, assuming a Cu_2O layer, is calculated as 505 Å. For this calculation to be accurate a specimen with a known oxide thickness has to be used. A non exposed part of the copper strips is used as a standard. Under ambient conditions copper oxidises very slowly and it tends to be an almost constant value after several days. This constant value is approximately 50-60 Å. A value of 60 Å is taken as reference for the X-ray calculations.

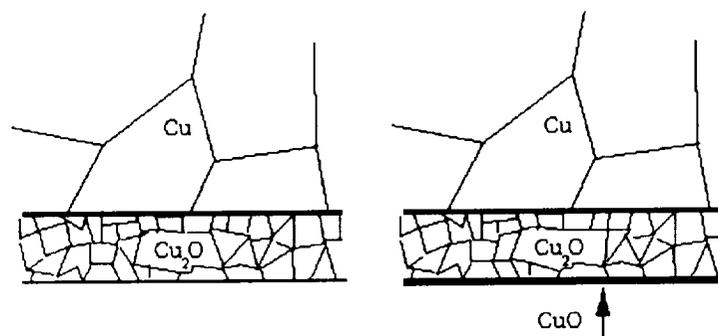


Figure 6. *Left: pure copper oxidised at low pressure or in air above 1025 °C. Right: pure copper oxidised in air below 1025 °C.*
(from ref. 5)

The third method of oxide thickness determination is the depth profile during Auger-XPS measurements. This method depends on knowledge of the sputtering rates of the materials under ion bombardment. A clean copper sample was ion etched under the same depth profiling conditions as the LDEF samples. After 38000 seconds

of etching a step of 5 μm was measured on the copper surface yielding a sputtering rate of 1.3 $\text{\AA}/\text{s}$ for copper. Taking into account the different molecular mass and density of Cu_2O as opposed to copper, the sputtering rate of Cu_2O is estimated lower than the one for copper. A value of 1 $\text{\AA}/\text{s}$ is taken for Cu_2O . Depth profiles of four LDEF samples are given in figure 7. Using the calculated sputter rate the copper profile and the oxygen profile of sample E10 reveal an oxide layer thickness between 500 and 600 \AA .

The colour as seen by the naked eye does not enable us to deduce the oxide thickness with confidence. The results of the X-ray and Auger-XPS measurements are combined and displayed in table II. The validity of the values given in table II has to be judged against the accuracies of the method employed. Both methods (X-ray and Auger depth profiling) depend on the knowledge of the type of oxide layer. Studies show that copper oxidised at low temperature exhibits a Cu_2O layer with a large non-stoichiometry (reference 6). The X-ray method of depth calculation depends on an accurate knowledge of the X-ray generation depth, which depends among others on the electron escape depth. The X-ray generation depth in the surface layer relies on the density, the mean atomic mass and the mean atomic number of this layer. Also very elaborate methods for the calculation of the thickness of layers on substrates, such as the PAP model from reference 7, require a realistic description of the depth distribution function.

Accurate depth profile measurements using Auger-XPS depend on obtaining a flat bottomed crater during ion sputtering of the calibration sample. The accuracy measured using a Talystep on the copper calibration sample is $\pm 20\%$. This measurement was not possible on the oxide layer and correction procedures in the calculation of the sputtering yield were used. The expected accuracy on the thickness determination is not better than $\pm 30\%$.

Table II. Individual And Average Results In \AA On Thickness Determination

Strip nr.	X-ray on thin films	Auger-XPS profiling	Colour of surface	Average
E02	167	150		158
C06	299	350		325
D07	491	500		495
E10	505	525	400-500	515

The average result from table II is graphically displayed in figure 8, where the thickness is plotted against the atomic oxygen fluence at the end of mission for each sample investigated. A logarithmic function can be fitted to the data points. Direct logarithmic or inverse logarithmic relationships are usually found for the oxidation of copper oxidised at low temperature and small film thicknesses.

