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Evaluation of Space Environmental Effects on Metals and Optical Thin Films on EOIM-3

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ABSTRACT

Metals and optical thin films exposed to the space environment on the Third Flight of the Evaluation of Oxygen Interactions with Materials (EOIM-3) payload, onboard Space Shuttle mission STS-46 were evaluated. The materials effects described in this paper include the effects of space exposure on various pure metals, optical thin films, and optical thin film metals. The changes induced by exposure to the space environment in the material properties were evaluated using BRDF, specular reflectance (250 nm to 2500 nm), ESCA, VUV reflectance (120 nm to 200 nm), ellipsometry, FTIR and optical properties. Using these analysis techniques gold optically thin film metal mirrors with nickel undercoats were observed to darken due to nickel diffusion through the gold to the surface. Also, thin film nickel mirrors formed nickel oxide due to exposure to both the atmosphere and space.

INTRODUCTION

The harsh environment in low Earth orbit (LEO) affected the optical and mechanical properties of many of the spacecraft materials flown on the Long Duration Exposure Facility (LDEF),[1,2] returned in 1990 after 69 months of space exposure. Ground simulators are being developed to simulate various aspects of the space environment to evaluate candidate materials. Because it is difficult to combine some of the environments to study synergistic effects on materials, it is always beneficial to expose materials to the space environment to understand short-comings of ground simulators and verify that these simulators correctly reproduce effects caused by actual space exposure.

Various pure metals, optical thin films, and optically thin film metals were exposed to the space environment as part of the Evaluation of Oxygen Interaction with Materials Experiment, third flight, (EOIM-3) on board the STS -46 shuttle flight. The STS-46 shuttle flight started July 31, 1992 and concluded Aug. 8, 1992. It included the electrodynamic testing of the Tether Satellite System (TSS-1), the deployment of the European Retrievable Carrier (EURECA), and the exposure of the EOIM-3 payload to the Space Shuttle velocity vector. The EOIM-3 experiment pallet carried numerous material samples and fixtures into space and exposed them to the space environment for a total of 42 hrs in the velocity vector. The space shuttle flew at an altitude of 197 km (123 nautical miles) near the end of STS-46

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mission exposing the EOIM-3 experiment to a directed atomic oxygen fluence of 2.2 x10^{20} atoms/cm^2 with a total of 7.6 equivalent sun hours (ESH) of synergistic near and far ultraviolet radiation. During those 42 hours the EOIM-3 experiment received the majority of its atomic oxygen exposure. However, a small amount of atomic oxygen exposure was received during the deployment and release of the EURECA.

EOIM-3 also received simultaneous exposure to solar ultraviolet radiation, thermal cycling, particulate radiation, and micrometeoroid/space debris impacts. EOIM-3 received 30.6 equivalent sun hours (ESH) during the STS-46 mission with 7.6 ESH exposure simultaneous with direct atomic oxygen impingement. Due to the short duration and orbit of the STS-46 mission the particulate radiation dose was negligible. During the STS-46 mission the EOIM-3 pallet experienced about 120 sun to shadow cycles which include those cycles during EURECA and TSS deployment. Molecular contamination due to thermal cycling was minimized by vacuum baking all materials for 24 hours prior to flight. Post-flight analysis did not reveal any detectable evidence of micrometeoroid/space debris hits greater than 0.25 mm diameter.

EOIM-3 DESCRIPTION AND ANALYSIS PROCEDURE

The EOIM-3 experiment tray, shown in Fig.1 , consisted of fifteen passive trays, three trays heated to 60°C, 120°C and 200 °C, respectively, and various active experiments. Marshall Space Flight Center supplied to the EOIM-3 experiment three passive trays which contained a total of 138 samples, several individual samples to be integrated into the heated trays, and three active experiments. The optical thin films and optical thin film metals were found primarily on the passive trays. The pure metals (bulk sheet stock or shim stock) and
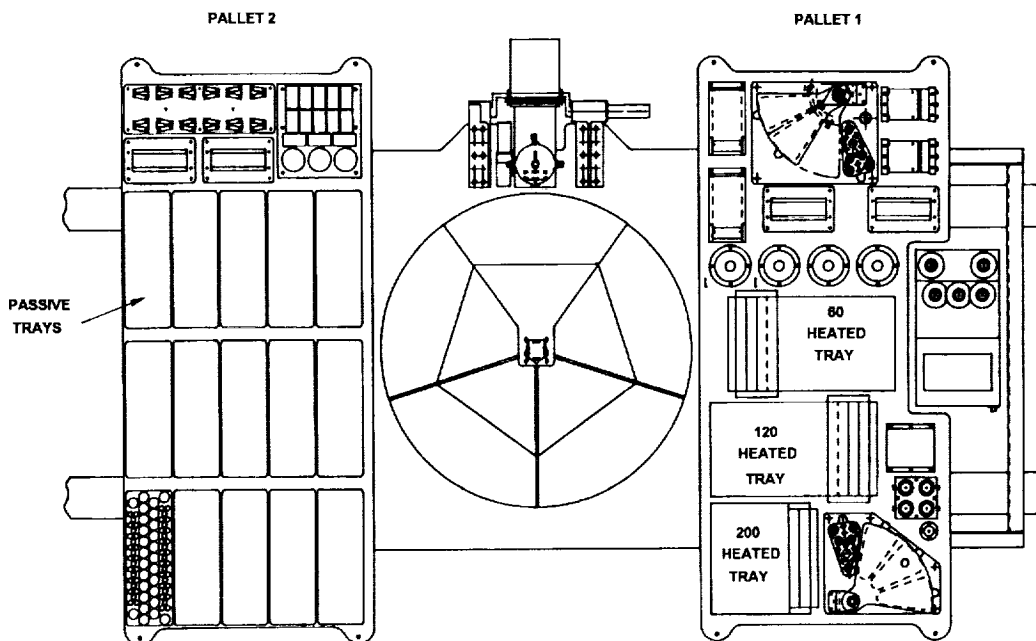

