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ATOMIC OXYGEN EROSION CONSIDERATIONS FOR SPACECRAFT MATERIALS SELECTION

Ann F. Whitaker and Rachel R. Kamenetzky
NASA/Marshall Space Flight Center
Huntsville, Alabama

INTRODUCTION

The Long Duration Exposure Facility (LDEF) satellite carried 57 experiments that were designed to define the low-Earth orbit (LEO) space environment and to evaluate the impact of this environment on potential engineering materials and material processes. Deployed by the Shuttle *Challenger* in April of 1984, LDEF made over 32,000 orbits before being retrieved nearly 6 years later by the Shuttle *Columbia* in January of 1990.

The Solar Array Passive LDEF Experiment (SAMPLE) AO171 contained approximately 300 specimens, representing numerous material classes and material processes (ref. 1). AO171 was located on LDEF in position A8 at a yaw of 38.1° from the ram direction and was subjected to an atomic oxygen (AO) fluence of 6.93×10^{21} atoms/cm^2. LDEF AO171 data, as well as short-term shuttle data, will be discussed in this paper as it applies to engineering design applications of composites, bulk and thin film polymers, glassy ceramics, thermal control paints, and metals subjected to AO erosion.

DEFINITIONS

The terms associated with AO erosion as set forth in this paper need to be clearly defined in order to provide nonambiguous data for the design engineer. AO *fluence* is defined in terms of the ratio of the number of oxygen atoms incident to sample surface exposed area. A particular material's *reactivity* is defined in terms of a change in material thickness per AO fluence. Some materials react with AO in a manner such that long-term AO effects can not be linearly predicted from short-term data. These materials are often described in terms of a *nonlinear reactivity* which is defined as the ratio of a material's change in mass to the AO fluence. *Accommodation*, which is a term used particularly for oxidizing metals, is defined in terms of the number of atoms of AO reacted to the number of incident atoms of AO.

COMPOSITES

LDEF experiment AO171 included 33 composites (Table 1), 27 of which were carbon fiber composites configured in various layups in order to provide a potentially more complete analysis of both fiber and matrix strengths. These composites were the most promising types in the 1978 to 1980 timeframe when samples were chosen for this flight experiment. These samples included both high strength (HMS series) and high modulus (HMF series) composites as well as the P75S/934 composites, which were used for the focal plane structure of the Hubble space telescope. Also included in the sample list were six "S" glass epoxy composites, three of which were covered with a protective aluminum thermal control tape.

Table 1. Experiment A0171 composites fiber/matrix/layup (number of samples).

• HMF 322 / P1700 / ±45° (5)
• HMS / 934 / 0° (5)
• HMS / 934 / 90° (6)
• P75S / 934 / 90° (6)
• P75S / 934 / 0° (5)
• "S" Glass Epoxy (3)
• "S" Glass Epoxy with Aluminum Thermal Control Tape (3)

Exposure to the LEO environment tended to darken the exposed composite surfaces and make them more optically diffuse. For the carbon fiber composites, matrix erosion was greater than that of the carbon fibers. Reactivity data based on erosion of the carbon fiber was approximately half that which was generated for short-term shuttle flight data where sample erosion is confined to the matrix rich top surface of the composite. The epoxy resin in the "S" glass composites was generally protected from AO attack by the glass fibers, but ultraviolet (UV) radiation degraded the thermal/optical properties of the composite. Composites covered with the aluminum thermal control tape were completely protected from AO erosion in the taped area (ref. 2), though a slight amount of AO undercutting along the unprotected edges of the sample was evident. Table 2 contains AO reactivity and percentage change in the ratio of absorptivity to emissivity generated for the space exposure of all the AO171 composites.

Table 2. Experiment A0171 composite space environmental exposure data.

Sample	AO Reactivity (cm^3/atom)	Percentage Change in (α/ε)
Graphite/Epoxy	1.0×10^{-24} *	–3 to 8 percent
"S" Glass Epoxy	0.13×10^{-24}	+9 %
"S" Glass Epoxy with Aluminum Thermal Control Tape	Tape Protected Composite	–8 percent (Aluminum Tape)

* Based on erosion of carbon fiber.

POLYMERS

AO171 polymers (ref. 3) consisted of thin films of 5-mil Kapton™, 1-mil black Kapton™, 0.5-mil FEP Teflon™, and 1-mil white Tedlar™, of which only a residual film of the white Tedlar™ survived the space exposure. Bulk polymers included various configurations of Halar™, polyetherether ketone (PEEK), and RTV 511. In addition, TFE Teflon™ washers, which were used to secure flight samples to the experiment tray, were also evaluated for AO erosion effects. AO171 polymers also included samples of Kevlar 29™ and Kevlar 49™ configured in the form of woven fabrics, and polysulfone, which served as the matrix for the HMF 322 composites.

