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Review
Effect of low earth orbit atomic oxygen on spacecraft materials

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This review attempts to bring together the published data and analysis related to the effect of low earth orbit (LEO) atomic oxygen (AO) interaction with spacecraft materials. The basic interaction mechanism of AO with spacecraft materials and quantification of its effect on materials performance are briefly discussed. After providing a list of materials susceptible to the LEO environment, the paper focuses on the degradation mechanism of various spacecraft materials. Particular emphasis is given to the protective mechanisms for AO-susceptible materials and development of AO-resistant materials for long-term LEO spacecraft applications. Ground-simulation testing requirements and their present status are reviewed briefly. The need for further research is emphasized.

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1. Introduction

Early space shuttle mission have brought to light somewhat unforeseen physical phenomena occurring at low earth orbit (LEO) altitudes [1–3]. Examinations of returned satellite hardware have shown that atomic oxygen (AO) within the orbital environment can interact with many spacecraft materials to produce surface recession and mass loss. The dominant chemical constituent of the LEO environment is AO and its erosive potential is substantially increased by the high speeds of the spacecraft in the LEO [4]. Flight experiments were conducted during space shuttle flights STS-5 [5–8], STS-8 [9], STS-17 [9], STS-32 [10], STS-41 [10] and STS-44 [11]. Long Duration Exposure Facility (LDEF) [12–15] and Limited Duration Candidate Exposure (LDCE) material exposure experiments [16] were conducted to develop fundamental understanding of the deleterious effects of the exposure of a variety of materials to the LEO environment. These experiments have demonstrated that although the ambient density of AO is quite low at altitudes where LEO spacecraft typically operate, the orbital speed of the spacecraft results in high incident fluxes and collisional energies large enough to interact with and degrade many material surfaces. Results of these experiments have also shown that prolonged exposure of sensitive spacecraft materials to the LEO environment will result in degraded system performance, which can significantly affect mission performance and may even result in premature mission failure. The accurate prediction of the AO environment and quantification of its effect on performance of spacecraft materials can significantly aid designers in selecting suitable materials and designing reliable spacecraft systems for the desired mission life at LEO altitudes. The need to understand and negate the adverse effects of AO erosion on spacecraft materials is of significant importance. Development of new materials and protective coatings which are stable in the LEO environment is an appealing approach to solving the AO degradation problem.

This paper reviews the effects of AO environment on the performance of various spacecraft materials using the available data from both space experiments and laboratory investigations. Focus is on identification and development of AO-resistant spacecraft materials.

The review is arranged as follows. Section 2 briefly reviews the AO interaction mechanism with spacecraft materials and quantification of its effect on the performance of materials for the desired LEO mission lifetime.

Various materials susceptible to AO attack and their degradation mechanism are discussed briefly in Section 3.

Section 4 discusses and reviews the different protective mechanisms and AO-resistant materials for different spacecraft materials. The present development status of the coatings and their performance in protecting spacecraft materials from the AO environment are also discussed briefly.

Ground simulation testing requirements and their present status are discussed briefly in Section 5.

The paper ends with a summary of conclusions and the need for further research is emphasized.

2. Interaction mechanism of AO with spacecraft materials

AO is produced due to photodissociation of the diatomic oxygen molecules present in the upper

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atmosphere by absorption of solar u.v. radiation in the wavelength range 100–200 nm [17]. Photodissociated AO has a very high probability of long-term survival in the low earth altitudes because there is an appropriate O_2 density here to facilitate reasonable AO production and low probability of interaction with neighboring atoms or molecules. The average thermal velocity of the gas molecules at low earth altitudes is very low and the collision energy produced due to impact with spacecraft surfaces is very low and may not initiate any changes in surfaces, but the spacecraft orbiting in the LEOs ram into the AO environment at a velocity of 8 km s^{-1} and produce collision energies between the spacecraft surfaces and oxygen atoms of 4.5–5 eV [18]. The AO collision with the spacecraft surfaces with this energy initiates numerous chemical and physical events on the surfaces. The AO may simply scatter off the surface either in its original or altered charged state. It may chemically react with nitrogen atoms on the spacecraft surfaces or while impinging upon the surface to form nitrous oxide in the excited state, which can de-excite by producing glow [19]. The impinging AO may be captured by a potential well at or below the surface where it chemically reacts to form an oxide, which migrates from the surface into the bulk of the material.

Reactions of AO with different polymeric materials have been shown to occur by various mechanisms [20]. The basic mechanisms are abstraction, addition, elimination, insertion and replacement. *Abstraction* is the process by which AO abstracts an atom such as hydrogen from the compound. *Addition* describes the process by which an oxygen atom adds or attaches itself to an organic compound. This has been observed in the reaction with a typical alkene and the initial product is a vibrationally excited molecule which can then undergo *elimination* of the hydrogen atom. AO has also been observed to lodge between two bound atoms such as hydrogen and carbon in an organic molecule (*insertion*). *Replacement* is the mechanism by which an oxygen atom attaches to the molecule and a portion of the original molecule departs (usually as a radical). Oxygen in effect replaces a group originally present on the molecule producing alkoxy and alkyl radicals. The details of degradation mechanisms of different spacecraft materials due to AO impact are discussed later.

The interaction of AO with spacecraft surfaces will result in mass loss or gain and changes in surface morphology and optical, mechanical and thermal properties. The quantification of AO effects with spacecraft materials has generally been performed by measuring the AO effect and materials reaction probability. The energetic AO reacts with spacecraft surfaces forming oxidative compounds. These compounds may be volatile in the case of polymers, carbon and osmium or oxides which are not adherent and spall in the case of silver. Both types of surface oxide contribute to net surface erosion. AO reacts with high oxidative metals like aluminium, nickel, etc., and inorganic polymers like silicones forming their strong adherent oxides on the surface. In these cases the surface may grow. The chemistry of the remaining or reacted surface may be analysed at the surface in terms of composition and optical and mechanical characterization (of modulus and elasticity). If net erosion of the material surface occurs, the volume or mass loss is quantified and used to calculate an erosion or surface recession per incident atom. Depending on the functional requirement of the material surface, the necessary property changes are also measured and correlated with the total effect of AO exposure.

3. Spacecraft materials susceptible to AO attack

Spacecraft surfaces directly exposed to the LEO environment are mostly affected by AO interaction. Table I lists the spacecraft materials affected by LEO AO impact and the degradation mechanisms of these materials are discussed below.

3.1. Composite materials

Advanced composites have been used extensively for spacecraft structural, payload, power and thermal control subsystem applications. Composites of interest for spacecraft applications are mainly polymer matrix composites, because of their combination of light weight, dimensional stability, high structural rigidity and low thermal expansion. Polymer resins include a variety of epoxies, polyimides, polysulphones and phenolics. The resin determines the interfibre mechanical properties. Reinforcements include glass, aramid, graphite and boron fibres. Typical applications of polymer composites for spacecraft structures include primary truss assemblies, core structures, booms, sandwich panels, bulkheads and stiffeners. Types of payload advanced composites especially for dimensional stability include communication antennae reflectors, radio frequency components, optical telescope components, space-based radar and precession mounting payload platforms and support structures. Rigid structural support for photovoltaic solar arrays and for solar dynamic power systems concentrators also now utilize composites [21].

The high-energy AO interacts with both carbon/graphite fibres as well as the resin matrix. The degradation of polymer matrices at high levels of AO fluence is mainly due to polymer bond breaking and subsequent molecular fragmentation leading to the erosion of the polymer matrix. The high-energy AO reacts with the carbon/graphite fibres resulting in formation of volatile oxides on the surface, which leads to surface recession. These effects are mainly responsible for reduction of mechanical strength, and changes in surface morphology and optical and thermal properties.

Various types of composites were exposed to the LEO environment in space shuttle flights [22, 23] and LDEF missions [24–28]. These included a range of low-, medium- and high-modulus mesophase pitch and polyacrylonitrile (PAN) carbon and graphitic and Kevlar (aramid) fibres, and cured and post-cured thermoplastic and thermoset resin matrices, especially

TABLE I Spacecraft materials susceptible to AO

1. Polymer matrix composite materials
    - carbon fibres
        - pan-based fibres
        - mesophase pitch based fibres
    - Kevlar fibres (polyamide fibres)
    - thermoplastic resin matrix
        - polysulphone
        - polyethersulphone
    - thermoset resin matrix
        - epoxy
        - polyimide
        - poly(arylacetylene)
2. Tribomaterials
    - lamellar solids
        - MoS_2
    - soft metals
        - silver
        - lead
        - indium
    - polymers
        - PTFE
        - phenolics
        - epoxy
        - polyimide
3. Thermal control components
    - metallized polymers
        - Ag/FEP Teflon
        - Al/FEP Teflon
        - Al/Kapton
    - organic paints
        - white paints
            - Chemglaze A276
            - silicone S13G/LO
        - black paints
            - Chemglaze Z302
            - Chemglaze Z306
4. Optical components
    - metallic coatings
        - silver
        - aluminium
        - rhodium
        - iridium
        - nickel
        - niobium
        - gold
        - chromium
        - copper
        - osmium
        - palladium
        - tantalum
        - titanium
        - tungsten
        - zirconium
    - dielectric coatings
        - magnesium fluoride
        - thallium fluoride
        - zinc sulphide
        - calcium fluoride
5. Space power components
    - photovoltaic solar array
        - Kapton film
        - silver interconnects
        - CFRP
        - fibreglass composites
    - solar dynamic power components
        - reflective
            - silver
            - aluminium
            - CFRP
        - refractive
            - silicones
            - acrylic
            - fluoropolymers
            - polycarbonates

unidirectional and multidirectional composites. Most composite constructions were either cloth laminates or varying angle fibre wraps [29].

Various types of carbon fibres ranging from a high-modulus, highly graphitic (Gr) fibre to a low-modulus amorphous carbon fibre were exposed to the LEO environment on the STS-8 mission. Post-flight results show that carbonaceous materials oxidized upon exposure to the LEO environment at shuttle altitudes [23]. The extent of surface and in-depth oxidation appears to depend on precursor-pitch, polyacrylonitrile (PAN), mesophase pitch and the degree of graphitic order [23].

PAN-based fibres with a low tensile modulus had shown the greatest surface, transverse and longitudinal and internal oxidation, and a decrease in oxidation rate with increasing tensile modulus and density. The surface sheen of the low-modulus PAN fibres after oxidation appears to be a fibril structure [23]. The degree and extent of oxidative attack was reduced for the fibres with an intermediate modulus and even more so for the filament with a high modulus. The post-oxidative characteristics of mesophase pitch carbon fibres appear to be similar to the PAN-based high-modulus carbon fibres. The extent of surface oxidation on carbon fibres appears to be dependent on the degree of graphitic order and the type of precursor.

The ground-simulated experimental results on carbon samples show that oxygen had diffused into the bulk of the carbon [30, 31]. Although diffusion had been seen, it was expected that all the oxygen atoms that were reacted with the carbon surface would leave the surface as CO or CO_2; with oxygen dissolved in carbon, it is possible that there could be latent effects that would lead to further erosion [30]. The reaction efficiencies of different types of carbon samples derived from both space and ground-based laboratory experiments are given in Table II. Ground simulated laboratory AO experiments with an AO fluence of 7×10^{18} atoms m^{-2} have shown that carbon fibres were degraded due to oxidation. Surface composition analysis of carbon fibres after AO exposure shows that there is an increase of 30% in surface oxygen concentration [32].

Kevlar fibres are made from polyamide polymer and are spun similarly to textile fibres. There are two types of Kevlar fibres available commercially, namely Kevlar 29 and Kevlar 49. Both have low density and high strength, but the modulus of Kevlar 49 is approximately twice that of Kevlar 29. Both fibres were exposed to the LEO environment on space shuttle

TABLE II AO reactivity coefficients of composite materials

Composite material	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	AO reactivity coefficient (cm^3 atom^{-1}) (10^{-24})	Ref.
Kevlar 29	STS-8	03.0	1.1	34
Kevlar 29	LDEF	69.3	1.5	34
Kevlar 49	LDEF	69.3	4.0	34
Carbon film	STS-4	00.65	1.4–4.3	31
Carbon vitreous	STS-5	00.99	0.23	31
Graphite (basal-oriented)	STS-8	03.0	0.63	31
Carbon film	STS-8	03.0	9.0	31
Glassy carbon	STS-8	03.0	1.3	92
Graphite (single-crystal)	STS-8	03.0	1.4	92
Graphite (pyrolytic carbon)	Ground simulation	00.1	29–36	30
Graphite (highly oriented pyrolytic)	Ground simulation	00.1	9.2	30

TABLE III AO reactivity coefficients of polymer matrix composites

Composite Fibre/resin	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	AO reactivity coefficient (cm^3 atom^{-1}) (10^{-24})	Ref.
Graphite/epoxy				
T300/5208	STS-8	03.0	2.9	22
T300/934	STS-8	03.0	2.6	22
T300/934	LDEF	69.3	0.3	37
AS/3501-6	LDEF	69.3	0.8	37
HMS/934	LDEF	76.8	0.9	34
P75S/934	LDEF	76.8	1.0	34
T300/934	LDEF	03.0	2.0	68
Graphite/polyimide				
C6000/PMR-15	LDEF	69.3	1.3	37
Graphite/LARC160	LDEF	69.3	0.9	37
Graphite/thermoplastic				
T300/P1700	LDEF	69.3	1.1	37
HMF322/P1700	LDEF	76.8	1.6–3.8	34

[23] and LDEF missions [26, 33, 34]. Post-flight results showed mass loss of Kevlar fibres and a change in optical properties and surface morphology. The AO reactivity coefficients derived for Kevlar fibres from space tests are given in Table II. The data show a distinct difference between Kevlar 29 and 49. Kevlar 49, whose reactivity is higher, is a more stressed material than Kevlar 29, suggesting a connection between stress and AO reactivity [34]. The surface sheen of the Kevlar 29 fibre was dulled and solar absorptance and emissivity values decreased. A mechanical strength loss of 25–30% was observed after exposure to the LEO environment [23].

