Results from Optical Coatings Flown on MISSE-1 and MISSE-2 and other Flight Experiments

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Selected optically transparent materials and coatings flown on a number of low Earth orbit (LEO) materials flight experiments will be reviewed and discussed. Effects of flight exposure for both magnesium fluoride and lithium fluoride specimens will be presented. Individual specimens of magnesium fluoride were flown on the EOIM III Space Shuttle experiment, the Long Duration Exposure Facility (LDEF), the Optical Properties Monitor and Passive Optical Sample Assembly experiments on Mir, and MISSE-1 and MISSE-2 International Space Station packages. Subsequent to the LDEF retrieval and EOIM III experiment in 1992, the question of atomic oxygen reaction with magnesium fluoride was raised.

Atomic oxygen and solar exposures, molecular contamination levels, and varying exposure durations will each be considered in evaluating any observed changes in optical properties. A comparison of the thermodynamics of oxidation of magnesium fluoride and lithium fluoride will be summarized. Elemental composition as a function of depth, as determined using XPS, will be discussed for selected specimens, to gain insight into reactions that are thermodynamically allowed under the LEO conditions.

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NSMMS
June, 2006

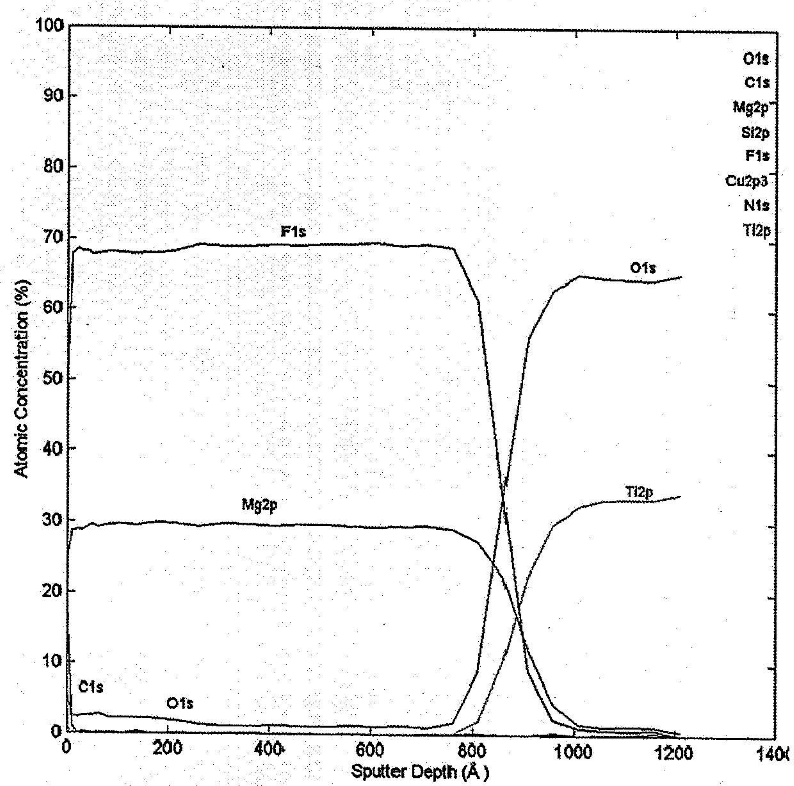
Purpose: Describe results of post-flight examination of optically transparent materials and mirrors from the MISSE-1 and MISSE-2, POSA (Passive Optical Sample Assembly) I & II, Optical Properties Monitor, and EOIM (Effects of Oxygen Interaction with Materials) III experiments