Fig. 1   Schematic of EOIM-3 Experiment

some metallic thin films presented in this paper were flown on the heated trays. The active experiments, the thermal control coatings, and polymer materials that MSFC provided on the EOIM-3 experiment are presented in detail in other papers found in these proceedings.

Most of the samples provided by MSFC for integration on the heated and passive trays were nominally 2.54 cm dia., except for the pure metals which were 1.27 cm dia. The optical thin film metals and the optical thin films found on both the heated and passive trays were covered with a half moon aluminum cover. This provided a control surface that was exposed to both the same thermal and vacuum environments as the exposed portion of the samples. The samples were weighed and optically pre-characterized prior to flight.

Following EOIM-3 de-integration from the orbiter, the samples were kept in desiccators until optical property and mass data could be measured. Optical property data were measured at MSFC using an AZ Technology laboratory portable spectroreflectometer (LPSR) and a Gier-Dunkle DB100 emissometer, and the mass properties were measured using a Mettler AT250 balance. Both the optical thin film metals and the optical thin films were examined using a TMA Quickscan scatterometer to calculate the Bi-directional Reflectance Distribution Function (BRDF) for both the unexposed and exposed region of each sample. Using this function the RMS roughness changes could be examined. To complete the reflectance analysis of the samples, spectral vacuum ultraviolet (VUV) reflectance measurements (120 nm to 200 nm) were made. After completing the series of reflectance measurements, numerous other more destructive analysis techniques were used, including surface analysis by laser ionization (SALI), proton induced x-ray emission spectroscopy (PIXE), rutherford backscatter spectroscopy (RBS), fourier transform infrared reflectance spectroscopy (FTIR), and electron spectroscopy for chemical analysis (ESCA).

PURE METALS

Numerous 99.9999% pure metals were flown on both the 60°C and 120° C heated trays. Included in these pure metals were copper, gold, nickel, niobium, silver, tantalum, tungsten, and vanadium. Silver and tungsten were also flown on the 200 ° C tray. Also included on EOIM-3 were two aluminum/lithium alloys: 2090 Al/Li and Weldalite®. All the pure metals had an exposed area of 0.71 cm². The aluminum/lithium alloys were 2.54 cm dia. samples, but the 2090 alloy was half covered while the Weldalite sample was covered with a "D" ring. A "D" ring was a 2.54 cm dia cover with a small straight edge at one edge of the sample. The goal of the "D" ring was to provide a step edge for monitoring the presence of oxide growth or perhaps erosion due to atomic oxygen with maximized exposure area.

Table I lists the results of both changes in mass and optical properties for all the pure metals flown by MSFC on EOIM-3, following exposure to the space environment. The two metals expected to be most affected by the space environment were copper and silver since both have a history of atomic oxygen effects from LDEF[1,2] and earlier EOIM flights[3]. Both the copper and the silver demonstrated the largest changes in solar absorptance (α) of the pure metals which was attributed to oxidation. However, it appears that the short exposure received by EOIM-3 did not produce an oxide layer thick enough on the copper sample to be