Polymer matrix composites exposed to the LEO environment showed thickness loss and optical, mechanical and thermal property changes. Polymer matrix composite reactivity coefficients were derived from the space shuttle and LDEF missions data and are given in Table III.

The AO reactivity coefficient of composite materials is generally computed from the known composite density and exposure area and the measured mass loss and computed AO fluence. The erosion depths are probably somewhat higher than predicted because the samples might have resin-rich surfaces and the epoxy, which has a lower density than graphite fibres, erodes at a higher rate than the fibres. Composites prepared by different processes and under different surface conditions show various degrees of degradation due to AO attack [35]. It appears that the fibre content and surface conditions are more important variables than the graphite fibre type or epoxy matrix type in determining the susceptibility of graphite/epoxy to AO erosion [35]. The estimated erosion of graphite epoxy matrix composites is much less than the predicted erosion based on monolithic polymer reactivity [36].

The estimated reactivity coefficients of graphite/epoxy, graphite/polysulphone and graphite/polyimide composites show that the polyimide matrix-based composite suffered more surface erosion than epoxy and polysulphone composites. The thickness loss of the composites varies in the order polyimide > epoxy

> polysulphone [28]. The lower surface recession of epoxy and polysulphone composites may be attributed to the white residue formation on the surfaces after exposure to the LEO environment [37–39]. This ash-like residue coating on the composite surface may act like a barrier layer which may slow down the composite erosion [38]. Chemical analysis of the ash residue on graphite/epoxy and graphite/polysulphone composites shows that sodium sulphate appears to be a major component [37]. The source of this compound appears to be the remnant of sulphates from the diaminodiphenylsulphone (DDS)-based curing agents used in the epoxy and polysulphone matrix composites and residual sodium contamination during manufacture of graphite. This sodium sulphate may form on the surface as an AO-resistant layer. The exact chemical composition of this sulphur-containing species has not yet been established [38, 39].

Post-flight results for carbon fibre reinforced with poly(arylacetylene) composite samples tested in the LDEF have shown that the composites were eroded to a depth of 25–125 μm [40]. The erosion morphology was dominated by crevasses parallel to the fibres with triangular cross-sections of 10–100 μm in depth. The reason for the crevass formation may be the faster oxidation rate of the resin compared with that of the fibres. Carbon fibre/organic matrix composites with epoxy, polyimide and polysulphone matrices were reported to have erosion of 50, 75 and 50 μm respectively [41]. The experimental data indicate that the carbon fibres play an important role in crevass initiation and enlargement and in overall erosion rate [40]. Molecular composition analysis of the composites tested at the leading edge of the LDEF mission shows that there is a very small increase in oxygen concentration on the surface. This may be due to formation of volatile oxide products upon AO interaction on the surface; subsequently they may evaporate [40].

Graphite/epoxy composites of IM6/R6376, T300/E600 and T300/5208 with high-strength fibres and GY70/934 with high-modulus fibres were tested in a ground-simulated AO facility with an AO fluence of 5×10^{20} atoms cm^{-2} [42]. Composites of IM6/R6376, GY70/934 and T300/5208 were reinforced with tetraglycidyl-diaminodiphenylmethane/diaminodiphenylsulphone resins and T300/E600 composites were reinforced with bisphenol-A-diglycidylether/acidanhydride resins. The X-ray photoelectron spectroscopy (XPS) results of the graphite/epoxy surface show that chemical changes occurred on the irradiated surfaces, which were attributed to AO interaction. The surface mainly contained the free radicals of O–C=O (carboxyl), C=O (carbonyl), C–O, CH–CH from the epoxy resin and C–C from the carbon fibre. The carbonyl groups are formed mainly due to dehydrogenation of alcohol groups in the epoxy resin. The methylene carbon and carbonyl bonds might have dissociated due to AO impact and subsequent addition of oxygen lead to the formation of carboxyl groups. The composition analysis shows that the oxygen content was enriched from 16.2 at % in the pre-irradiated sample to 23.2 at % in the irradiated samples [42].

Two types of erosion morphology were observed in polymer matrix composites tested in LDEF experiments. Preliminary observations suggest that the erosion features may be a function of the fibre modulus or structure [35]. Deep AO erosion grooves with erosion fragments with "Christmas tree" or cone-like features were observed in composites containing high-modulus graphite fibres of GY70 (4.82×10^{11} N m^{-2} modulus) and PS75S (5.17×10^{11} N m^{-2} modulus). The rows of erosion fragments on these samples run parallel to the fiber direction with the apex of the cones or Christmas tree pointing in the direction of AO flux impact. A fine and more acicular appearance with randomly arranged AO erosion fragments was observed in composites containing low-modulus graphite T300 or Celion 6000 fibres ($2.1–2.4 \times 10^{11}$ N m^{-2} modulus) [35]. The erosion morphology of composites has been discussed in terms of a 2-step erosion process [40]. In the first step the outer layer of the organic matrix might have been removed at a faster rate – roughly at the same rate as the monolithic reactive polymers. In the second step, when the carbon fibres became exposed, a lower reaction efficiency for the fibres led to a lower overall erosion rate and contributed to the development of highly irregular surface morphology [40].

The AO erosion of graphite/epoxy composites exposed directly to the AO environment at the leading edge of the LDEF experiments resulted in a 20–30% reduction in the strength and modulus, and the graphite/bismalimide composite (T300/V378A) had a 60% reduction in strength. The short beam shear strength of graphite/epoxy and T300/V378A composites decreased by 10% [25, 35]. The effect of AO erosion on mechanical performance for the different polymer composite orientations has been studied in LDEF experiments [37]. The results show that the loss of 1 ply thickness on unidirectional (0°) reinforced ply on the surface would result in performance reduction. This may be due to surface erosion of both fibre and the epoxy, which allows the underlying ply to pick up the load from the eroded surface whereas a (0°, 90°) and (0°, ± 45°) angle ply stacking sequence shows that after erosion of 0° ply, the ply underneath is a continuous reinforcement in the load direction. These orientations show no change in flexure modulus or strength. The results clearly show that ply orientation plays a very important role in flexure strength behaviour when AO erosion is involved [37].

3.2. Tribomaterials

The tribological requirements of different mechanical assemblies of spacecraft vary depending on the function of the mechanisms. Almost all spacecraft mechanisms are in two general categories: (a) high-cyclic and (b) low-cyclic mechanisms. Low-cyclic mechanisms are customarily one-shot devices and the tribomaterials are not seriously affected (deployment of antennae, solar arrays and large booms). Advanced tribomaterials used for the following high-cyclic mechanisms need to be carefully selected:

(a) *control moment gyros* – for stabilizing satellite movement/control

(b) *gimbal bearings* – allow multidirectional movement of components or systems

(c) *despin bearings* – allow a portion of the platform to be stationary with respect to earth while the body of the spacecraft spins for stability

(d) *sliprings* – allow transmission of signal/power from rotating to stationary components.

Lubrication selection is very limited for long-term space applications without maintenance for refurbishment or replenishment. Many lubricants cannot perform well in the space environment. Therefore solid lubricants are being considered for environmentally exposed surfaces.

Solid lubricants can be either organic or inorganic. The latter can be further separated into metallic (Pb, Au, Ag and In) and non-metallic. The LEO-exposed lubricants react with high-energy AO resulting in chemical degradation. Degradation can occur through oxidation and erosion or loss through evaporation of volatile oxide elements. Early experimental space results show that solid lubricants are at risk, particularly when in the form of thin films, since even a low erosion rate would cause their removal in a comparatively short time. The susceptibility of solid lubricants to AO attack has been addressed in the literature [43]. Table IV summarizes the reaction efficiencies in terms of volume material lost per incident oxygen atom of some selected tribomaterials [44]. Very limited data are available on solid lubricants tested both in space as well as ground simulation experiments. It is clear from Table IV that polymer materials such as perfluorinated lubricants, soft metals and epoxy bonded laminates will be affected. To date the most extensive study of AO effects on solid lubricants has been performed on molybdenum disulphide (MoS_2). In the laboratory tests the samples were exposed to very low-energy oxygen atoms [45, 46]. Molybdenum disulphide reacts with AO forming molybdenum oxides and the release of sulphur oxide was also observed during the test [45]. The oxides comprised mainly MoO_3 and to a lesser extent MoO and were restricted to the surface layer. Tribological measurements have shown that the oxidized MoS_2 exhibits higher friction and a higher wear rate. The values of wear and friction are determined by the oxidation rate and the duty cycle of the exposed component. Table IV indicates that silver which is used as a lubricant is heavily attacked by AO resulting in an oxidized metal, which is lost by flaking and spallation. Indeed any material with a susceptibility to oxidation seems likely to suffer in similar fashion. Organic compounds would appear to be particularly susceptible to AO-induced degradation. This susceptibility may prohibit the use of those organic compounds that are used as lubricants or as binders of solid lubricants.

3.3. Thermal control components

There are two basic approaches to the design of a spacecraft thermal control system, passive and active. The former operates by using appropriate materials and surface finishes, such that the temperature of the spacecraft components remains within acceptable limits over the range of geometries and irradiation levels experienced. Active systems use mechanical or thermoelectric devices and have moving parts. Passive thermal control systems are mainly exposed to the LEO environment. The choice of materials and coatings constituting the surface of the spacecraft must take into account both the solar spectrum and spacecraft thermal radiation characteristics. In this regard a knowledge of two important properties, solar absorptivity and infrared emissivity, is necessary. For example a component requiring low temperatures in the solar earth environment can use a highly reflecting and highly emitting white surface (low-α and high-ε). Similarly a component operating at a high temperature might use a high-absorptance and low-emittance metallic surface. Passive thermal control surfaces may be conveniently divided into the following categories:

(a) *solar reflector*: a surface which reflects the incident solar energy and emits infrared energy, low-α, high-ε and low-$\alpha/\varepsilon < 1$

(b) *solar absorber*: a surface which absorbs solar energy and emits a small percentage of the infrared energy, high-α low-ε, and high $\alpha/\varepsilon > 1$

(c) *flat reflector*: a surface which reflects the energy incident upon it throughout the spectral range from u.v. to far-infrared, low-α and ε and $\alpha/\varepsilon = 1$

(d) *flat absorber*: a surface which absorbs the energy incident upon it throughout the spectral region from u.v. to far infrared, high-α and ε and $\alpha/\varepsilon = 1$.

TABLE IV AO reactivity coefficients of tribomaterials

Material	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	AO reactivity coefficient (cm^3 $atom^{-1}$) (10^{-24})	Ref.
Silver			10.5	157
Epoxy	STS-8	03.5	1.7	157
Polysulphone	STS-8	03.5	2.4	34
	LDEF	69.3	2.3	34
PEP	STS-8	03.5	0.05	34
	LDEF	69.3	0.35	34
TFE	STS-8	03.5	0.05	34
	LDEF	69.3	0.20	34

The above requirements are met by using metallized polymer films (second surface mirrors (SSMs)), organic paints and thermal control coatings.

The high-energy AO can cause severe damage to thermal control components in the form of thermo-optical property degradation and mass loss, particularly to traditional polymeric films (FEP Teflon and Kapton) and organic paints, which are used extensively passive thermal control applications on spacecraft [47].

3.3.1. *Metallized polymer films*

Silver-backed fluorinated ethylene propylene (FEP) Teflon and aluminized Kapton and FEP Teflon are used as flexible SSMs and as multilayer thermal insulation blankets (MLIs).

The SSM is derived from its dual function as thermal emitter and solar reflector. They typically cover the areas of the spacecraft beneath which are the radiators for heat producing equipment such as travelling wavetube amplifiers, output multiflexers and batteries. MLIs consist of multilayers metallized on one or both sides of Kapton or FEP Teflon foil. MLIs are used to stop heat getting in on the sun-facing sides and to stop it getting out on the shadowed sides. The antenna reflectors reflect the energy on to the east and west sidewalls. To protect against this radiation the walls are covered with MLIs. MLIs are used to protect the spacecraft from hydrazine thruster heating and to isolate the components to maintain a specified temperature. Astronomical telescopes are generally wrapped in an MLI to reduce thermal distortion.

3.3.1.1. Silvered Teflon (Ag/FEP) SSMs. Silver-backed FEP Teflon is used as an SSM, because it has the lowest solar absorptance of any high-emittance space-proven material. The outer layer is FEP Teflon which is a transparent polymer film. Solar radiation passes through it and is reflected by either silver or aluminium backing. This results in low absorption of solar radiation. The thermal emittance is a function of the FEP Teflon infrared absorption and is dependent therefore on the thickness of the FEP Teflon.

The degradation of FEP Teflon surface thickness due to AO impact will affect the functional performance by decreasing emittance and changing optical properties. Space shuttle experiments have shown that the FEP Teflon appears to be resistant to AO erosion. FEP Teflon samples returned from the solar maximum mission satellite suffered noticeable damage such as cracking and yellowing [48]. The optical properties of the FEP Teflon samples were significantly degraded. On the other hand the data from STS-5 and STS-8 showed very little degradation [49, 50]. Ground-simulation test results show that FEP Teflon degrades when samples are exposed to both AO and u.v. radiation [51]. The Ag/FEP blankets tested in the LDEF remained functional as a thermal control system over the lifetime of the mission [52–60]. Post-retrieval analysis of the silvered FEP Teflon thermal control blanket material indicated that AO had oxidized at higher rates than had been predicted on the basis of previous low AO fluence flight data. The average FEP Teflon recession rate due to AO exposure was calculated at different locations around LDEF surfaces and the average value of erosion rate appears to be 3.65×10^{-25} cm^3 atom^{-1} [54]. The recession due to AO will eventually leave the FEP Teflon layer thin enough so that the emissivity will decrease. The AO erosion yield of FEP Teflon was found to vary with angle of incidence of AO, i.e. $Re = 3.65 \times 10^{-25} (\cos\theta)^{0.32}$ [56].