DEPTH PROFILE OF LDEF EXPOSED CU SAMPLES

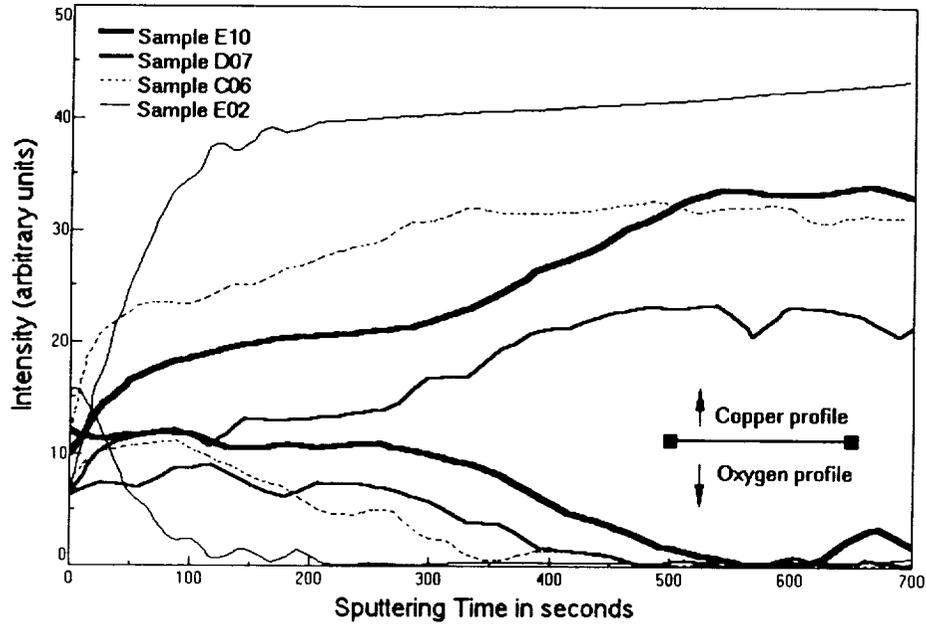


Figure 7. Depth profile of Copper and Oxygen from the Cu samples exposed on LDEF. The four upward curves are the Cu profiles and the four downward curves are the oxygen profiles.

OXIDE THICKNESS vs ATOMIC OXYGEN FLUENCE

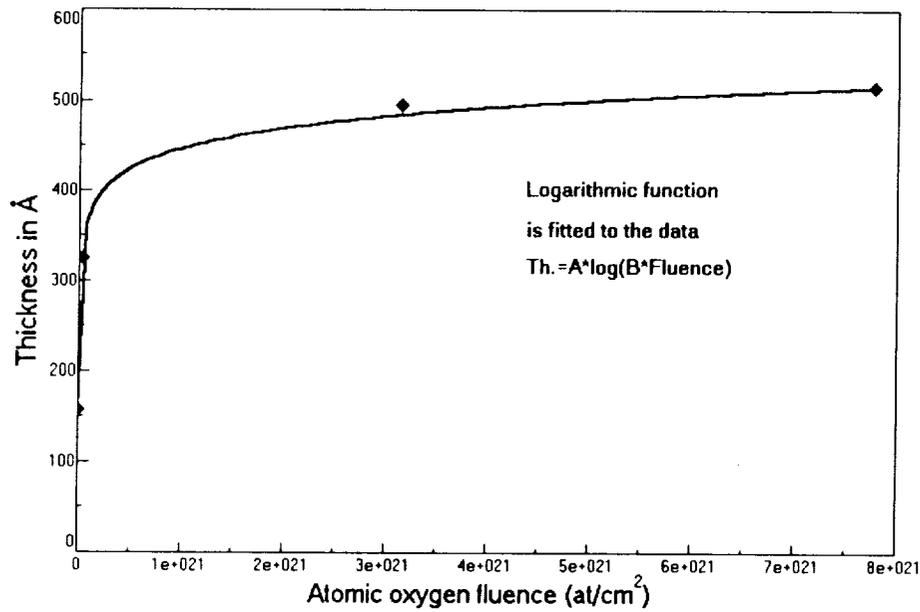


Figure 8. Thickness of oxide film measured on copper after exposure in low earth orbit.