Table I Pure Metals Mass Loss and Optical Property Summary

Sample Material	Δm (mg) (± 0.02)	$\Delta m/A$ (mg/cm²) (± 0.03)	α_i (± 0.01)	α_f (± 0.01)	ε_i (± 0.01)	ε_f (± 0.01)
Copper						
60°C Tray	-0.03	- 0.042	0.49	0.56	0.01	0.03
120°C Tray	-0.07	- 0.098	0.47	0.52	0.02	0.03
Gold						
120°C Tray	+0.01	+ 0.014	0.19	0.18	0.02	0.02
Nickel						
60°C Tray	-0.05	- 0.071	0.33	0.34	0.02	0.02
120°C Tray	-0.05	- 0.071	0.33	0.31	0.02	0.02
Niobium						
60°C Tray	-0.05	- 0.071	0.33	0.34	0.03	0.03
120°C Tray	-0.03	- 0.042	0.33	0.34	0.03	0.03
Silver						
120°C Tray	+0.23	+ 0.323	0.11	0.80	0.01	0.46
Tantalum						
60°C Tray	-0.05	- 0.071	0.38	0.39	0.03	0.02
120°C Tray	-0.01	- 0.014	0.38	0.37	0.03	0.02
Tungsten						
60°C Tray	-0.15	- 0.210	0.46	0.48	0.02	0.02
120°C Tray	-0.02	- 0.028	0.46	0.46	0.02	0.02
200°C Tray	-0.04	- 0.051	0.46	0.55	0.02	0.01
Vanadium						
60°C Tray	-0.42	- 0.589	0.68	0.70	0.06	0.05
120°C Tray (pre-ox.)	-0.04	- 0.051	0.64	0.66	0.06	0.06
Al/Lithium						
60°C Tray	-0.51	- 0.155	0.15	0.14	0.05	0.05
120°C Tray	-0.53	- 0.162	0.15	0.14	0.05	0.05
Weldalite						
Passive	-0.15	- 0.090	0.13	0.15	0.05	0.05
Trays	-0.17	- 0.102	0.13	0.13	0.06	0.05

detected by either mass changes or infrared emittance changes or the oxide layer was lost due to flaking. The pure silver sample on the 120 °C heated tray developed a dark black silver oxide layer which is represented in the mass gain and large change in emittance (ε). All other pure metal samples seemed to change uniformly in reflectance proportional to the change in solar absorptance over the entire wavelength range measured.

Two vanadium samples were flown. One was pre-oxidized prior to flight and the other was cleaned of any oxidation layer. The pre-oxidized vanadium sample had a blue tint prior to flight and the other a yellow/gold tint. Upon retrieval neither sample changed much in appearance, as indicated by the solar absorptance data, but the sample which was not pre-oxidized saw a large decrease in mass. Because the sample decreased in mass and did not demonstrate any change in emittance, it is unlikely than an oxide layer was produced. The decrease in mass is most likely a result of out gassing or water desorption from the surface, but more tests are planned to understand this result.

Two different types of aluminum-lithium materials were flown on EOIM-3 by MSFC: a 2090 aluminum-lithium alloy and Weldalite®. The 2090 Al/Li alloy samples were flown on the 60 °C and 120 °C trays, while the Weldalite samples were flown on the passive trays. Both aluminum-lithium alloys lost significant amounts of mass. The 2090 alloy samples which were flown at elevated temperature lost the most weight. The loss in weight with these materials is most likely attributed to lithium loss from the samples caused by atomic oxygen exposure. The amount of lithium lost seems to be a function of temperature. More tests are underway to examine the effects of atomic oxygen exposure on these materials.

OPTICAL THIN FILM METALS

Several optical thin film metals were flown on EOIM-3 by MSFC. Included were gold, iridium, platinum, and nickel thin films, 750 Å thick with a 100 Å chrome undercoat which were flown on the passive trays. Also, samples of these same thin films 250 Å thick with a chrome undercoat and without a chrome undercoat were flown, but they are still under investigation and will not be presented in this paper. Other gold thin film mirrors ($\approx$ 1000Å) with nickel undercoat were flown on all three of the heated trays. All thin film samples flown on both the passive and heated trays were half exposed during flight, providing a control surface to compare to both exposed and pre-flight measurements.

Table II Optical Property Summary for Metallic Thin Films

Sample	α_c	α_e	ε_c	ε_e
Gold				
Passive Tray	0.20	0.21	0.07	0.07
60 °C	0.17	0.17	0.03	0.03
120 °C	0.17	0.17	0.06	0.06
200 °C	0.18	0.23	0.05	0.04
Platinum				
Passive Tray	0.24	0.25	0.06	0.07
Iridium				
Passive Tray	0.24	0.25	0.11	0.12
Nickel				
Passive Tray	0.31	0.31	0.05	0.08

Table II is a summary of the optical properties data, solar absorptance (α) and infrared emittance (ϵ), measured for the four different thin film metals. The measurements made in the control region of the sample are indicated with subscript "c" and the measurements made in the exposed region are indicated with an "e". Two interesting observations made from the optical property data were the increase in solar absorptance of the gold sample, which was flown on the 200°C tray, and a small increase in the nickel sample in emittance. The change in emittance on the nickel sample could be within the resolution of the instrument; however, data will be presented later that confirm the presence of a thin oxide layer.