Compare results from these flight experiments

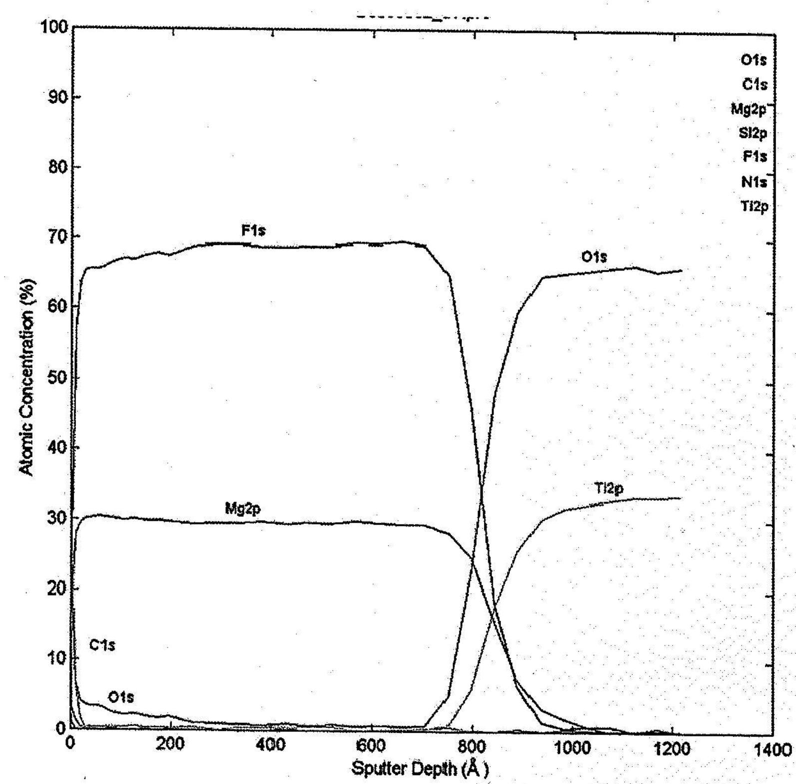
Consider the thermodynamic limitations on oxidative reactions on these surfaces