DEPTH PROFILE of SAMPLE D01

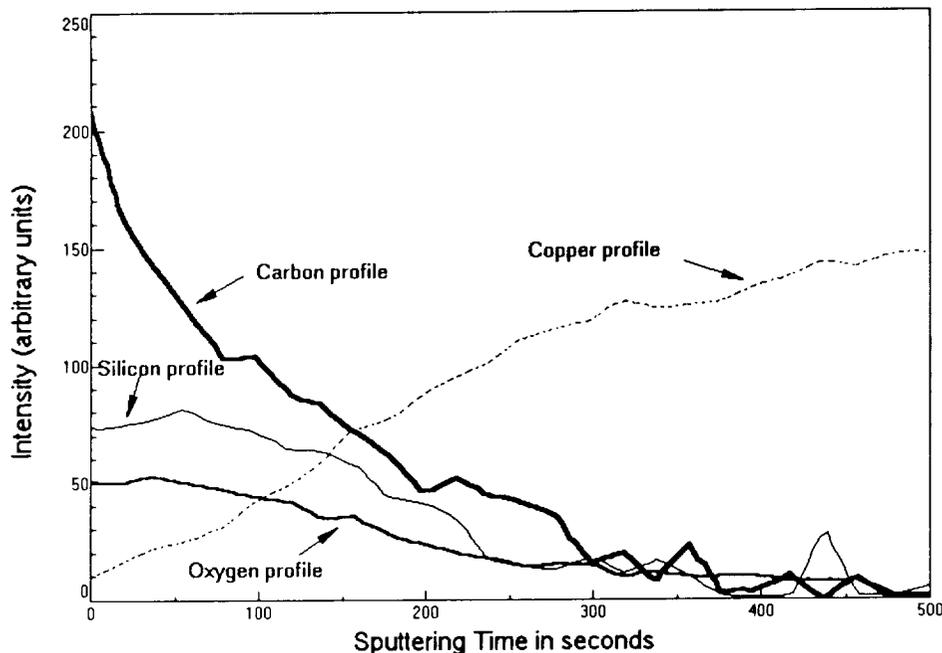


Figure 9. Depth profile of Carbon, Copper, Silicon and Oxygen from sample D01. The Carbon, the Silicon and the Oxygen decay in the same manner.

The thickness of the oxide layer of four of the five samples could be measured. X-ray measurements on the sample from tray 1 (D01) revealed the presence of high amounts of carbon and silicon. The depth profiles of the elements present in the surface layer are shown in figure 9.

The copper signal starts off much lower than the oxygen signal as opposed to the signal seen in figure 8. The carbon, the silicon and the oxygen signals decay in the same manner reaching zero intensity at the same sputtering time. When the intensities of these three signals are negligibly small the copper signal approaches its maximum. This indicates the presence of a silicon oxide instead of a copper oxide. The silicon oxide contains significant amounts of carbon, so probably the silicon oxide originated from a silicone contaminant. This contamination occurred very early in the mission because no significant traces of a copper oxide layer are found.

CONCLUSION

The silver samples, being part of the UHCRE thermal blanket, were oxidised through holes in the outer Teflon A-FEP layer. The micro-meteoroids that caused these holes evaporate the FEP locally. The shock wave, induced by the impact, redistributes the evaporated FEP over the underlying silver in a circular pattern with high and low density regions of fluor/carbon. The areas of low density are subsequently oxidised by reflected atomic oxygen.

Copper is oxidised by atomic oxygen to thicknesses that exceed the ones found for standard atmosphere oxidation. The oxide was found to be adherent to the surface and consisted of Cu_2O and can be removed mechanically by rubbing. The top layer of CuO was probably formed during ground storage after retrieval of LDEF.

More accurate thickness determinations are needed to calculate the growth of the oxide layer under atomic oxygen bombardment. Controlled samples and probably optical techniques should be used to achieve this.

ACKNOWLEDGEMENT

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