The gold sample from the 200 °C tray was visibly dark in the exposed region. Figure 2 is a comparison of the diffuse reflectance curves taken by the LPSR showing the 200 °C gold sample to have a much higher solar absorptance. Two different theories are possible to explain the unexpected darkening: 1)Diffusion or migration through micropores of the nickel substrate through the gold activated by the heat and atomic oxygen or 2)Contamination from a foreign source. FTIR and SALI measurements were made on both the exposed and unexposed regions of this sample. FTIR and SALI results from this sample indicated only trace amounts of hydrocarbons or surface contaminants on either the exposed or unexposed portions of the sample, which was later confirmed by ESCA analysis. SALI measurements did indicate nickel oxide present on the surface of the sample in the exposed region and only trace amounts of nickel in the unexposed. This result indicates the nickel diffused or migrated through the gold during space exposure due to the elevated temperature of the samples. RBS measurements on the gold thin film flown on the 120 °C tray indicated trace amounts of nickel in the bulk and on the surface. Attempts to reproduce the diffusion
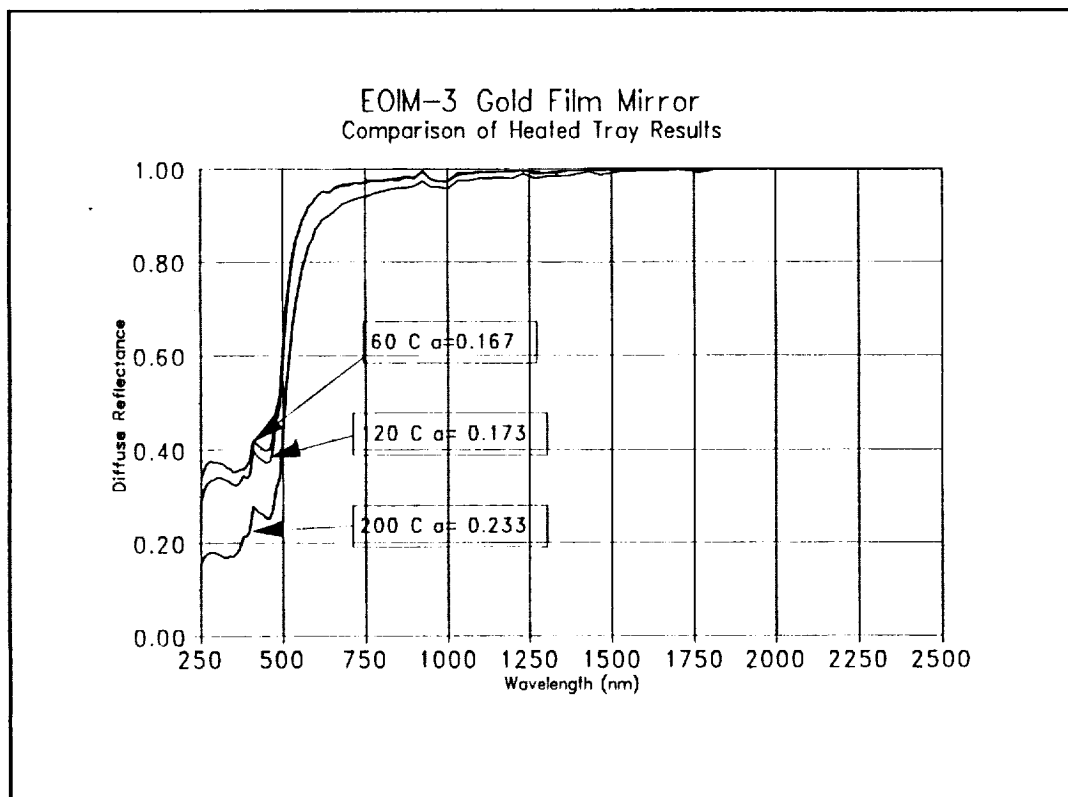

Figure 2 Comparison of Reflectance Data of Gold Thin Films on Heated Trays

Sample	Gold Control	Gold (60°C) Control	Gold (60°C) Exposed	Gold (120°C) Control	Gold (120°C) Exposed	Gold (200°C) Control	Gold (200°C) Exposed
Contamination Layer	NONE	7Å	13Å	10Å	15Å	-	-
Nickel Layer	10Å	25Å	65Å	35Å	90Å	-	250Å

**Table III   Nickel Depths on Gold Mirrors from the 60°C, 120°C, and 200°C Trays**

process in the lab by heating a gold sample to nearly 200 °C were successfully verified using RBS, but the sample did not darken as did the flight sample. The darkening of the sample is due to the oxygen exposure as verified by ESCA analysis.

All three gold mirrors with nickel undercoats and a control were analyzed in both the exposed and unexposed regions using SALI and ESCA. The gold mirrors flown on the 60 °C, 120 °C and control gold mirrors were analyzed using ESCA with sputtering capabilities for depth analysis, and the 200 °C mirror was analyzed using SALI. Results showing the depth of nickel found on the surface in both the control and exposed sides of the flight mirrors are shown in Table III. The control mirror had no detectable contamination layer while all gold mirrors had very small contamination layer on the order of 10 to 15 Å. Thin nickel layers were detected on the surface of all four gold mirrors. The control mirror had a 10 Å layer on the surface of the mirror possibly from cross deposition during the evaporation process. ESCA verified the presence of nickel in both the unexposed and exposed regions of the 60°C and 120°C mirrors similar to the SALI analysis on the 200 °C mirror which suggests that the nickel diffuses through the gold driven by the sample temperature. Because the exposed region has thicker nickel layer in the exposed region, it is believed that the oxidation reaction between the nickel and the atomic oxygen is producing the darkening. This hypothesis is supported by the stoichiometric breakdown from the ESCA analysis which found oxygen in only the exposed region of the gold mirrors exposed in both the 60 °C and 120 °C trays.