FEP Teflon thermal control blanket surfaces underwent significant changes in appearance, where the colour changed to a diffuse whitish appearance. This may have been due to the eroding effect of AO resulting in a rough light scattering surface. The roughening of the surface texture of the FEP Teflon layer dramatically increased the diffuse component of reflectance. Samples exposed to a high level of AO were dominated by diffuse reflectance, whereas samples exposed to a low level were dominated by specular reflectance [54]. Small changes in solar absorptance have occurred as a result of low AO fluence exposure and a slight reduction occurs in thermal emittance when samples are exposed to high level of AO fluence. This may be mostly due to reduction in the emitting FEP Teflon thickness [52].

Significantly greater erosion yields were observed for FEP Teflon thermal blankets from the LDEF in comparison with space shuttle results, suggesting a strong AO/u.v. radiation synergism in the degradation of this material. Exposure to solar u.v. radiation and v.u.v. radiation embrittles the FEP Teflon surface resulting in a decrease in elongation to failure and ultimate tensile strength. The test results for FEP Teflon samples exposed at the trailing edge of the LDEF where the samples were exposed to a very low level of AO and more u.v. radiation indicated that the tensile strength of the samples decreased about 30% and elongation about 25% [54]. XPS data of FEP Teflon samples exposed at the trailing edge of the LDEF mission show that they degraded significantly. This degradation was attributed to damage to the carbon backbone of the FEP Teflon resulting in molecular weight degradation, new chain terminations, branching and crosslinking through free radical reactions. The chemical analysis of the samples showed a decrease in $-CF_2$ functional groups and an increase in CF_3, CF, $C-(CF_n)_4$ functional groups. The solar u.v. radiation exposure of LDEF surfaces is thought to have caused this FEP Teflon surface degradation [57]. Chemical analysis of the FEP Teflon samples tested in ground-simulated u.v. radiation shows that increased u.v. exposure increases the fraction of $-CF$ and CF_3 functional groups at the expense of the CF_2 groups. The structural changes are associated with the increased crosslinking and embrittlement of the near-surface material [61, 62].

Blankets exposed simultaneously to u.v. radiation and AO had mass loss and became thinner. These specimens show only small decreases in tensile strength and elongation in comparison with unexposed specimens from the same blanket [53]. This may be explained as follows: solar u.v. radiation of sufficiently short wavelengths has enough energy to break C–C bonds (chain scission) and C–fluorine bonds in the FEP Teflon backbone and induce cross-linking in the polymer, making it more brittle. Under simultaneous exposure, u.v.-induced bond breaking provides reaction sites for the AO to attack the polymer backbone producing volatile products which then leave the surface exposing new reaction sites. This process will recur and results in thickness loss [58]. The ground-simulation test results show that the FEP Teflon exposed to v.u.v. radiation only possessed a hard embrittled surface layer; it was absent in the sample exposed to v.u.v. and AO. These results show that there is a strong synergistic effect between v.u.v. and AO [54].

XPS measurements on the surface of FEP Teflon samples exposed to the LEO environment on the LDEF at different locations show that composition of the FEP Teflon varies with exposure to AO fluence and u.v. sun hours [54]. Samples exposed to v.u.v. radiation and less AO fluence show a decrease in fluorine content and an increase in both oxygen and carbon concentration, whereas samples exposed to a high level of AO fluence and u.v. radiation show the bulk FEP Teflon concentration with a small amount of oxygen. This may be due to partial oxidized species on the surface. The u.v. damaged material might have been removed due to AO erosion leaving the original FEP Teflon on the surface. The u.v. degradation of FEP Teflon could have occurred at a slow rate during the entire mission but the erosion of the material would have occurred more rapidly near the end of the mission as the altitude of the LDEF dropped and the AO flux rapidly increased [57]. Table V gives the AO reactivity coefficient derived from different experiments and the change in optical properties due to AO effects is given in Table VI. It is clear from the data that samples degrade due to exposure to the AO environment, but the functional performance of FEP Teflon mainly depends on the level of AO fluence and u.v. radiation exposure. No significant change was observed on samples tested in space shuttle missions, whereas samples retrieved from solar maximum mission and the LDEF had mass loss and significant changes in optical properties. In particular the effect is more significant on thinner samples of FEP Teflon. A slight increase in absorptance was observed in LDEF samples. This may be due to deposition of contamination on these surfaces, which was observed on all surfaces in the LDEF experiments. Detailed study is needed to understand the synergistic effects of the LEO environment on degradation of FEP Teflon [63].

TABLE V AO reactivity coefficient of FEP Teflon

Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	AO reactivity coefficient (cm^3 atom^{-1}) (10^{-25})	Ref.
STS-4	00.65	1.0	50
STS-5	00.99	0.5	50
LDEF	77.8	3.5	52
LDEF	51.6	2.6	52
LDEF	31.6	2.3	52
LDEF	31.6	2.0–4.7	54
LDEF	66.3	2.8–3.8	54
LDEF	77.8	3.2–4.0	54
LDEF	51.6	2.8–4.6	54
Ground simulation	8.0×10^{-5}	0.8	51
	1.5×10^{-3}	0.7	51

TABLE VI Change in optical properties of FEP Teflon after exposure to AO

Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	Optical properties change		Ref.
		$\Delta\alpha$	$\Delta\varepsilon$	
STS-41G	03.0	+ 0.08	+ 0.11	48
LDEF	83.2	+ 0.053	+ 0.10	94
LDEF	12.0	+ 0.04	+ 0.07	94
LDEF	03.64	+ 0.06	+ 0.03	94
LDEF	80.0	+ 0.09	− 0.2	82
LDEF	80.0	+ 0.02	− 0.03	82
LDEF	1.09×10^{-7}	+ 0.009	− 0.006	52
LDEF	77.8	+ 0.042	− 0.088	52
LDEF	00.493	+ 0.001	− 0.001	92
LDEF	00.493	+ 0.003	− 0.02	92
LDEF	87.2	− 0.012	− 0.027	60
LDEF	87.2	+ 0.013	+ 0.003	60
STS-8	03.5	+ 0.006	0.0	22
Ground simulation	185.0	+ 0.05	− 0.19	64
	99.0	+ 0.06	− 0.06	64
	56.0	+ 0.07	− 0.01	64

3.3.1.2. Aluminized Kapton film. Aluminized Kapton is used as an external thermal control material on almost every satellite. In this configuration aluminium in the back surface acts as a reflector and Kapton is used to limit the emittance of the light.

Kapton is one of the most studied materials susceptible to AO degradation in the LEO environment. A very large amount of data are available from space experiments [50, 64–69]. In fact, Kapton is often considered as a reference standard for comparison between experiments and between ground-simulation laboratory tests and flight experiments.

Kapton is an organic poly (N,N′-(P,P′-oxydiphenylene)pyromellitimide) film. A possible explanation for the observed degradation of Kapton film in the LEO environment could be an oxidation reaction involving the breaking of bonds within the backbone of the macromolecule. The mechanism of this reaction may proceed via an intermediate hydroperoxide (involving hydrogen abstraction) with this intermediate then decomposing into low molecular weight fragments that are volatile under space vacuum conditions [70]. The removal of volatile oxidized material is efficient and in the case of organic surfaces there is no evidence for the formation of a stable oxidized boundary layer which might preclude further degradation. During AO exposure tests CO and CO_2 gases were detected by mass spectroscopy [73]. It is speculated that these gases are released from the Kapton surface by imide ring decomposition. The mechanism of thickness loss for Kapton films due to AO is considered to be a result of the aromaticity disappearing after the imide rings are decomposed. Ground simulated test results also confirmed the above observations [74]. Analysis of the polyimide determined from the XPS data has shown that both carbon and nitrogen were deficient. Oxygen on the other hand was in excess in both STS-8 and LDEF flight samples [71, 72].

Space tests have shed some light on the degree to which the Kapton reactivity coefficient is dependent on various environmental factors. The effect of angle of incidence of AO flux on Kapton reactivity shows that the material erosion rate varies more with $\cos(\theta)^{1.5}$ than $\cos(\theta)$ [75]. The reactivity coefficient is unaffected by solar radiation, charged species, Kapton thickness, and AO flux [20]. The AO energy dependence of the reactivity coefficient is not measured in the space tests because the LEO configuration produces AO energies only in the range 4–5 eV. However, the ground simulation tests show that the Kapton erosion rate increases with increasing energy of incident AO beam to the 0.68 power [76] and is found to be proportional to $e^{-0.38}$ of the impact energy [69]. The AO reactivity coefficient of Kapton derived from various experiments given in Tables VII and VIII gives the change in optical properties after AO exposure. The increase of absorptance in LDEF Kapton samples appears to be due to contamination deposition on the Kapton surfaces.

3.3.2. Organic paints

Various types of organic paint are used on spacecraft for thermal control applications. White paints are used on the outer surfaces of parabolic communication antennae, since an excess of absorbed thermal radiation would distort the antenna by thermal expansion and cause defocusing of the beam. Space telescope support systems also use white paints. Black paints are generally used on internal spacecraft components. Space telescope light shields and baffles for stray light suppression, and payload aperture doors to minimize the scattered light entering the optical payloads and on the rear side of the solar panels to improve the thermo-optical properties, are typical examples of where black paints are exposed to the LEO environment.

TABLE VII AO Reactivity coefficient of Kapton film

Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	AO reactivity coefficient (cm^3 atom^{-1}) (10^{-24})	Ref.
STS-3	02.16	2.0	50
STS-3	02.16	2.5	50
STS-4	00.65	2.8	50
STS-4	00.65	2.7	50
STS-5	00.99	1.5	50
STS-5	00.99	2.2	50
STS-5	00.99	2.8	50
STS-8	02.98	3.5	50
STS-8	02.98	3.2	50
STS-8	02.98	3.7	49
STS-41G	03.0	2.5	48
Solar max.	06.9	2.8	48
Ground simulation	03.0	3.0	157
	02.24	3.06	74
	02.16	2.99	74

TABLE VIII Change in optical properties of Kapton film after exposure to AO

Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	Optical properties change		Ref.
		$\Delta\alpha$	$\Delta\varepsilon$	
STS-41G	03.0	+ 0.08	– 0.01	48
Solar max.	06.9	+ 0.09	+ 0.01	48
LDEF	83.2	+ 0.034	-	93
LDEF	66.3	+ 0.129	-	93
LDEF	83.2	+ 0.013	-	93
LDEF	66.3	+ 0.134	-	93
LDEF	00.493	– 0.04	+ 0.02	92
LDEF	00.493	– 0.03	+ 0.01	92
LDEF	12.0	00.00	– 0.08	94
LDEF	03.64	00.00	– 0.06	94
LDEF	87.2	+ 0.091	+ 0.028	60
LDEF	87.2	+ 0.046	+ 0.013	60
Ground simulation	03.0	+ 0.07	-	84
	03.0	+ 0.06	-	84
	03.0	+ 0.05	-	84
	11.8	– 0.23	– 0.57	64
	185	– 0.23	– 0.59	64

Space shuttle mission experiments demonstrated the effects of AO exposure on organic thermal control paint degradation [77–79]. LDEF experiments also showed that thermal control organic paints degrade significantly after exposure to the harsh LEO environment. Organic paints are generally degraded due to u.v. exposure and are susceptible to AO erosion. Of the available organic thermal paints, polyurethane-based paints and some silicone-based paints were degraded significantly in the LEO environment. The degradation mechanisms of various organic paints are discussed briefly below.

Chemglaze A276 is a white thermal paint, which consists of titanium dioxide pigment in polyurethane binder. Degradation of A276 was observed on samples tested on the STS-5 mission [77–79]. Post-flight results show that the surface had a porous and powdery appearance, which may be due to AO reaction with polyurethane binder. Similar surface degradation and mass loss was observed in ground-simulation tests [84]. LDEF results have shown that the organic paint A276 had a mass loss and change in thermo-optical properties due to AO attack [80, 81]. Table IX gives the mass loss data and Table X the change in thermo-optical properties of A276 paint derived from both

TABLE IX Mass loss of thermal control organic paints after exposure to AO

Organic paint	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	AO reactivity coefficient (mg atom^{-1}) (10^{-21})	Ref.
A276	STS-8	03.5	1.0	77
	LDEF	69.3	0.14	34
	LDEF	02.6	2.3	89
	Ground simulation	03.0	2.45	84
Z302	STS-8	03.5	5.8	77
	LDEF	69.3	0.57	34
	Ground simulation	03.0	3.96	84
Z306	STS-8	03.5	1.0	77
	LDEF	69.3	0.23	34
	LDEF	02.6	2.6	89
	Ground simulation	03.0	2.3	84
A971	Ground simulation	03.0	3.6	84
S13G/LO	LDEF	03.0	1.9	89
S13G/LO-41	Ground simulation	20.0	18	123
S13G/LO-1	Ground simulation	20.0	27	123
S13G/LO-51	Ground simulation	20.0	21	123

space tests and ground simulated experiments. Samples tested at the leading edge of the LDEF show that there was no observable change in optical properties after exposure to the LEO environment. This may be due to erosion of degraded polyurethane binder in the A276 paint, because the u.v. degraded surface layers may be eroded away faster due to AO bombardment than they degrade due to u.v. radiation. Sampair and Berrios [80] and Golden [83] studied the effect of both AO fluence and u.v. radiation at different locations of the LDEF mission. A276 paint samples displayed a varying degree of thermo-optical property degradation. The specimens located at the leading edge of the LDEF where the samples were exposed to a high level of AO fluence and u.v. radiation showed that the organic binder of the A276 paint had been broken down by AO leaving a white chalky pigment on the surface. The specimens located on the trailing edge, where the samples were exposed to a low level of AO fluence and high u.v. radiation, had developed a hardened dark-brown finish.