Unlike the Kapton™, black Kapton™, and FEP Teflon™ thin films, white Tedlar™ contains self-shielding inert particles which served to protect the film from complete AO erosion. Table 3 contains the reactivity values generated for the AO171 polymers along with reactivity values from previous shuttle flight data where available. Though no reactivity values were generated for RTV 511 due to outgassing of the specimens, SEM evaluation of the exposed surfaces clearly showed features characteristic of AO erosion. Although previous short-term shuttle data could not clearly distinguish TFE and FEP reactivity values, TFE data from LDEF experiment AO171 and FEP data from LDEF experiment SOO69 indicate a clear and definitive AO erosion difference between the two Teflons™, with FEP being the more reactive. LDEF reactivity values for the Halar™ and polysulfone specimens agree well with short-term shuttle values, indicating that these pure polymers erode linearly with AO fluence. The larger reactivity values for Kevlar 49™, a higher stressed state material than Kevlar™ 29, suggests a connection between stress and AO reactivity. This possible connection between stress state and AO reactivity has also been seen in data generated for other material types.

Table 3. Polymers AO reactivity data.

Polymer	AO Reactivity (10^{-24} cm^3/atom)		Comments
	AO171	Shuttle Flights	
White Tedlar™	0.29	----	Inert particles retarded erosion.
TFE Teflon™	0.20	< 0.05 (estimated)	Data taken from AO171 washers.
FEP Teflon™	0.35	<0.05	Data from S0069.
PEEK	2.3	3.7 ± 1.0	Shuttle flight material was thin film with low emittance.
Halar™	2.1	2.0	
Kevlar™ 29	1.5±0.5	1.1 ± 0.2	Shuttle data based on STS-8 tether mass loss.
Kevlar™ 49	4.0	----	Shuttle data based on STS-8 tether mass loss.
Polysulfone	2.3	2.4	

GLASSY CERAMICS

Approximately 30 silver and aluminum solar reflectors with thin coatings of various glassy ceramics were flown on this experiment. Many of these samples were configured so that only half of the sample surface was exposed to the environment.

Table 4 summarizes sample changes in solar reflectance and film thickness for the solar reflectors induced by exposure to the LEO. In general, all exposed sample surfaces experienced a small decrease in reflectivity. Angstrometer data revealed a general decrease of up to 160 Å in film thickness in the exposed region with corroborating evidence from low energy Rutherford back-scattering indicating a densification of the exposed film. In addition, a conversion of SiO to SiO_2 was identified for many of the specimens. Reactivity values, based on the assumption that the observed effects were the result of AO attack and that no other mechanism was involved, ranged from 0.40 to 2.3×10^{-28} cm^3/atom.

Table 4. Property changes in glassy ceramics.

Coating/Solar Reflector	Percentage Change in Solar Reflectance (%)	Decrease in Film Thickness (Å)
SiO_2/Ag	– <1	40
SiO_2/Al	– <1	50
SiO – SiO_2/Enhanced Al	– 2.0	125
SiO/Al	– 1.5	150
MgF_2 – Sapphire/ Enhanced Al	+ 1.5	25
MgF_2 – Sapphire/Ag	–5 to –10	150
Dielectric/Ag Alloy	–1 to –5	160

PAINTS

Experiment AO171 contained eight different paint specimens including several different polyurethane specimens, a black epoxy specimen, two tiodized specimens and a S13GLO specimen. All the paint samples were configured such that only half of the sample surface was exposed to the environment. Table 5 summarizes visual observations made for both the unexposed and exposed regions.

All the paints except the S13GLO lost mass as a result of the space exposure. Table 6 summarizes the thermal property changes and reactivity values (based on mass loss) for the AO171 paints and compares these values to data generated, where available, from previous shuttle flights. As evident from the data, AO reactivity is clearly nonlinear, with the implication that long-term reactivities cannot be predicted from short-term exposures. From a positive standpoint, the nonlinear erosion, coupled with a slight increase in emittance, indicates that the paints will remain effective as a thermal control coating longer than previously suggested by short-term shuttle data.

Table 5. A0171 summary visual observations on exposed paints.

Paint	AO171 - Visual Observations	
	Unexposed Region	Exposed Region
Z306	Diffuse, Black	More Diffuse
Z302	Specular, Black	Diffuse, Light Gray (Substrate)
Z853	Specular, Dark Yellow	Diffuse, Light Yellow
A276	Specular, White	Diffuse, Bright White
401-C10	Diffuse, Black	More Diffuse
Tiodized K17 Black	Diffuse, Black	Diffuse, Gold/Brown
Tiodized K17 White	Diffuse, White	Diffuse, White
S13GLO	Diffuse, White	Diffuse, Light Tan (UV Degradation)

Table 6. A0171 and shuttle flight paint thermal properties and reactivities.