Vacuum ultraviolet (VUV) reflectance data measured at MSFC indicated no significant change within experimental error in measurements on the unexposed, exposed side of the gold passive tray sample, the platinum sample, or the iridium sample. A typical VUV reflectance data set is shown in Fig. 3. This figure shows reflectance data measured for the platinum thin film mirror for which no significant changes in the reflectance were found. However, VUV reflectance data for the nickel sample, which is shown in Fig. 4, showed consistent change in VUV reflectance over all wavelengths from pre-flight measurements, as well as, unexposed and exposed measurements after flight. The sample remained in atmosphere for nearly six months prior to flight. The change in VUV reflectance and emittance data shown in Table II is a strong indication of nickel oxide growth caused by both atmospheric exposure as well as space environmental exposure.
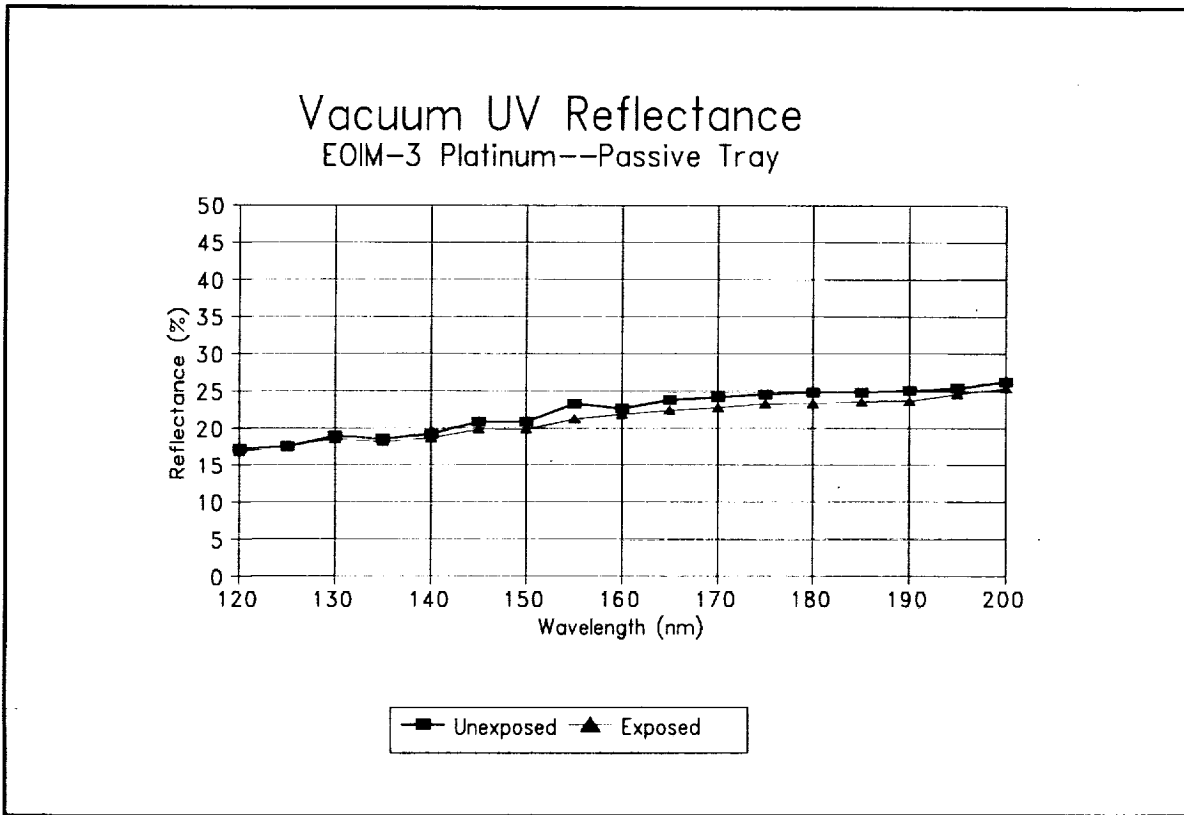
Figure 3   VUV Reflectance Data for Platinum Thin Film Mirror
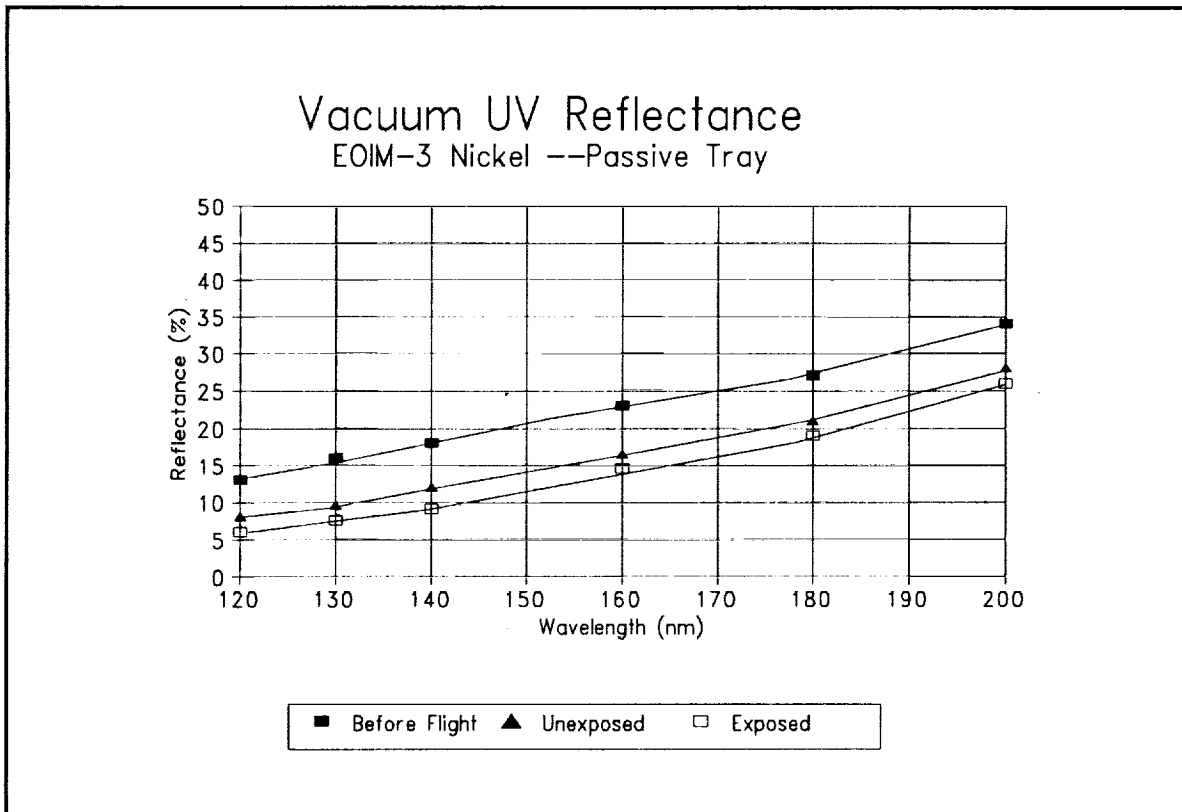
Figure 4   Vacuum Ultra Violet Reflectance Data for Thin Film Nickel