Exposure of polyurethanes to u.v. radiation results in autoxidation of the urethane chains to a quinone-imide structure. A consequence of these chemical changes is a deepening in colour from colourless to yellow to amber and on extensive exposures even to brown [82]. The effects of u.v. radiation on the optical properties of titanium dioxide (TiO_2) have been studied by Firle and Flangan [88]. The reflectance spectra of TiO_2 degraded significantly more in the visible than in the infrared region, but the samples recovered almost completely to pre-irradiation values after exposure to an oxidizing atmosphere [88]. The absorptance of the paint exposed to only u.v. radiation and low AO fluence is approximately twice that of the control samples, but the samples exposed simultaneously to AO and u.v. radiation show very little change in thermo-optical properties. Wilkes *et al.* [82] reported that absorptance of A276 paint might have increased during the early low AO flux portion of the LDEF mission but, as the orbital altitude began to decay, the AO flux began to increase rapidly. The u.v. degraded polyurethane binder might have been removed due to AO erosion during this period and brought A276 absorptance to the normal value. The erosion of the organic binder significantly degraded the mechanical integrity of the paint coatings. LDEF results show that the emissivity of A276 paint showed no significant change from the control samples, even though there was a severe colour change. This can be attributed to the emissivity of the painted coatings being more a function of the coating thickness and chemical matrix (i.e. material infrared absorption band) than other factors such as colour [83]. The increase in absorptance on LDEF samples exposed an AO fluence level of 8.99×10^{21} atoms cm^{-2} might be due to contamination deposition on powdery pigment.

Chemglaze Z302 [71] is a glossy black paint and Z306 [75] is a flat black paint. Both contain polyurethane as binder and carbon as pigment. Space experiments have demonstrated that black paints degrade significantly due to u.v. exposure and are susceptible to AO erosion [34, 77, 82, 89]. Degradation of black paints Z302 and Z306 was observed in ground-simulation tests also [84]. The black paints were almost completely eroded away from the surface on the samples tested on the LDEF mission, leaving little powder on the surface [68]. Mass loss data for black paints are given in Table IX and the change in thermo-optical properties is given in Table X. The degradation of these paints is mainly due to polyurethane binder degradation upon u.v. exposure and erosion of both polyurethane and carbon due to AO exposure. Table X shows that there is no significant change in absorptance of black thermal coatings of Z302 and Z306 after AO exposure and a marginal increase in thermal emittance was observed. This might be due to roughening of the surface by non-uniform erosion of the paint.

White silicone thermal paint S13G/LO consists of zinc oxide in a methyl silicone binder. Space shuttle AO experiments on STS-5 and STS-8 did not reveal

TABLE X Change in optical properties of organic paints after exposure to AO

Organic paint	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	Optical properties change		Ref.
			$\Delta\alpha$	$\Delta\varepsilon$	
A276	STS-8	03.5	– 0.002	–	77
	STS-8	03.5	– 0.023	– 0.01	22
	LDEF	89.9	+ 0.016	– 0.03	89
	LDEF	69.3	– 0.05	–	34
	LDEF	80.0	– 0.01	+ 0.03	82
	Ground simulation	03.0	+ 0.0023	–	84
Z302	STS-8	03.5	+ 0.043	–	77
	LDEF	02.0	+ 0.043	–	89
	LDEF	80.0	+ 0.01	+ 0.01	82
	Ground simulation	03.0	+ 0.01	–	84
Z306	STS-8	03.5	+ 0.028	–	77
	STS-8	03.5	+ 0.022	0.0	22
	STS-41G	03.0	+ 0.01	+ 0.03	48
	Solar max.	06.9	+ 0.01	+ 0.05	48
	LDEF	87.0	– 0.02	+ 0.04	87
	LDEF	89.9	– 0.02	+ 0.01	89
S13G/LO	LDEF	69.3	+ 0.14	–	34
	LDEF	89.9	+ 0.033	– 0.01	89
	LDEF	80.0	+ 0.19	– 0.01	82
	LDEF	83.2	+ 0.26	– 0.02	94
	LDEF	12.0	+ 0.25	– 0.01	94
	LDEF	03.64	+ 0.31	– 0.01	94
	LDEF	83.2	+ 0.053	–	93
	LDEF	66.3	+ 0.02	–	93
	LDEF	87.2	– 0.001	+ 0.118	60
	LDEF	0.493	+ 0.25	–	92
	LDEF	0.663	+ 0.085	–	81
	Ground simulation	03.0	+ 0.005	–	84

any noticeable degradation to S13G/LO and there was no measurable AO erosion of the surface. Samples tested on LDEF missions have shown significant degradation [34, 80, 81, 89]. The mass loss data and change in thermo-optical properties derived from the space experiments and ground-simulation experiments are given in Tables IX and X respectively. They show that silicone S13G/LO paint degraded significantly. This was attributed to u.v. radiation degradation of methyl silicone binder and little change was due to ZnO pigment degradation. When exposed to u.v. radiation the methyl silicone binder exhibits induced u.v.-visible absorption and there was no recovery upon exposure to the AO environment, indicating that the degradation is not limited to the bleachable surface defects but the result of bulk polymer degradation [90]. ZnO also degrades upon exposure to u.v. radiation. Gilligan [91] explained the infrared optical behaviour of ZnO on the basis of the free carrier absorption mechanism. Absorbed photons create electron-hole pairs in a depletion zone with the holes discharging adsorbed oxygen from the surface of the pigment particles. The ZnO pigments therefore become electron-rich with electrons accumulating in the infrared active conduction band resulting in an increase in the infrared absorption. The increase in solar absorptance may be mainly due to silicone binder degradation after exposure to the AO environment [92–94]. Surface analysis of S13G/LO paint shows that significant changes occurred in the methyl silicone binder after exposure to the AO environment. The loss of methyl groups accompanied by an increase in the O : Si ratio is consistent with oxidation of methyl silicone to silica after exposure to the AO environment. The surface has developed a cracking network and the extent of cracking is related to the degree of oxidation. The most likely explanation is that cracks developed due to a density change as a result of oxidation of the methyl silicone binder to silica. Surface erosion of S13G/LO may be due to spalling of the degraded surface [89]. The change in absorptance is mainly due to degradation of silicone and possibly due to contaminant deposition on the LDEF surfaces.

The reactivity values for short- and long-term exposures and ground data are given in terms of milligrams per incident atom rather than conventional reactivity units of volume lost per incident oxygen atom. The organic paints that were exposed to the AO environment are optically diffuse. This diffuseness may be due to the presence of inert components which do not erode due to AO attack, so thickness loss is not as sensitive a measure of AO reactivity as mass loss. As expected the long-term reactivities are non-linear so they cannot be predicted from short-term exposures. With increased exposure more inert material is exposed, thus providing increased self-shielding which results in apparent decreased reaction of incident AO. It appears that the organic paints may survive longer than predicted from short-term exposures.

The above discussion shows clearly that organic paints degrade due to u.v. exposure and are susceptible to AO erosion. For long-term satellite application organic paints need careful selection of materials and/or protective coatings.

3.4. Optical components

Optical systems are used for different spacecraft applications including astronomical, atmospheric and earth observations. Optical coatings have wide application for mirrors, gratings, filters, beam splitters, antireflection coatings and optical windows. Alterations of optical properties due to AO interaction are of great concern in design and development of spacecraft instruments for long-term applications in the LEO orbit. Different metallic coatings have been exposed to the LEO AO environment during STS-8 and STS-17 missions. Post-flight results show that most of the optical coatings degraded due to AO in the LEO environment [5, 95, 96]. A variety of optical components were exposed to the LEO environment on LDEF experiments to study AO effect on performance. The post-flight results show that several metallic materials whose oxidation or space environmental stability was either unknown or undetectable in short-term exposures were found to be measurably affected.

Thin films of optical-quality silver coatings were typically converted to transparent silver oxide with the film thickness expanding greatly (55%). The literature indicates that thick oxide formations appear to create considerable stresses in the exposed areas, which produce buckling or scaling which in turn limit or modify further oxidation [5]. Debonding and sometimes flaking of silver oxide were also observed. Debonding from the silver apparently limited further reaction at the interface. Different samples behaved differently. Both refractive index and absorption coefficient changed considerably after exposure to the LEO environment [95]. Silver films coated on quartz were exposed to the LEO environment on LDEF experiments. The post-flight results show that silver oxidized and was removed from the surface [97].

Osmium films are very good reflectors for vacuum u.v. optics. Osmium films have been shown to disappear or rapidly evaporate during orbital exposure, presumably due to the formation of volatile osmium tetraoxide (OsO_4) [95]. Osmium films of 60 nm on quartz substrate were degraded after exposure to the LEO environment on the LDEF at an effective AO fluence level of 2×10^{20} atoms cm^{-2}. The films were oxidized completely and removed by evaporation of volatile oxides [73].

Thin films of aluminium [95], nickel [96], palladium [96], copper [96, 98], gold [96], chromium [96], tantalum [99], iridium [957], niobium [95, 100, 101], tungsten [99], molybdenum [34], titanium [34] and zirconium [99] were exposed to the LEO environment. The post-flight results indicate that all these metal coatings converted to metal oxide coatings on the surface. Aluminium converted to Al_2O_3, copper to Cu_2O [98] and nickel to NiO. Ta_2O_5 was observed on the tantalum surface, W_3O formed on tungsten and ZrO_2 was observed on the zirconium surface due to LEO AO interaction. Changes in the optical refractive index and optical absorption coefficient were observed. Oxidation of palladium and gold was observed in LDEF experiments but not in space shuttle experiments. The AO reactivity coefficients derived from different space missions for various metals are given in Table XI. The values were derived from the experiments based on linear behaviour of oxidation rate with AO fluence but all metals appear to oxidize non-linearly with AO fluence. These values are given with the object of providing some comparative measure of the observed effects. The results of the LDEF experiments show that the AO effects are mostly dependent on temperature and microstructure of the samples than total incident AO effect.

LEO exposed soft uncoated optical substrate materials like thallium bromide (KRS-5 and KRS-6) experienced gross physical degradation, which is mainly due to AO degradation of the samples [102].

Dielectric optical coatings of MgF_2, CaF_2 and ThF_4 were exposed to the LEO environment in the LDEF [103]. The results indicate that the coatings degraded by converting MgF_2, CaF_2 and ThF_4 into their oxides. The LEO AO replaced all fluorine atoms in the material. These results indicate that the use of MgF_2, CaF_2 and ThF_4 coatings as antireflection and protective coatings requires AO-resistant coatings to survive in the long term in the LEO environment [104].

Silicon/aluminium oxide-coated high-reflectance mirror coatings were exposed to the LEO environment on LDEF missions. Post-flight reflectance measurements show that there is a slight reduction in reflectance at a design wavelength of 2.8 μm. The reflectance loss of the mirror at longer wavelengths (3–4 μm) appears somewhat greater. The reflectance loss at longer wavelengths may possibly be due to surface oxide formation [105].

Zinc sulphide/aluminium oxide and zinc sulphide/thorium fluoride-coated laser mirrors showed significant reductions in reflectance at the design wavelength after exposure to the LEO environment on LDEF missions. The spectral shift of reflectance maxima to the shorter wavelength was observed. This shift might be due to refractive index reduction with oxide formation and also thickness reduction of the zinc sulphide layer [106].

Aluminium metallic mirrors protected with MgF_2 have shown a relative reflectance loss varying from 16 to 23% after exposure to the LEO environment on LDEF experiments. Dielectric MgO/MgF_2 mirrors centred at 250 nm have shown approximately 38% relative bandwidth change after exposure to the LEO environment [105]. The reflectance loss of the aluminium mirrors might be due to a change in the refractive index of the MgF_2 after conversion into MgO.

Optical filters (except neutral density filters) exposed to the LEO environment in the LDEF have shown a reduction in transmission. Al–MgF_2 layers deposited on MgF_2 substrate used for half wave filters at wavelengths centred around 121.6 and 127 nm have shown 51% and 30% relative transmission losses respectively [105]. This reduction may be due to degradation of the cement used in their construction and conversion of MgF_2 into MgO. In the case of neutral density filters, the filter characteristics were not changed except for a slight increase in transmission. This behaviour may be due to slight erosion of the metal film used in the construction of the neutral density filters [105].

3.5. Space power generators

Two concepts, photovoltaic and solar dynamic, are being considered as potential power sources for spacecraft applications. Solar photovoltaic array systems directly convert solar energy to electrical power using solar cells. In the solar dynamic system, solar radiation is collected by concentrators and used to drive heat engines which in turn generate electrical power.

3.5.1. Solar photovoltaic arrays

Planar photovoltaic arrays can effectively be subdivided into two broad categories, rigid and flexible. Rigid arrays are photovoltaic arrays that are mechanically stiffened with a honeycomb structure, usually made of aluminium, and sandwiched between two graphite epoxy face sheets, and a Kapton film is fixed on the cell laying side of the solar panel for electrical isolation of the solar cells from the conductive substrate [107]. Flexible arrays are typically a Kapton substrate which is sandwiched between photovoltaic solar cells and electrical circuitry.

The highly reactive AO would limit the useful life of the solar array mainly due to its effect on silver solar cell interconnects, Kapton film, graphite fibre epoxy composite facesheets and glass fibre epoxy composites and MgF_2 coatings.