MgF_2 coated sample from OPM flight Experiment

Ground control

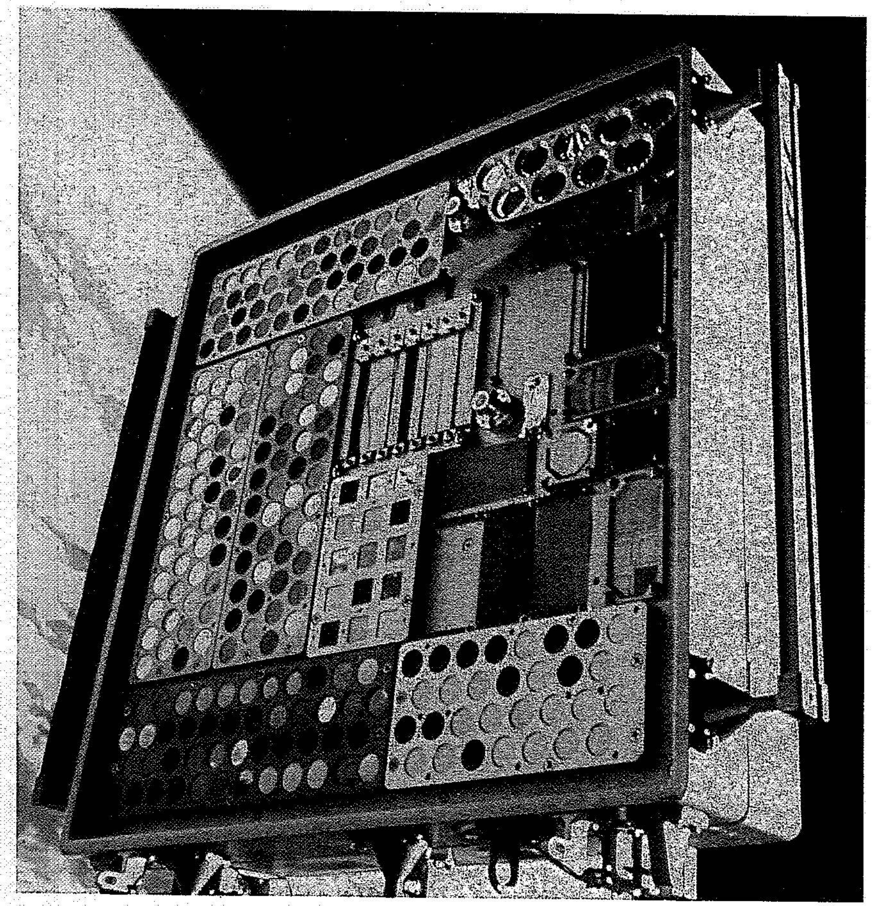


Flight sample



Slight increase in oxygen, decrease in fluorine for 20-30 nm on flight specimen relative to ground control. Small increase in surface carbon on flight specimen.