Ellipsometer measurements were made to investigate the presence, if any, of an oxide layer on all the metal thin films, particularly the nickel sample. Only a single layer substrate program which measures the substrate index of refraction (N_s) and the substrate extinction coefficient (K_s) was available for use. The results of these measurements are presented in Table IV.

Measurements of both N_s and K_s were made in both the unexposed and exposed region of the samples. The measured reflectance shown in Table IV was taken from the data file of the TMA quick scan scatterometer which is used to make BRDF measurements using the same 632.8 nm laser as the ellipsometer. Using the N & K values measured at 70 ° by the ellipsometer as input to a computer model designed to calculate the reflectance of the sample, comparisons of the calculated and measured reflectance were made. The computer model solves the basic Fersnel equations for the variables N, K, the incident angle, and the thickness of the coating. This model can be used for multi-layer thin film calculations. Any change indicated between the calculated reflectance and the measured reflectance would tend to indicate some anomaly with the surface.

Sample	N_s	K_s	Measured Reflectance (632.8 nm)	Calculated Reflectance (632.8 nm)
	70°	70°		
Platinum Unexposed	2.030	-4.643	0.741	0.736
Platinum Exposed	1.867	-4.399	0.735	0.729
Gold Unexposed	0.228	-3.458	0.939	0.932
Gold Exposed	0.224	-3.455	0.942	0.933
Iridium Unexposed	2.566	-4.162	0.654	0.658
Iridium Exposed	2.479	-4.143	0.659	0.661
Nickel Unexposed	1.819	-3.657	0.663	0.659
Nickel Exposed	1.681	-3.465	0.660	0.650