TABLE XI AO reactivity coefficient of metal films

Metal film	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	AO reactivity coefficient (cm^{3} atom^{-1}) (10^{-27})	Ref.
Copper	LDEF	69.3	8.7	34
Molybdenum	LDEF	69.3	1.4	34
Tungsten	LDEF	69.3	0.44	34
Tantalum	LDEF	69.3	6.0	34
Titanium	LDEF	69.3	3.9	34
Niobium	LDEF	69.3	1.4	34
Silver	LDEF	69.3	2.9	34
Iridium	STS-8	03.5	8.33	95
Aluminium	STS-8	03.5	2.29	95
Niobium	STS-8	03.5	3.7	95
Niobium	STS-8	03.5	2.29	95
Nickel	STS-8	03.5	2.58	95
Tungsten	STS-8	03.5	2.0	95

Space results have shown that AO interaction with Kapton will degrade its performance. The degradation mechanism of Kapton due to LEO AO impact is discussed in Section 3.3.1.2.

On reaction and surface erosion of graphite fibres and epoxy resin the composite may decline in performance through a weakening of its mechanical and thermo-optical properties. The degradation mechanism of composite materials is discussed in Section 3.1.

Silver foil of 12.5 or 35 μm thickness is generally used to connect the solar cells to the electrical network. AO reacts with silver forming silver oxide on the surface. The lattice spacing of silver oxide is approximately 55% greater than the bulk silver. Thus strains are developed at the interface, which results in removal of the oxide layer from the surface. The degradation mechanism of silver due to AO interaction is discussed in Raja Reddy *et al.* [107]. The AO reactivity coefficient of silver interconnects derived from different space experiments are given in Table XII.

Fibreglass epoxy composites are used as a mast to extend and retract the flexible solar array blanket and to provide structural support and rigidity when extended. Ground-based simulation tests show that the epoxy at the surface of the composite was oxidized, exposing individual glass fibres. These fibres are very brittle and can break off due to flexure [108].

Magnesium fluoride is commonly used as an antireflection coating on the outer surface of the coverglass. These covers are used to protect solar cells from space radiation environment degradation and serve to increase the emissivity of the cell. LDEF results show that MgF_2 layers may degrade due to loss of fluorine component and perhaps the incorporation of oxygen [109]. This consequence of thin fluoride to oxide conversion is a change in the performance of the coating from antireflection to reflection enhancement. The refractive index of MgO is much higher than that of MgF_2 and also higher than the coverglass. Increasing the fluoride to oxide conversion will increase reflectance which results in a decrease in light transmission through coverglass in proportion to the power reduction.

3.5.2. Solar dynamic power systems

The components most sensitive to AO effects on the solar dynamic system are the reflector and concentrator surfaces. Solar dynamic concentrators are of

TABLE XII AO reactivity coefficient of silver interconnect

Material	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	AO reactivity coefficient (cm^{3} atom^{-1}) (10^{-24})	Ref.
Silver cold-rolled ribbon	LDEF	69.3	0.275	34
	STS-41G	01.1	1.4	10
	STS-8	03.0	1.4	77

TABLE XIII Change in solar transmittance of Fresnel lens materials after exposure to AO

Material	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{22})	Transmittance loss (%)	Ref.
Silicones				
RTV-615	Ground simulation	6.7	− 8.8	110
RTV-615		6.7	− 7.7	110
RTV-670		6.7	− 4.5	110
DC93500		6.7	− 5.7	110
Fluoropolymers				
ETFE	Ground simulation	4.73	+ 4.7	110
PFA		4.73	+ 2.4	110
FEP		4.73	+ 1.6	110
KEL-F		5.26	+ 3.2	110
Other organics				
Lexan PC		3.66	+ 2.6	110
UVA 11 acrylic		6.73	+ 3.2	110

two types, reflective and refractive. Reflective surfaces must maintain high specular reflectivity over the wavelength range 200–2500 nm during the mission lifetime in the LEO environment. Refractive lens material must maintain high specular transmittance. Among the reflective surfaces silver- and aluminium-coated surfaces show the maximum reflectance in the wavelength range required. Reflective surfaces of silver and aluminium form their oxides on exposure to the LEO AO environment. Silver oxide is loosely adhered to the surface and flakes away from it. Aluminium forms aluminium oxide after reacting with the LEO AO environment. Aluminium oxide is transparent in the wavelength range and reduces the reflectance. Different organic materials which include silicone, polycarbonate, acrylic and various types of fluoropolymers are considered for Fresnel refractive lens applications. All refractive Fresnel lens samples degraded when they were exposed to the AO beam in ground-simulated laboratory facilities [110]. Table XIII gives data on the change in solar transmittance of different Fresnel lens materials after exposure to the LEO environment. Total transmittance was found to decrease 4–8% for silicones and there was a slight increase of 1–3% in the fluoropolymers. Polycarbonate and acrylic polymer specular transmittance decreased significantly following AO exposure, falling from 25 to 50% of the initial value. Silicone surfaces deteriorated badly, the colour changing slightly yellow; a significant amount of surface cracking was also observed. The fluoropolymers exhibited somewhat different behaviour: a slight increase in total transmittance initially followed by a more pronounced and rapid decrease in specular transmittance. This may be due to mass loss and erosion at the sample surface. The roughening of the surface due to AO impingement reduces the total amount of front surface reflectance, which results in an increase in the total light transmitted. Mass loss measurement following AO exposure indicates that the fluoropolymers lose 20–40% of their initial mass. The polycarbonates also behave similarly to the fluoropolymers, except that there is a very gradual decrease in specular transmittance. Polycarbonates lost approximately 56% mass after exposure to the AO environment.

4. Protective mechanisms for AO-susceptible materials

Most of the spacecraft materials discussed above are susceptible to AO erosion. The extent of degradation of materials due to AO attack clearly shows that most of the materials are unacceptable for long-duration use in LEO spacecraft applications. Mitigation techniques would ideally avoid the use of AO-sensitive materials and/or orient the critical spacecraft surfaces to avoid the direct impingement of the AO environment. Unfortunately, these solutions may not always be possible and it is therefore necessary to apply protective mechanism, which can reduce the amount of damage or replace with AO-resistant materials.

The basic requirements of the protective mechanisms and their development status and performance in the LEO environment and ground simulation facilities have been discussed. The development status of AO-resistant materials for different spacecraft subsystems and their durability in the LEO environment are discussed below.

The selection of a protective mechanism candidate is primarily based on the following requirements:

(a) it should be resistant to AO attack
(b) it should be thin, light weight and adhere strongly to the base material
(c) it should be free from defects, pores and scratches
(d) it should be non-contaminating
(e) it should not alter the basic properties of the base material
(f) it should have good physical integrity with the base material to withstand ground handling and manufacturing loads and also orbit loads
(g) it should be stable in the LEO environment synergism which includes particulate radiation, u.v. radiation, micrometeoroids and orbital debris impact, plasma charging and thermo-vacuum cycling

(h) the application process should not damage the base material
(i) it should be cost-effective and easily scaleable to large dimensions.

The application of a thin protective coating to base material is one of the most commonly used methods of preventing AO degradation. The purpose of the coating is to provide a barrier between the base material and the AO environment or, in some cases, to alter AO reactions to inhibit AO diffusion. The effectiveness of a coating depends on its continuity, porosity, degree of adhesion and durability in the environment. In addition to the technicalities of forming an effective barrier, such factors as cost, convenience of application and ease of repair are important considerations in the selection of a coating for a particular application.

Numerous coatings and layer combinations are currently used for AO protection. Essentially, each coating falls into one of three categories according to composition: (1) metallic, (2) inorganic compound and (3) organic compound.

4.1. Protective mechanisms for composite materials

The extent of polymer composite degradation in the LEO AO environment appears to be serious and it is risky to use them in long-term LEO spacecraft applications. It is necessary to apply protective mechanisms in order for the composites to survive long term in the LEO environment.

A wide variety of oxidation concepts for protecting composite materials have been explored. AO protection can be achieved effectively by any one or a combination of the following: (a) protective coatings, (b) a thin outer wrap of bonded aluminium, (c) aluminium cladding.

The application and durability of different coatings on composite surfaces have been studied. Table XIV lists the various coatings used on different composites to protect against AO degradation. Sputter-deposited coatings of Ni, Ni/SiO_2 and Al/Al_2O_3 were applied to graphite/epoxy composites and their durability tested in space shuttle mission STS-8 [22]. Sputter-deposited coatings of Al, Al/Ni, Ni/SiO_2, Al/Ni/SiO_2 and Cr/SiO_2 were applied to composite surfaces and their durability tested in LDEF experiments [89]. Post-flight analysis indicated that all these coatings provide good protection to polymer composite materials.

Plasma-deposited coatings of amorphous silicon and its inorganic compounds silicon nitride and silicon oxynitride on graphite/epoxy composite substrates were tested in ground-simulated AO beam [111]. The results show that these coatings provide good protection to underlying composites. Upon being exposed to the AO environment they form a very thin barrier layer or a scale of silica glass, which will act as a protective barrier for AO diffusion and limit further AO attack. Though these coatings are efficient in protecting polymer composites, their application on composites imposes severe constraints. Their thermal expansion coefficients differ markedly from those of polymer composite substrates. As a result cracks develop in the coatings on thermal cycling and AO can penetrate through them to the substrate. Various internal and overcoat glassy sealants can be used to prevent oxygen from reaching the substrate through the cracks. Typical sealants are based on silicate or borate glasses. Sometimes the coatings themselves are

TABLE XIV AO protective coatings for composite materials

Composite material	Protective coating	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{21})	Ref.
Graphite/epoxy				
T300/5208	Ni	STS-8	0.3	22
	Ni/SiO_2	STS-8	0.3	22
	Al/Al_2O_3	STS-8	0.3	22
	TiO_2	LDEF	6.63	35
T300/934	Al_2O_3	LDEF	8.72	39
	Z306	LDEF	8.72	39
	A276	LDEF	8.72	39
	BMS10-60	LDEF	8.72	39
GY70/X30	In-Sn	LDEF	6.63	39
Gr/epoxy	Al	LDEF	8.99	89
	Al/Ni	LDEF	8.99	89
	SiO_2/Al/Ni	LDEF	8.99	89
	SiO_2/Cr	LDEF	8.99	89
Graphite/thermoplastic				
T300/P1700	TiO_2	LDEF	6.63	35
	ZnO	LDEF	6.63	35
T350/PES	TiO_2	LDEF	6.63	35
	ZnO	LDEF	6.63	35
W722/P1700	TiO_2	LDEF	6.63	35
	ZnO	LDEF	6.63	35
Graphite/polyimide				
CELION 6000/PI	ZnO	LDEF	6.63	35

multilayered with glasses or glass formers in them, or transition layers of other materials are employed between the coating and the substrate to reduce the coefficient of thermal expansion (CTE) mismatch and compatibility to anchor the coating better to the substrate. Alternatively various inhibitors are added to the polymer matrix itself. These function both as oxygen providers and as glass formers. They typically consist of silicon, boron, zirconium, etc., and various compounds of these materials [112].

A thin (100 nm) coating of plasma-sprayed fluorinated ethylene–propylene copolymer was applied to carbon epoxy composites and tested in STS-41G [115]. The post-flight test results indicated that the coatings provide some resistance. This may be due to exposure of the samples to the LEO environment for a few days only.

Different types of thermal control coatings were applied to composite substrates and tested on LDEF missions to study their durability to protect the composites from LEO environment degradation [114]. The post-flight results of white thermal coatings containing polyurethane binder and titanium dioxide pigment show that they protected the graphite/epoxy composite panel from AO attack. This is mainly due to the AO-resistant nature of the titanium dioxide pigment in these coatings. Upon exposure to the AO environment, the polyurethane binder reacts with AO significantly and becomes eroded from the surface leaving the titanium dioxide pigment on the surface. The black thermal control coating Z306 which contains carbon pigment and polyurethane binder was severely eroded as both carbon pigment and the polyurethane matrix are reactive with AO. Some initial attack of the substrate under this coating was observed. Thermal control coating containing ZnO pigments appears to provide good protection, but the durability of the coatings mainly depends on defects and the physical integrity with the substrate material. Alloy coatings of In–Sn also provided good protection from AO attack [114].

Monte Carlo models have been used to predict the undercut profiles on composites through cracks in the coating. Carbon fibre epoxy composite materials protected with aluminium oxide coatings were used to study the undercut profiles through the defects in the coating [115]. These samples were tested in the LDEF and exposed to an AO fluence level of 8.72×10^{21} atoms cm^{-2}. The AO reactivity coefficient of carbon fibre epoxy composite under defect sites in the protective coating was estimated and the average appears to be 2.5×10^{-24} cm^3 atom^{-1}, which is approximately twice that of the unprotected CFRP composite. Monte Carlo modelling assumptions used to predict the ground simulated laboratory plasma asher results appear to be inadequate for predicting the LDEF results accurately. Several mechanistic assumptions were used in the modified Monte Carlo modelling based on the LDEF results to predict the experimentally observed results. The reaction probability of AO with polymeric material at the interface between the protective coating and the polymeric substrate appears to be the same as with the bulk material. The AO reaction probability for thermally accommodated AO is probably not greater than 0.003 [115]. The AO may not be fully accommodated on first impact with organic materials, thus scattering with sufficient energy to significantly contribute to the undercutting.

Tubular truss members are generally used for spacecraft structural applications. Electroplated Ni protective coatings were applied on the tubes and tested in the ground-simulated experiments to study their effectiveness in protecting composite tubes from AO degradation. The results indicate that the coatings provide good protection but their adhesion to the composite tubes appears to be poor during exposure to the LEO environment, suggesting a limitation to their use. Application of other coatings like SiO_2 on large sections of the tubes required large vacuum coaters. An alternative approach to protecting the composite tubes is cladding the polymer epoxy composite with metal foil. The most advantageous and space-durable metal film is aluminium foil, which can be coated by either phosphoric or chromic acid anodization [116]. The latter can be easily tailored to meet a variety of optical parameters by varying anodizing parameters. Phosphoric acid anodizing is not as versatile. The anodized aluminium foil can be bonded along a lengthwise seam using adhesive bonds, but concern remains about pinholes and delamination of this bonded seam. This problem can easily be circumvented by using a seamless aluminium tube as the outer environmental protection for the composite tube. Here the thickness of the aluminium is higher for damage tolerance and AO durability [117]. Aluminium clad graphite epoxy tubes are manufactured as follows; an aluminium tube with prespooled collimated dry graphite fibre can be inserted into an outer larger diameter aluminium tube. Epoxy resin is then injected into the annulus between the two tubes. Pressurized hot water is pumped through the inner tube to provide the resin cure heat. Subsequent chem milling of the tube can provide the desired wall thickness. The outer surface should then be anodized to obtain the proper coefficient of thermal expansion and absorptivity/emissivity requirements.