Paint	Absolute Change in Absorptivity		Absolute Change in Emissivity	AO Reactivity (Nonlinear) (mg/incident atom)	
	Shuttle Flight	LDEF AO171	LDEF AO171	Shuttle Flight	LDEF AO171
Z306	–0.02	–0.01	+0.02	1.0×10^{-21}	2.3×10^{-22}
Z302	+0.04	~0.00	+0.02	5.8×10^{-21}	5.7×10^{-22}
Z853	+0.04	–0.07	+0.04	0.90×10^{-21}	1.4×10^{-22}
A276	~0.00	–0.05	+0.03	1.0×10^{-21}	1.4×10^{-22}
401-C10	+1.5 ±0.5	+0.01	+0.00	0.86×10^{-21}	1.6×10^{-22}
Tiodized K17 Black	Unavailable	+0.03	–	No Data	Unavailable
Tiodized K17 White	Unavailable	–0.15	–	No Data	Unavailable
S13GLO	+1.1 ± 2	+0.14	–0.04	Negligible	Negligible

METALS

AO171 metal specimens included 1-in diameter bulk pure metals, metal alloys in both the as-received and preoxidized condition, and cold-rolled silver ribbon both thermally heat sunk and thermally isolated configured with and without a stress loop. All the bulk metal specimens were well heat-sunk to the less than 100 °F flight structure.

All nonpreoxidized metals gained mass as a result of the nearly 6 years of exposure to the LEO environment. Macroscopic oxidation effects were observed on both the bulk copper and bulk silver specimens. SEM photographs of the exposed silver specimens indicated a surface morphology which varied radically with sample microstructure and thermal configuration. Reactivity and accommodation numbers for all the metals as well as thermal properties are shown in Table 7. Although metals oxidize in a nonlinear process, all reactivity values calculated were based on a linear oxidation process in order to provide a relative means of comparison. In general, reactivity values for all but the silver specimens were less than 1×10^{-26} cm^3/atom. Accommodation numbers (calculated based on the assumption that the mass gain was due to the formation of the most thermodynamically favorable oxide) for all but the cold rolled silver ribbon stress loop were less than 10 oxygen atoms reacted per 10^4 incident. Reactivity and accommodation values for the cold rolled, stressed, thermally isolated silver were an order of magnitude greater than that for the same material which had no applied stress and were well heat sunk to the LDEF tray, suggesting that AO effects are more dependent on temperature and microstructure than on total incident AO.

Table 7. Thermal/optical property changes and AO reactivity and accommodation values for A0171 metals.

Metal	Thermal/Optical Properties		AO Reactivity (10^{-26} cm^3/atom)	AO Accommodation, (AO/10^4 incident atoms)*
	Change in Absorptivity, (%)	Change in Emissivity, (%)		
Copper	+57.1	+11.4	0.87	3.6
Molybdenum	+20.4	+ 1.89	0.14	2.8
Tungsten	+ 3.08	+ 9.09	0.04	~1.0
HOS 875	+ 6.92	- 2.90	0.29	2.5
Pre-Ox HOS 875	+ 0.39	+16.0	TBD	TBD
Tophet 30	+33.2	- 3.33	0.55	5.0
Pre-Ox Tophet 30	- 0.22	+ 0.69	–	–
Ni-Cr-Al-Zr Alloy	+10.8	+51.0	TBD	TBD
Pre-Ox Ni-Cr-Al-Zr Alloy	+ 2.93	+ 1.86	–	–
Tantalum	- 0.87	- 5.98	0.60	8.3
Titanium 75A	+ 5.17	- 2.97	0.39	4.4
Mg AZ31B	- 5.26	+ 1.54	0.45	2.0
Niobium	+ 2.58	+ 0.94	0.14	2.0
Silver disk-fine grain	+247.0	+262.0	2.90	8.4
Silver-cold rolled ribbon in stress loop	–	–	27.5	80.0

* Accommodation strongly dependent on temperature and stress; numbers are tentative pending confirmation of oxide identity.

CONCLUSIONS

The LDEF satellite proved to be a valuable source of information on the durability of potential engineering materials exposed to the LEO environment for an extended period of time. Coupled with short-term shuttle data, material degradation due to AO attack can be predicted with a greater level of confidence.

Data from experiment AO171 indicated that long term AO erosion of carbon composites can be predicted from carbon reactivity. Glass fiber composites tend to become self-protecting and would thus perform well in an AO environment. In addition, AO171 data indicated that thermal control tapes worked well in protecting the underlying composite from AO attack. Data on the AO171 polymers, coupled with short-term shuttle polymer data, indicated that the unfilled "pure" polymers react linearly with AO such that long-term AO erosion can be predicted from short-term shuttle data. AO171 glass ceramics underwent a densification accompanied by a decrease in film thickness of less than a few hundred angstroms as a result of the space exposure. The role of AO in this densification process is not clearly understood. Data on the AO171 paints indicated that the AO erosion process is nonlinear. However, thermal/optical property data, in which emissivity values increased slightly while solar absorptivity values generally decreased slightly, indicates that the paints would last longer than previously predicted from short-term shuttle data. AO interactions with AO171 metals clearly showed a nonlinear relationship which is strongly dependent on temperature, stress, and material microstructure.

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