Table IV   Summary of Ellipsometry Measurements on Metallic Thin Films

Most of the ellipsometer measurements shown in Table IV show no change within experimental error between the unexposed side and the exposed, and there is good agreement between the measured reflectance and the reflectance calculated using the measured values of N_s and K_s at 70 °. One inconsistency which is evident in the table is the small but statistically significant difference between the measured reflectance and calculated reflectance of the exposed nickel thin film. Although the difference between the measured and calculated reflectance data is close, there is other data (the VUV reflectance data) which indicate there is a significant change on the surface. FTIR analysis showed no evidence of contamination. LDEF results indicate the presence of nickel oxide on nickel samples due to space exposure[4]. SALI measurements on the EOIM-3 nickel thin film mirror indicated about 60 Å of oxide on the unexposed side after flight and 100 Å on the side exposed during flight. The SALI measurements were confirmed by calculating the reflectance at 121.6 nm and comparing it to measured reflectance data. Table V is a comparison of the calculated and measured reflectance data at 121.6 nm at an angle of incidence of 16 ° which is approximately the angle used to measure the reflectance at the VUV wavelength. The measured reflectance data shown in this table is from Fig. 4. The calculated reflectance from the computer model previously mentioned used the literature values for unoxidized nickel N and K (N=1.220 and K= -3.330)[5] at 121.6 nm. The N and K for nickel oxide were assumed to be similar to those measured for typical metal oxides. By choosing the thickness which provided the best match to the measured reflectance data, the thickness of nickel oxide on the surface was determined. The pre-flight reflectance measurements indicated that 10 Å of oxide was already present. After the EOIM-3 flight, the reflectance measurements indicated that even without exposure to the space environment the oxide thickness grew 60 Å from just atmospheric exposure. Exposure to atomic oxygen resulted in an additional 30 Å of oxide being produced for the short exposure experienced by the EOIM-3 experiment.

Sample Measured	Measured Reflectance (%)	Calculated Reflectance (%)	Nickel Oxide Thickness (Å)
Pre-Flight	13.0	13.9	10
Unexposed After Flight	6.67	6.64	70
Exposed After Flight	4.95	4.91	100

Table V   Comparison of Measured and Calculated Reflectance Data at 121.6 nm and 16° Angle of Incidence on nickel thin film on zerodur

Included in the materials flown on the passive trays by MSFC were several optical materials including magnesium fluoride/Al/fused silica (MgF_2) mirrors and CaF_2, LiF and MgF_2 coated on beryllium substrates. Also, a luminescing phosphor which has wide spread use in VUV applications, sodium salicylate, was included in the samples. Because of the complexity of some measurements only initial results of the sodium salicylate will be touched on in this paper. In general, the CaF_2, LiF and MgF_2 coatings on Be did not lose significant mass or change optically. Future work will concentrate on using RBS measurements to detect any changes in the surface and bulk materials due to space exposure.

Visual inspection of the sodium salicylate on a quartz substrate after flight indicated that the surface roughness of the samples had changed. The most striking change observed was found by the BRDF scatterometer in the transmission mode measuring the bi-directional transmission distribution function (BTDF) for the sodium salicylate sample in both the unexposed and exposed regions (Fig. 5). The data cannot be used to determine the surface roughness, but it does indicate that the sample has lost material. Mass loss data indicated a 1.27 mg decrease in mass. Because sodium salicylate is used for its luminescing capabilities in many VUV applications, fluorescence measurements were also done. The spectrofluorometer at MSFC has been used in the past to study the fluorescence changes in
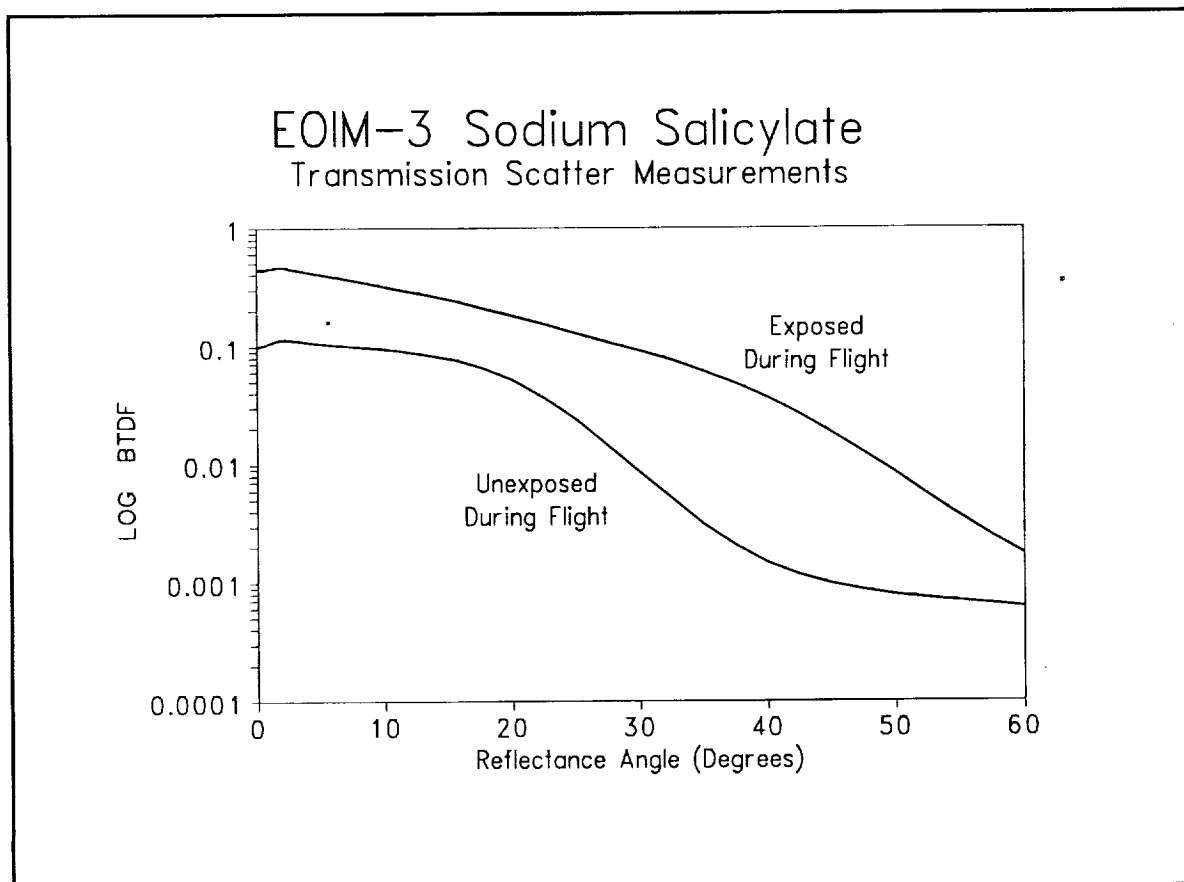