Alternative materials for polymer composites are metal matrix composites, ceramic matrix composites and the development of AO-durable resin matrices for composite application.

Metal matrix composites of graphite/Al and graphite/Mg were exposed to the LEO environment in the space shuttle STS-8 mission [22]. The post-flight results showed that graphite/Al composites oxidized and there was no change to graphite/Mg composites. Samples flown on the LDEF showed that both graphite/Al and graphite/Mg oxidized due to AO interaction [118]. Graphite/Al composites showed stable, linear thermal expansion behaviour with near-zero thermal hysteresis over the LDEF temperature range. Prolonged thermal cycling on the LDEF also stabilized the thermal expansion of graphite/Al over wide temperature ranges. In contrast, graphite/Mg composites, even after extensive cycling during orbiting, showed non-linear, unstable behaviour with significant hysteresis. Thermal bending of graphite/Mg composite materials was observed. This may be due to their low thermal conductivity. More study is needed to develop very good thermally stable structures for space application. It appears that graphite/Al composites offer advantages for space structure application because of their good CTE, thermal hysteresis and thermal conductivity.

One of the alternatives to polymer composites are ceramic matrix composites. In this system carbon fibres are reinforced with glass or glass ceramic compositions. These composites exhibited good stability when exposed to the LEO environment with AO reactivity coefficients less than 0.02×10^{-24} cm^{-3} atom^{-1}. In order to assess the durability of the ceramic composites for long-term LEO applications a few samples were tested on the LDEF mission [119]. Analysis of the ceramic matrix composites indicated that they experienced negligible weight loss resulting from surface carbon fibre erosion with no change in flexural strength or thermal expansion behaviour. Only the fibres that were exposed at the surface of samples were eroded away with the ceramic matrix providing good protection for interior fibres. In fact, even fibres near the surface that were covered by only a thin layer (5 μm) of the ceramic matrix were fully intact following exposure. This inherent resistance to the effects of AO suggests that the ceramic matrix composites will not require any additional protective measures, such as coatings, making them very attractive for space applications requiring long-term durability [119]. However present technology appears insufficient to replace all polymer with ceramic composites because of the difficulty in preparing different shapes of spacecraft components.

A modified polymer matrix with siloxane appears to be resistant to AO attack and precludes the degradation of composites in the LEO environment [120]. A siloxane molecular composite is a composite of a flexible organosiloxane copolymer and an intrinsically rigid macromolecule. This is conceptually similar to a fibre-reinforced plastic, except that the organo-siloxane copolymer is molecularly reinforced by the rigid macromolecule such that the thermomechanical reinforcement of the siloxane copolymer is achieved with the lower surface energy siloxane-enriched surface [121]. After exposure to the LEO environment, the siloxane segments convert to a ceramic-like silicate which provides a protective overcoat to the composite. Of the materials evaluated so far, only siloxanes in the form of crosslinked poly(dimethyl siloxane) and poly(siloxane-imide) copolymers were stable in the LEO environment.

4.2. Protective mechanisms for tribomaterials

Most of the tribomaterials used on spacecraft are mainly shielded from direct exposure to the environment. The LEO environment-exposed tribomaterials should be either protected by applying protective mechanisms or replaced with AO-resistant materials. Application of thin protective coating to tribomaterials may not provide the same lubrication behaviour as the original material because the lubrication characteristics of the tribomaterials are mainly limited to surface characteristics. One possible way to protect AO-susceptible materials is to use flexible AO-protective covers. Recent test results show that tungsten disulphide appears to be resistant to AO degradation [122]. Ceramic-based AO-resistant materials appear to be the substitute for AO-susceptible lubricants. More emphasis should be given to developing and qualifying the AO-resistant tribomaterials for long-term LEO spacecraft application.

4.3. Protective mechanisms for thermal control components

4.3.1. *Protective coatings for metallized polymer films*

SSMs based on FEP Teflon and Kapton films require protective coatings to protect them from AO attack and to survive for the mission life. Table XV gives the various coatings studied to protect FEP Teflon from AO degradation. Ion beam sputter-deposited thin conductive coatings of In_2O_3 on the FEP Teflon side appears to provide both the conductivity required to avoid charging of the surfaces with atmospheric plasma interaction, and protection from AO attack. The post-flight results of the samples tested on LDEF experiments indicate that these coatings provide some protection. This may be due to defects in the coating, which act as reaction sites and interact with the base material. The sheet resistance of samples increased from 900 to 2000 Ω/□ but there was no measurable change in solar absorptance and/or thermal emittance [92]. The resistance increase might be due to increasing the oxygen content in the coating. Protective

TABLE XV AO protective coatings for metallized FEP Teflon

Protective coating	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{21})	Change in optical properties		Ref.
			$\Delta\alpha$	$\Delta\varepsilon$	
ITO	LDEF	8.72	+ 0.005	− 0.001	60
ITO	LDEF	8.72	− 0.006	+ 0.002	60
In_2O_3	LDEF	8.72	− 0.013	+ 0.006	60
In_2O_3	LDEF	8.32	+ 0.017	–	93
In_2O_3	LDEF	6.63	+ 0.026	–	93
SiO_2	Ground simulation	2.0	+ 0.01	0.0	123
SiO_2		2.0	+ 0.01	+ 0.02	123
CeO_2		2.0	+ 0.05	+ 0.02	123
			+ 0.03	+ 0.03	123

In_2O_3 coatings applied to FEP Teflon and tested in other experiments also exhibited similar behaviour [60, 93].

ITO-coated FEP Teflon had been eroded in some places, which may be due either to erosion of the ITO layers by AO or to damage of the coating during prehandling [60].

Protective coatings of SiO_2 and CeO_2 applied FEP Teflon samples were tested in a ground-simulated plasma asher facility for AO durability [123]. The test results indicate that for SiO_2-protected samples there is negligible change in emittance and a slight increase in solar absorptance. Some surface cracks were observed during AO plasma ashing, but these do not appear to be detrimental to AO protection. Cerium oxide-protected samples showed an increase in both emittance and absorptance upon exposure to plasma asher. A significant amount of surface erosion was observed on the surface in addition to a large number of defects and cracks in the coating. These results show that cerium oxide coating is not a viable candidate for protecting FEP Teflon from LEO AO degradation.

Aluminized Kapton film required protective coatings to perform as thermal control components for mission life in the LEO environment. Different protective mechanisms have been studied and tested both in space missions and ground-simulated facilities. The coatings studied to protect Kapton film due to AO degradation are shown in Table XVI.

Aluminized Kapton covered with sputter-coated ITO and SiO_2 were exposed to the LEO environment in STS-8 experiments [48]. The surface resistivity of the ITO samples decreased by a factor of 5 (a drop from 11.25 to 2.11 $G\Omega\square^{-1}$). Similar behaviour has been observed in both ground-simulated tests and LDEF experiments [60, 94, 124]. STS-8 test results showed that the ITO coating protected the Kapton film from surface erosion during AO impact by a factor of 10 compared to the unprotected Kapton. The limitation of ITO protective coating is mainly due to defects and the higher oxidation rate of ITO [60]. Kapton samples covered with In_2O_3 coatings were tested in the LDEF and the post-flight results show that these coatings provide good protection [60, 94].

Various silicon and silicon compound coatings were applied to Kapton film and tested in both ground simulation facilities and space tests. The test results show that silicon-based coatings appear to provide good protection but the limitation is mainly due to defects in the coatings. There was no significant change in thermo-optical properties [125].

Among the inorganic polymer coatings, silicone polymers appear to provide good protection. Silicone coatings may crack after long exposure to the AO environment and due to thermal cycling. Spalling of cracked coatings will result in thickness loss. This process continues till the coating fails. These coating materials therefore have a definite life time for long duration missions determined by their thickness and AO fluence. Additionally silicones produce a lot of contamination due to outgassing and polymeric scissioning of the bulk coatings. Thermal control coatings

TABLE XVI AO protective coatings for Kapton film

Protective coating	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{21})	Change in optical properties		Ref.
			$\Delta\alpha$	$\Delta\varepsilon$	
ITO	STS-8	0.35	+ 0.006	+ 0.004	78
C6-1104	STS-8	0.35	− 0.01	− 0.01	78
ITO	STS-41G	0.245	+ 0.01	0.0	68
ITO	STS-41G	0.245	0.00	0.0	68
In_2O_3	LDEF	8.32	+ 0.003	–	93
In_2O_3	LDEF	6.63	− 0.005	–	93
ITO	LDEF	8.72	+ 0.049	+ 0.027	60
S13G/LO	LDEF	8.21	+ 0.26	− 0.02	94
	LDEF	1.20	+ 0.25	− 0.01	94
	LDEF	0.364	+ 0.31	− 0.01	94
RTV-615	LDEF	8.32	+ 0.24	− 0.01	94
	LDEF	1.20	+ 0.1	− 0.01	94
	LDEF	0.364	+ 0.17	− 0.01	94
SiO_x	LDEF	1.2	+ 0.02	+ 0.01	94
20 nm	LDEF	0.364	+ 0.02	+ 0.02	94
50 nm	LDEF	1.2	+ 0.01	0.0	94
	LDEF	0.364	+ 0.04	+ 0.03	94
70 nm	LDEF	1.2	0.0	− 0.01	94
	LDEF	0.364	+ 0.04	+ 0.03	94
100 nm	LDEF	1.2	+ 0.01	− 0.01	94
	LDEF	0.364	+ 0.07	+ 0.03	94
SiO_2	LDEF	0.0493	+ 0.023	0.0	92
96% SiO_2 4% PTFE	LDEF	0.0493	+ 0.017	0.0	92
Al_2O_3	LDEF	0.0493	+ 0.028	0.0	92
a:Si:H	Ground simulation	0.3	+ 0.01	+ 0.02	125
P:SiN		0.3	0.0	0.0	125
P:SiO_2		0.3	0.0	0.0	125
pp:HMDSO		0.3	− 0.05	0.0	125

of S13G/LO and Z306 were applied to the Kapton surface and their AO durability tested in LDEF missions. Post-flight results show that Z306 coatings appear to degrade significantly and S13G/LO coatings also degraded but the magnitude appears to be less [94].

There is a need to develop both AO and u.v. radiation stabilized materials for long-term space applications. Polysiloxane-modified materials and thermoset siloxane materials with high glass transition temperatures offer possibilities for AO-stabilized materials. Use of phosphate pendent groups on polymer chains should enhance oxidative stability because the phosphate group is already oxidized and is large enough to block access to the main chain atoms. For u.v. stabilization candidates include polyphosphazenes, u.v.-stabilized fluorocarbons such as perfluorophenyls, low colour polyimide polymers (optically transparent) and aromatic polyimides.

4.3.2. Protective coatings for organic paints

Various coatings were studied for protecting organic paints from AO attack (Table XVII). Polyurethane coatings of A276 white paint and Z302 black paints were protected by applying silicone adhesive RTV-670 and OI 650. The effectiveness of the coatings was tested in space shuttle and LDEF missions [77, 82, 126]. The post-flight results indicate that OI 650 glass silicone resin was successful in protecting paints, whereas the RTV 670 was more reactive even though its mass loss was negligible. The mass loss of the paints with overcoating appears to be in the order of 1×10^{-24} g atom^{-1}. It appears that to protect these paints there is a need to study and develop suitable thin silicate overcoatings for AO protection. Durable flexible silicone coatings are needed for replacement of flexible S13G/LO paints. The inorganic white coatings Z93 and YB71 appear to have stable optical properties in the LEO environment. However, there is a need to develop new conductive and partially conductive coatings with acceptable optical properties.

4.4. Protective mechanisms for optical components

All-metal mirrors may be overcoated with protective layers and in some cases will serve to increase or decrease the reflectance of the underlying metal mirrors in a certain wavelength region. The most frequently used protective layers are films of silicon oxides, SiO, SiO_x, SiO_2 and Al_2O_3 [127].

Evaporated Al is the most frequently used coating for front surface mirrors for u.v., visible and infrared wavelength ranges. Thin films produced by evaporation of SiO and coatings of SiO_2 and Al_2O_3 deposited by electron beam evaporation are the most commonly used for evaporated Al mirrors.

Aluminium mirrors protected by SiO, SiO_2 and Al_2O_3 appear to have been provided with good protection without loss of performance of the underlying mirrors, but they showed a reduction in reflectance in the 8–12 μm wavelength region. At normal incidence the reflectance of the coated mirrors shows a reduction. Possible alternative materials that might lead to durable mirrors with high reflectance in the 8–12 μm wavelength range are Y_2O_3 and HfO_2. Evaporated protective coatings with $\lambda/2$ thickness at wavelength $\lambda = 550$ nm of HfO_2 and Y_2O_3 protected the Al mirrors [128].

Silver-coated mirrors are generally protected by SiO_2 coatings. Since SiO_2 coatings appear to have very poor adhesion to silver coatings there is the need for an intermediate buffer layer. Aluminium oxide appears to have the necessary properties to improve the adhesion without affecting the reflectance of the silver mirrors. Sputtered coatings of Al_2O_3 and SiO_2 of 95 nm thickness deposited on silver coatings of 25 nm were exposed to a ground-simulated AO flux of 1.0×10^{17} atoms cm^{-2} s^{-1}. The results indicate that the coatings protected the underlying silver only at an AO fluence level of 10^{20}–10^{21} atoms cm^{-2}. It is not clear whether increasing the thickness of the coatings proportionately increases AO resistance. Further study should focus on understanding the fundamental mechanism responsible for the degradation of these coatings [129]. Table XVIII gives the typical AO protective coatings for silver and aluminium mirrors.

Protective coatings with different combinations of layers not only protect against AO attack but also improve mirror reflectance. Rhodium mirrors coated with $SiO_2 + TiO_2$ have increased reflectance in addition to protection from AO attack. Coatings of $MgF_2 + CeO_2$, $Al_2O_3 + TiO_2$ and reactively deposited $SiO_2 + TiO_2$ are the most frequently used reflectance-enhancing film combinations for the visible range and

TABLE XVII AO protective coatings for organic paints

Organic paint	Protective coating	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	Change in optical properties		Ref.
				Δα	Δε	
A276	OI650	STS-8	2.9	+ 0.002	–	77
		LDEF	80.0	+ 0.34	– 0.01	82
	RTV-670	LDEF	80.0	+ 0.35	– 0.03	82
Z302	OI650	STS-8	03.5	– 0.001	–	77
		STS-41G	2.45	0.0	–	107
		LDEF	80.0	+ 0.01	–	82
	RTV-670	STS-8	03.5	– 0.004	–	77
		LDEF	80.0	+ 0.01	–	82
	RTV-602	STS-41G	2.45	– 0.004	–	107
	MN41-1104	STS-41G	2.45	– 0.002	–	107

TABLE XVIII AO protective coatings for optical metal films

Metal film	Protective coating	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{21})	Change in reflectance (%)	Ref.
Ag	SiO_2	LDEF	6.93	$- < 1$	34
Al	SiO_2	LDEF	6.93	$- < 1$	34
Al	SiO–SiO_2	LDEF	6.93	-2	34
Al	SiO	LDEF	6.93	-1.5	34
Al	MgF_2	LDEF	6.93	$+1.5$	34
Ag	MgF_2	LDEF	6.93	-5 to -10	34

films of $SiO_2 + HfO_2$ are suitable for increasing the reflectance of metal-coated mirrors in the u.v. range.

Various dielectric thin film materials used for optical application and their preparation and suitability as protective and reflectance-enhancing coatings on metals have been discussed by Ritter [130].

Thin coatings of various protective glassy ceramics were applied to silver and aluminium reflectors and exposed to the LEO environment on LDEF missions. Post-flight examination of samples revealed that a densification of the coating materials had occurred during AO exposure in the orbit. A conversion of SiO to SiO_2 was identified [34].

The application of a thin platinum coating appears to provide good protection to osmium films from AO attack. However, the durability of the protective coating depends mainly on the density of the defects [95].

4.5. Protective coatings for space power components

Protective mechanisms are needed for both photovoltaic solar arrays and solar dynamic power generators to protect against AO degradation.

4.5.1. Protective coatings for photovoltaic solar array

Protective mechanisms are required for silver solar cell interconnects, Kapton film, CFRP and fibreglass epoxy composites and magnesium fluoride coatings. Table XIX gives the various coatings studied for protecting photovoltaic solar array components from AO degradation.

TABLE XIX AO protective coatings for photovoltaic solar array components

Material	Protective coating	Spacecraft flown	Exposed AO fluence (atoms cm^{-2}) (10^{20})	Ref.
Silver interconnect	Al	STS-41G	2.45	107
	Pd	STS-41G	2.45	107
	Au	STS-41G	2.45	107
	DC1104	STS-41G	2.45	131
	CV1144	Ground simulation	2.42	131
	SWS V10		2.42	131
	DC100		2.42	131
Kapton	SiO_2	Ground simulation	3.5	143
			3.0	143
			3.0	143
		STS-8	3.5	143
		LDEF	4.92	143
	SiO_2 + FP	Ground simulation	3.5	143
			3.0	143
			2.21	143
		STS-8	3.5	143
		LDEF	4.92	143
	a:Si	Ground simulation	3.0	143
	P:SiN		3.0	143
	P:SiON		3.0	143
	Al_2O_3	STS-8	3.5	143
		LDEF	4.92	143
		Ground simulation	3.5	143
	SnO_2		3.0	143
	HMDS		3.0	143
	HMDS + FP		3.0	143
	RTV-1144		3.0	143
	ITO	LDEF	87.2	60
	In_2O_3	LDEF	87.2	60
Glass fibre composites	In–Sn	Ground simulation	88.0	108
	Ni/Au/In–Sn		88.0	108
	CV1144		88.0	108
	S13G/LO		88.0	108

Various types of metallic and polymer coatings were studied for protecting silver interconnects from AO attack [107]. Thin coatings of aluminium, gold and palladium were applied to silver and tested in the LEO environment. The post-flight results indicate that the applied metallization of aluminium, gold and palladium is inadequate for protecting silver under conditions of combined AO and thermal vacuum [107]. In general all metal coatings will have defects which act as active sites for oxidation. Once the oxygen diffuses through the defects in the coating to the underlying silver, oxidation of the silver is initiated. The thicker films seem to retard the onset of oxidation, but thicker metallization may change the flexibility and mechanical properties of the interconnects. Silicone coatings of DC-1200, DC1104, SWS-V10 and CV1144 were applied and their durability tested for the LEO environment in both ground-simulation [131] and flight tests. The results indicate that the silicone coatings provide good protection for the silver from AO attack. LDEF results showed that the silicones degrade significantly and are the source of contamination. The development of alternative materials for interconnects is of significant importance for spacecraft materials. There are few materials presently available to replace the silver interconnects for LEO spacecraft applications. Among the available materials molybdenum, Invar and Kovar appear to be potential candidates for interconnection. Silver-plated molybdenum appears to be a viable candidate because of its good space record and resistance to AO attack. Though Mo oxidizes in LEO environment its oxidation rate is very low relative to silver interconnect. The oxidation stability of Invar and Kovar interconnects yet to be determined. Aluminium alloy foils as solar cell interconnects are under development for LEO solar array application [107].

Various mechanisms for protecting Kapton film from AO attack were studied, and their durability was assessed in both ground-simulated laboratory facilities and in space experiments. The protective coatings studied included silicon dioxide with and without fluoropolymer (SiO_2, SiO_2 + FP) [132], Al_2O_3 [133], amorphous hydrogenated silicon (a: Si) [10], SiN [10], SiON [10], ITO [132], tin oxide with and without fluoropolymer (SnO_2, SnO_2 + FP) [132], diphenyldimethyl siloxane (CV1144) [132], hexadimethyl siloxane (HDMS) [111, 132], polydimethyl siloxane (DC93500) [134], polysiloxane-polyimides [135], polyphosphazenes [136] and germanium [137].

All inorganic coatings (SiO_2, Al_2O_3, ITO, SnO_2, SiN, SiON and Ge) appear to provide good protection to Kapton film because of their higher oxidation state and thermodynamic stability [132, 138]. However their brittleness places limitations on the flexibility of the coating. Because of their low strain to failure the inorganic coatings produce cracks when they are bent during handling and fabrication. These cracks may provide pathways for oxygen to diffuse through and attack at the Kapton surface resulting in undercuts, which may lead to the failure of both coating and Kapton film. A small amount of fluoropolymer mixed molecularly with these coatings appears to provide good flexibility [139]. Various internal and multilayer sealants can be used to block the defects and to prevent the AO reaching the substrate [140].

Siloxane coatings provide good protection to Kapton film from AO attack. The protection is achieved by the formation of inert silica on the surface of the coating during initial stages of exposure. Cracking of the coatings may occur after long exposure to the AO environment and due to thermal cycling. Spalling of the coating in the form of small debris and as free radicals of siloxane results in exposure of fresh siloxane on the surface. Condensed silicone monomers on sensitive optical components are likely to polymerize due to synergism of AO and v.u.v. radiation. The transparent silicone coatings turn brown after photopolymerization. As a result the transmission of light reduces through the contaminated layer [141].

Monte Carlo models have been applied to predict the performance of the Kapton film with defects in the coating. This model is modified based on LDEF results to predict the undercut profiles on Kapton film under protective coating [142]. Various protective coatings and their developmental status and the development of new AO-resistant materials for solar array application have been discussed previously [143].

Atomic oxygen resistant (AOR) polyimide films based on polysiloxane mixed polyimide copolymer films appear to be a viable alternative candidate for Kapton film to use in LEO spacecraft, since polysiloxane is a metal oxide former and metal oxides are proven to be highly resistant to AO attack [144, 145]. These films exhibit protective characteristics similar to those of the siloxane coatings, forming their own protective SiO_2 layer on the surface immediately after exposure to the AO environment. Ground simulated experimental results show that though siloxane-based polyimide shows better resistance it is unlikely to survive long term in the LEO environment [146]. An application of SiO_2 with fluoropolymer mix would improve the life of Kapton film and Kapton AOR film underneath would add a backup safety factor to the coating since AOR Kapton film is more durable than Kapton film.

Fibreglass composites exposed to the LEO environment were oxidized due to AO impact. The main effect is that the epoxy of the composite eroded away leaving the glass fibres on the surface. Protection of the fibres leaving the surface is required. Protection mechanisms including aluminium braid, In–Sn eutectic coating silicone adhesive CV-1144 and S13G/LO thermal control paints were studied for use in the protection of fibreglass composites [108]. All these coatings on fibreglass epoxy longerons were tested in ground-simulated tests and the results show that all coatings except aluminium braid provide some protection to the longerons. Aluminium braid is very open, which allows fibreglass epoxy to be directly exposed to the AO environment. Silicone coatings exhibit some induction period before the onset of oxidation degradation. In–Sn eutectic coatings appear to provide some protection, but this is mainly due to defects in the coatings. More study is required in application of defect-free continuous metal alloy coatings and selection of materials which can self-seal the defects in the coating [108].

Magnesium fluoride coating needs protection to limit conversion to magnesium oxide, and alternative coatings are under development [147].

4.5.2. Protective coatings for solar dynamic power generators

Protective coatings are needed for both concentrator substrate and reflective coatings. Different protective coatings were evaluated to protect CFRP concentrators from AO attack. Metal oxide coatings appear to provide protection to CFRP composites from the degradation effect of AO attack. The durability of the coatings was established by testing in both the LEO environment and in ground simulated laboratory tests. Metal matrix composites and an aluminium honeycomb sandwich with aluminium facesheets appear to be the alternative materials for concentrator substrates, because these materials are light weight and resistant to AO attack.

Various coatings including aluminium oxide, silicon dioxide and magnesium fluoride were studied for protecting both aluminium and silver reflective coatings from AO attack [148]. All the coatings were tested both in space experiments and laboratory simulated experiments [148, 149] to study their durability in the LEO environment. Tables XX and XXI list the various coatings studied for protecting solar dynamic reflector surfaces from AO degradation. The test results show that there is no change in the integrated reflectance of the reflective layers and good resistance to AO attack is exhibited. Though SiO_2 provides good protection for reflectors its poor adhesion necessitates a buffer layer in between the reflector coating and the protective layer. Aluminium oxide appears to provide both functions as buffer layer and protective coating. Thin multilayers of SiO_2 and Al_2O_3 coatings provide good protection to both Al and Ag reflective layers [150].

TABLE XX Change in reflectance of silver mirrors with protective coatings after exposure to AO

Substrate material	Protective coating	Exposed AO fluence (atoms cm^{-2}) (10^{22})	Reflectance loss (%)	Ref.
Glass	SiO_x	19.8	− 2.0	110
	SiO_x/MgF_2	19.8	− 3.6	110
	ITO	7.04	+ 1.0	110
	ITO/MgF_2	7.04	− 1.4	110
Aluminium	MgF_2	2.77	− 1.8	150
	SiO_2	1.94	− 2.1	150
	Al_2O_3	1.94	− 3.2	150
	Si_3N_4	1.25	− 8.1	150
Graphite/epoxy	SiO_x	5.63	− 3.2	110
	SiO_2	2.6	− 11.5	150
	MgF_2	5.63	0.0	110
		3.40	− 15.7	150
	Si_3N_4	1.25	− 11.2	150
	Al_2O_3	2.35	0.0	110
	RTV 655	4.73	− 6.2	110
Nickel	MgF_2	3.4	− 1.4	150
	SiO_2	2.6	− 8.6	150
	Al_2O_3	2.35	0.0	150
Beryllium/copper	MgF_2	2.77	− 1.5	150
	SiO_2	1.94	− 6.0	150
	Si_3N_4	1.25	− 3.6	150

TABLE XXI Change in solar reflectance of aluminium mirrors with protective coatings after exposure to AO

Substrate material	Protective coating	Exposed AO fluence (atoms cm^{-2}) (10^{22})	Reflectance loss (%)	Ref.
Glass	SiO_x	19.8	− 0.88	110
	SiO_x/MgF_2	19.8	− 5.2	110
	ITO	7.04	− 0.7	110
	ITO/MgF_2	7.04	− 3.7	110
Graphite/epoxy	MgF_2	5.63	− 0.5	110
	RTV 655	4.73	− 8.0	110

5. Ground-simulation testing requirements

Development and verification of AO-durable protective coatings and new AO-resistant materials for long duration use in the LEO environment requires both ground-based laboratory simulation testing and inflight experiments to ensure LEO environmental compatibility. Although inflight experiments provide valuable test data, the large matrix of materials and test conditions, short duration exposure, limited flight service availability and uncertain flight scheduling, now make it essential to develop and test the new technologies in ground-based laboratory simulation facilities. The economics and convenience of LEO simulation facilities will result in their extensive use provided there is adequate confidence in their ability to simulate the LEO environment and its effects on materials. As a result of a growing need for long-term space system durability and in order to assess the compatibility and durability of the new technologies for long-term space system applications in the LEO environment, numerous AO ground simulation laboratory facilities have been and continue to be developed [151–155].