Figure 5 BTDF Measured for Sodium Salicylate

thermal control coatings[6] with success. Spectrofluorometer measurements of sodium salicylate exposed to 260 nm light indicated only a slight change between the unexposed and exposed sides of the sample. However, when the fluorescence of the sample is measured at the vacuum ultraviolet wavelengths (120 nm to 200 nm) there is a consistent 50 % decrease in luminescence between the exposed and unexposed portion of the sample. This is consistent with the decrease in mass and transmission measured by the BTDF. Attempts to reproduce the loss of sodium salicylate were done in the laboratory by exposing samples to both 5 eV atomic oxygen and thermal atomic oxygen. While the samples did not lose mass as expected, the samples did turn yellow. After further investigation the yellowing was not due to contamination but was caused by intense VUV (130 nm) radiation from the atomic oxygen resonance line. This result did not provide any evidence to identify the cause of the thinning of the sodium salicylate but work is still continuing.

Preliminary Conclusion

General observation of all pure metals, optical thin metal films, and optical thin films indicates little or no contamination as reported by other EOIM-3 investigators. This result is backed up by numerous FTIR measurements on many samples.

Initial observations of the pure metal samples flown on EOIM-3 indicated most were unaffected by the short space exposure received. The copper and silver samples changed as expected. However, the vanadium and aluminum-lithium alloys indicated a decrease in mass by desorption of vanadium and lithium from the surfaces, respectively. Further work is required to confirm this observation.

Most of the optical thin metal films flown on EOIM-3 did not change due to the short duration space exposure. The gold thin film exposed to atomic oxygen on the 200 °C tray changed significantly in solar absorptance. ESCA, SALI, RBS, and FTIR data indicated that the darkening was not due to contamination but to diffusion or migration of the nickel substrate through the gold which was then oxidized by the atomic oxygen. The nickel thin film sample continuously grew oxide on the surface from the time it was first introduced into the atmosphere. Also, the oxide film grew when exposed to atomic oxygen during space exposure.

Sodium salicylate, which is used as a VUV phosphor, indicated some thinning in the exposed region of the sample confirmed by mass loss results, BTDF data, and VUV fluorescence measurements. More work is required to identify the cause of the thinning.

Acknowledgements

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References

[1] Levine, A.S., "LDEF--69 Months in Space: First Post-Retrieval Symposium Parts 1,2, and 3", NASA CP 3134, Kissimmee, Fl, June 2-8, 1991.

[2] Levine, A.S., "LDEF--69 Months in Space: Second Post-Retrieval Symposium Parts 1,2,3 and 4", NASA CP 3194, San Diego, CA, June 1-5, 1992.

[3] Visintine, J.T., edt., "Atomic Oxygen Effects Measurements for Shuttle Missions STS-8 and 41-G ", NASA TM 100459, Vol. 1-3, Sept. 1988.

[4] Franzen, W., Brodkin, J.S., Sengupta, L.C., and Sagalyn, P.L., "Ellipsometric Study of Oxide Films Formed on LDEF Metal Samples", NASA CP 3134, Part 2, pp. 1005-1021, June 2-8, 1991.

[5] Palik, Edward D., edt., Handbook of Optical Constants of Solids, Academic Press, Inc., pp. 317-323, 1985.

[6] Linton, R.C., Whitaker, A.F., and Kamenetzky, R.R., Fluorescence Observations of LDEF Exposed Materials as an Indicator of Induced Material Reactions", Published in the Proceedings of LDEF Materials Results for Spacecraft Applications Conference, Oct. 1992.