The types of capability needed from ground-based laboratory AO simulation facilities are as follows:

(a) they should have the capability to produce high beam energy (5–12 eV)

(b) the beam facility should have the capability to produce a beam flux of 10^{17}–10^{18} atoms cm^{-2} s^{-1}

(c) they should have the capability to produce an AO fluence level up to 10^{23} atoms cm^{-2}

(d) the AO beam area should be sufficiently large

(e) large area exposures should be possible

(f) *in situ* measurements of critical parameters should be possible

(g) thermal cycling and temperature control of the samples during AO exposure should be possible.

Currently, oxygen atom sources may be classified into five types: thermal, high-temperature electrical discharges (plasma torch), ion beams, beam–surface interactions and laser breakdown. These devices have been reviewed by Caledonia [156]. The advantages and limitations of the facilities are also discussed.

The extent of AO exposure system reliably replicates the mechanisms occurring in the LEO altitude environment can be judged by quantitative comparison of measurements of the surface texture, chemistry and erosion rate of various materials.

Most of the ground-simulation facilities are developed based on space results. The database provided by space experiments is limited in its application, because the total integrated AO flux (fluence) derived for space flights and used to determine materials reaction rates has been estimated using mass spectrometer and incoherent scatter (MSIS) thermospheric models to predict AO number densities within the orbital environment. Typically errors of ±25% or greater can be expected and these errors also appear in the surface erosion rates prediction.

Kapton thickness loss is normally used to measure the AO effect in ground simulated laboratory facilities.

The Kapton erosion rate of 3×10^{-24} cm^{-3} atom^{-1} derived from extensive experiments of both space and ground simulated experiments. The ground simulation test results show that the Kapton reactivity depends strongly on the translational energy of incident AO beam and increases with the energy of the AO to the 0.68 power. Thus, the Kapton erosion rate in ground simulated facilities with different incident energies would require AO levels of orders of magnitude different from those in space to obtain the same erosion rate observed in space.

Test results of ground simulated experiments show that some facilities are in near agreement with space results for a few materials only. There is no single facility in near agreement with space results for all spacecraft materials. However, the ground simulation facilities presently available give only qualitative rather than quantitative information. All the materials known to oxidize in the LEO environment also oxidize in the ground simulation tests but the relative rates of oxidation for various materials are not quantifiable in agreement with the LEO results. Additionally, all the materials known to be stable in the ground simulation tests are stable in the LEO environment. Thus, ground simulated AO experiment results only allow us to establish whether materials will survive or will be oxidized in the LEO environment, leaving the quantitative determination of the rate of degradation.

There are some complications associated with using the data derived from different ground simulation tests to predict the durability of the materials for long-term spacecraft applications. These may be due to exposure of the materials to improper AO energy, enhanced AO flux, use of ions instead of atoms, environmental gases in abundance dissimilar to that in space, metastable species and plasma effects. Nevertheless, the LDEF results show that the coatings and materials that were proved to be resistant to AO attack in ground simulation tests performed well in the LEO environment for 5 years 9 months. LDEF test results will be used as benchmarks for future ground studies.

Some of the ground simulated facilities have been developed to obtain the LEO environment AO fluxes and energies. Now, it is necessary to obtain the AO reaction data for various materials in long exposure, active orbital experiments using highly characterized surfaces and conditions to compare with laboratory data. Inflight experimental test data are indispensable to determine whether or not the ground simulated facility provides reasonable agreement in materials degradation rate. This information will give confidence that accelerated testing methods in ground simulated tests can actually be used to predict long-term AO exposure effects in the LEO environment.

The collective data from the available ground simulation facilities for different materials will provide better insight into understanding the mechanisms and the reactivity coefficient dependence upon AO energy, AO flux, AO effect, target temperature, metastable flux, charged species (O^+, O_2^{+1}, etc.,) flux, impact angle, environmental species (O_2, N_2, N, He, Ar, etc.,) and the synergistic effects of solar radiation. From this database it may be possible to identify the necessary exposure conditions which are important in the simulation of the LEO AO environment, in order to obtain results identical to those observed in space [157].

Future ground-based testing in well characterized facilities may resolve most of the issues and provide confidence in using the facilities for accelerated testing for long-term spacecraft applications.

6. Conclusions

1. Polymer composite materials are susceptible to mass loss and surface morphology changes due to AO impact. As a result of mass loss mechanical property degradation was observed. The surface morphology of the AO-eroded PMC surfaces does not resemble that of pure polymer specimens of similar chemistry to the PMC matrix resin. This is because of the different erosion rates of resin and carbon fibre. The AO degradation mechanism of polymer composites is different for different composites mainly due to the varying degree of susceptibility of various resin matrices and reinforced fibres to AO attack and different layup conditions. Metal and metal oxide coatings appear to provide good protection to PMCs from degrading effects of AO impact. Metal matrix and ceramic matrix composites prepared under optimum conditions appear to be alternative materials for PMCs for LEO spacecraft application. Modified resins with AO-resistant materials appear to survive long-term in the LEO environment.

2. Directly exposed solid lubricants appear to be affected by AO interaction. As a result of this interaction, the tribological properties of lubricants are changed and the performance also degraded. For long-term LEO spacecraft application the sensitive lubricants should be either replaced with AO-resistant materials or protected with flexible covers wherever the lubricants are necessarily exposed to the environment directly.

3. Polymer-based flexible SSMs were affected in the LEO environment. u.v./v.u.v. radiation exposure degrades FEP mechanical properties and provides reaction sites for AO interaction. The bulk properties of both the FEP and Kapton were not changed but there was mass loss and surface erosion. Metals and metal oxides and inorganic polymer coatings appear to provide good protection. The durability of the coatings was tested in both LEO experiments and in ground simulation laboratory tests. Materials stable for both AO and u.v. radiation need to be developed to replace SSMs with low α/ε. Most of the organic-based thermal paints are susceptible to AO degradation. Most prominent are polyurethane-based and silicone-based paints. The degradation is mainly due to mass loss of the binder materials. Thin silicate coatings appear to provide protection to organic paints from AO attack. There is a need to develop new conductive and partially conductive coatings with acceptable optical properties. Flexible white paints are needed to replace S13G/LO paint.

4. Most of the optical components are affected as a result of AO interaction. Significant changes in optical

properties were observed as a result of mass loss and surface morphology changes. The transmission characteristics of interference filters in visible and infrared wavelengths altered. The AO erosion caused detuning of the wavelength band width of the filters. Metal oxide coatings appear to provide protection to the optical components from AO attack.

5. Space power generator components were affected due to AO attack. As a result of AO interaction with silver interconnects, Kapton film and CFRP composites thickness loss and change in mechanical and thermooptical properties were observed. Optical transmission loss in refractive lens materials and change in reflectivity characteristics of silver and aluminium coatings were observed after exposure to AO environment. Various protective coatings were developed and tested to study their durability in both LEO environment and in ground simulated facilities. Siloxane substituted polyimides for Kapton film and metal matrix composites for CFRP and molybdenum interconnects for silver interconnects appear to be alternative materials. Metal oxide coatings appear to provide good protection from AO degradation to reflective surfaces of the solar dynamic systems.

7. Future research

1. Currently available AO interaction data have limited application because the flight data are limited in terms of the accuracy of the estimates of AO fluence. These were not measured during flight but calculated using MSIS thermospheric models; the model errors are included in the database. The environmental interaction database needs to be expanded and verified by means of both flight experiments and ground simulated laboratory investigations.

2. Space environmental models should be modified to predict AO, u.v. flux, particle impact rates and temperature variations within acceptable range.

3. Space environmental interaction models need to be developed to predict erosion yield, optical and mechanical property changes, etc. Detailed mechanistic models dependent on AO and u.v./v.u.v. impact, materials, temperature, time, etc., are required. The specific dependence of degradation and recession on AO and u.v. fluxes varies by materials type. These effects are strongly time- and temperature-dependent: activation energies will vary for different processes and the fluxes of u.v. radiation and AO change drastically over the solar cycle. At different times, different parameters are likely to dominate the rate-limiting processes. This is a very complex process in a materials-specific area. The main goal should be to develop a model which is able to make accurate lifetime performance predictions for materials with specific applications. This would improve the reliability of spacecraft and their chances of enduring and performing their missions long-term. Good models would also minimize the cost of testing by guiding selection of test parameters to focus on critical conditions.

4. Ground simulation testing facilities requirements are: (a) they must be capable of simulating space results; (b) synergistic effects must be included (simultaneously or sequential); (c) knowledge of how to extrapolate from ground testing to predict space performance; (d) quantification of acceleration artifacts for AO, u.v. thermal cycling, etc.

5. Flight experiments are needed: (a) on orbit monitoring of AO, u.v., temperature, etc.; (b) to study the LEO environmental effects both in active and passive experiments; (c) to test new, higher-performance and more durable materials; (d) to provide validation and phenomenology tests of ground test results; (e) to know how to extrapolate results of short-term flight experiments to predict long-duration performance.

6. Materials and protective coatings intrinsically stable under AO attack need to be developed. Accelerated full life testing on AO-resistant materials and protective coatings must be conducted in ground simulated laboratory experiments to ensure their long-term survivability in the LEO environment.

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Glossary

1. *Low earth orbit (LEO):* a circular orbit of low altitude typically less than 1000 km commonly.
2. *Space transport system (STS):* STS is a formal name for the American Space Shuttle. It is a reusable launch vehicle designed to carry personnel and payloads into orbit and return for refurbishment.
3. *Long duration exposure facility (LDEF):* LDEF was a passive payload of National Aeronautics and Space Administration (NASA) and was designed to test the various spacecraft materials and systems in the LEO environment. The experiments carried out by LDEF include various disciplines of materials, coatings and thermal systems, power and propulsion, space science and electronics and optics.
4. *Limited duration of candidate materials exposure experiment (LDCE):* LDCE was a small special shuttle payload to study the effects of the LEO environment on various inorganic and organic materials and coatings for limited duration exposure. The vertical height of a body above the surface of a plant (typically above sea level for earth).
5. *Composites:* a combination of two or more materials (reinforcing elements, fillers and composite matrix binders) differing in form or composition on the macroscale. The constituents retain their identities, i.e. they do not dissolve or merge completely into one another although they act in concert.
6. *Polyacrylonitrile (PAN):* used as a base material or precursor in the manufacture of certain carbon fibres.
7. *Kevlar:* an organic polymer composed of aromatic polyamides having a para-type orientation (parallel chain extending bonds from each aromatic nucleus).
8. *Control moment gyro:* a device used to control the attitude of the spacecraft.
9. *Gimbal:* a device used to provide angular movement in one or two dimensions.
10. *Slipring:* a device used to transfer the power/signal from rotating solar array to the stationary spacecraft.
11. *Boom:* as part of a spacecraft, a pole or spar designed to hold an instrument or detector required to operate some distance from the main body of the vehicle.
12. *Spin stabilized spacecraft:* a spacecraft which maintains its stability by rotating about its longitudinal axis.
13. *Mission:* a specific task assigned to a spacecraft. The duration of the mission of an unmanned spacecraft is measured in terms of its operational lifetime.
14. *Longeron:* a main longitudinal structural brace in a spacecraft structure.
15. *Second surface mirror (SSM):* SSM is a thermal control component on the surface of the spacecraft. The second surface is derived from its dual function as a thermal emitter and solar reflector. The front surface polymer film (Kapton or Teflon) works as a good emitter over the infrared spectrum, so thermal energy from the spacecraft can be conducted to the SSM and radiated into space from the outer first surface of the mirror. Most of the incoming solar radiation is reflected from the coated rear surface (the second surface).
16. *Multilayer insulation (MLI):* spacecraft thermal insulation comprising a number of reflective layers.
17. *Hydrazine thruster:* a propulsive device utilizing the chemical compound hydrazine as a propellant.
18. *Chemglaze A276:* a registered trademark of Hughson Chemicals, USA. A276 is a white organic thermal control paint used on spacecraft surfaces. It contains titanium dioxide pigment and polyurethane binder.
19. *Chemglaze Z302:* a registered trademark of Hughson Chemicals, USA. Z302 is a glossy black organic thermal control paint used on spacecraft surfaces. It contains carbon pigment and polyurethane binder.
20. *Chemglaze Z306:* a registered trademark of Hughson Chemicals, USA. Z306 is a flat black organic thermal control paint used on spacecraft surfaces. It contains carbon pigment and polyurethane binder.
21. *Silicone S13G/LO:* a white organic thermal control paint developed by Illinois Institute of Technology Research Institute (IITRI). It contains a ZnO pigment and methyl silicone binder.
24. *Z93 paint:* a white inorganic thermal control coating developed by IITRI. The coating contains ZnO pigment with potassium silicate binder.
25. *YB71 paint:* a white inorganic thermal control paint developed by IITRI. The coating contains a zincorthotitanate and potassium silicate binder.
26. *Outgassing:* the release of a gas from a material when it is exposed to an ambient pressure lower than the vapour pressure of the gas.
27. *Solar array:* an area of solar cells designed to provide electrical power to a spacecraft.
28. *Solar cell:* a device for the conversion of solar energy to electrical energy.
29. *Solar cell interconnect:* a metal foil used to interconnect the solar cells on the solar array in both series and parallel to obtain the required power for the spacecraft.
30. *Micrometeoroid:* any small celestial body of natural origin, about the size of sand or smaller.
31. *Orbital debris:* a blanket term for any man-made artefact discarded or accidentally produced in orbit. This includes satellites which have reached end of life, spent launch vehicle stages, hardware accidentally released by astronauts and the remnants of spacecraft which have exploded.

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