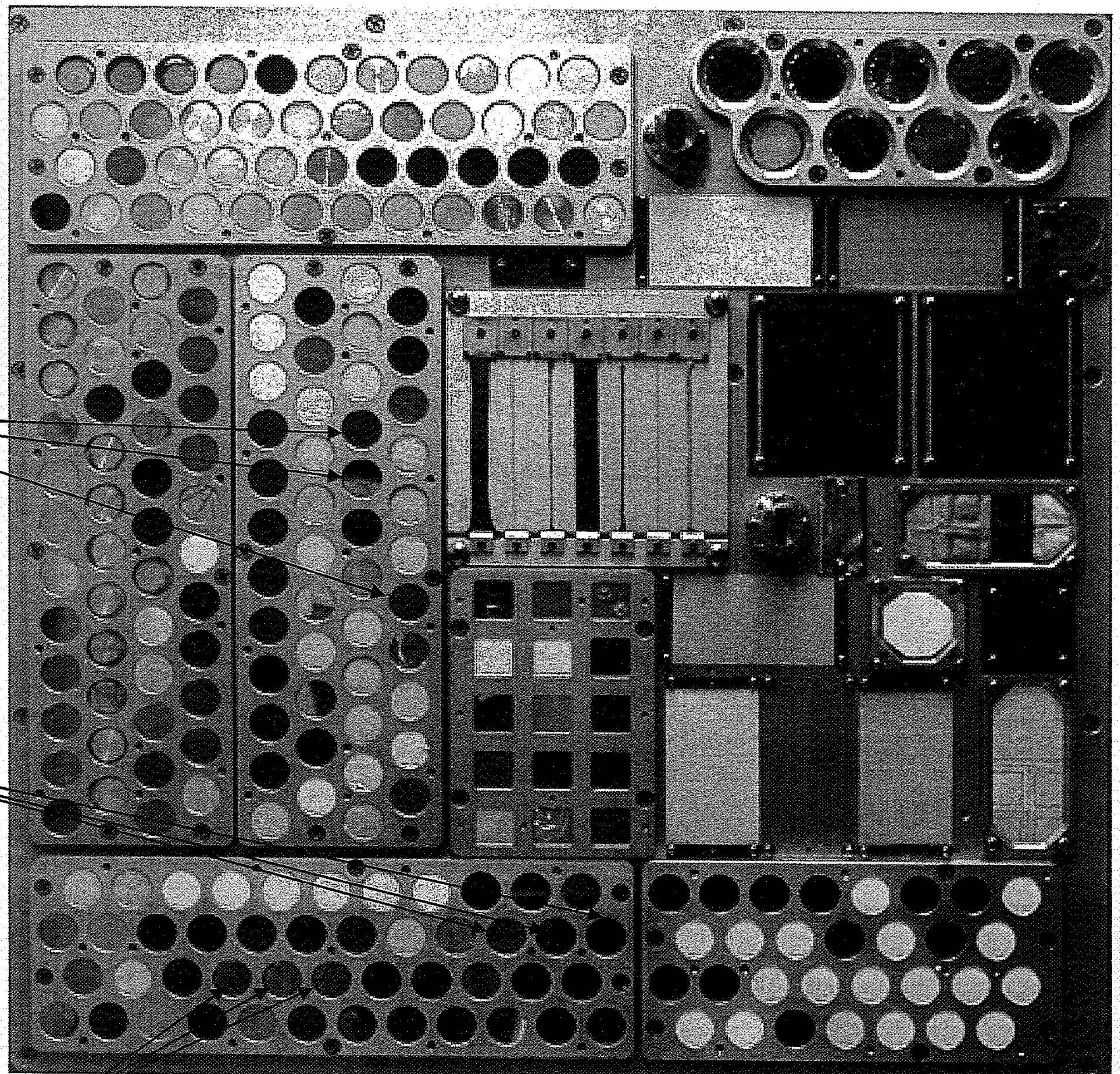
MISSE-2 AO-UV SIDE, on-orbit



AO fluence
at magnesium fluoride
Sample locations
~7 x 10^{21} atoms/cm^2

Locations of Magnesium Fluoride Windows on MISSE-2

Nominal "Ram," or AO/UV-side



E7-7,E7-15, E7-16

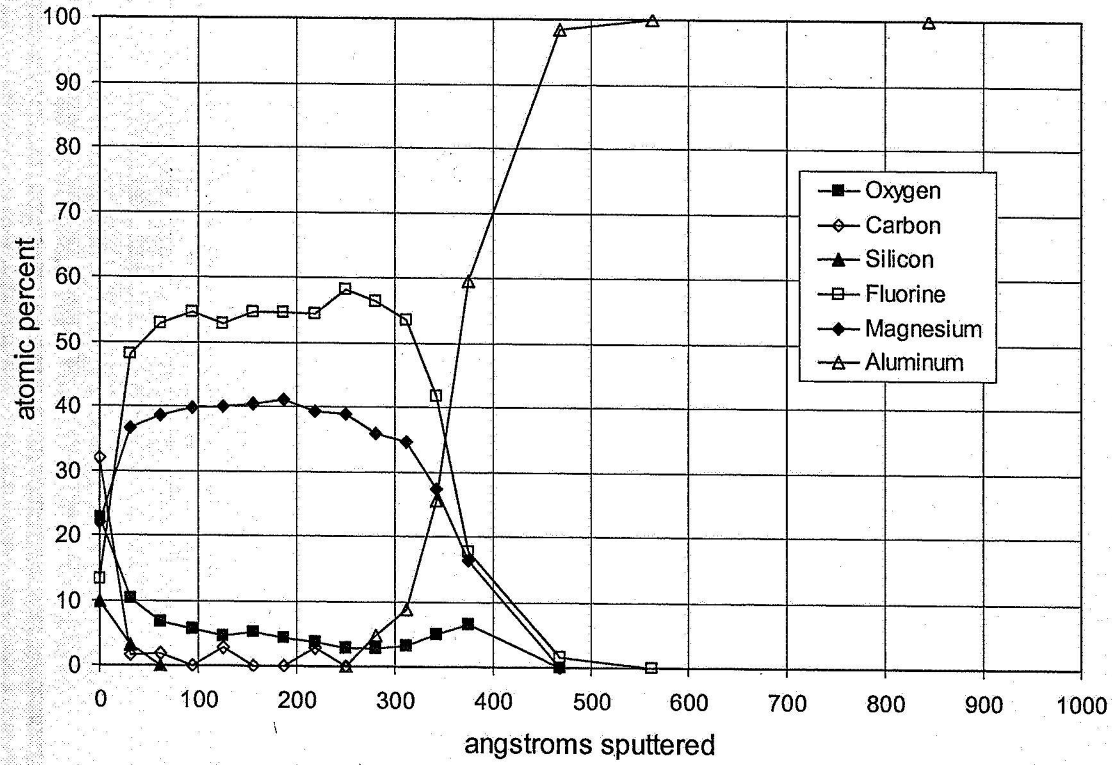
E8-21,E8-22, E8-23

E8-27,E8-28, E8-29

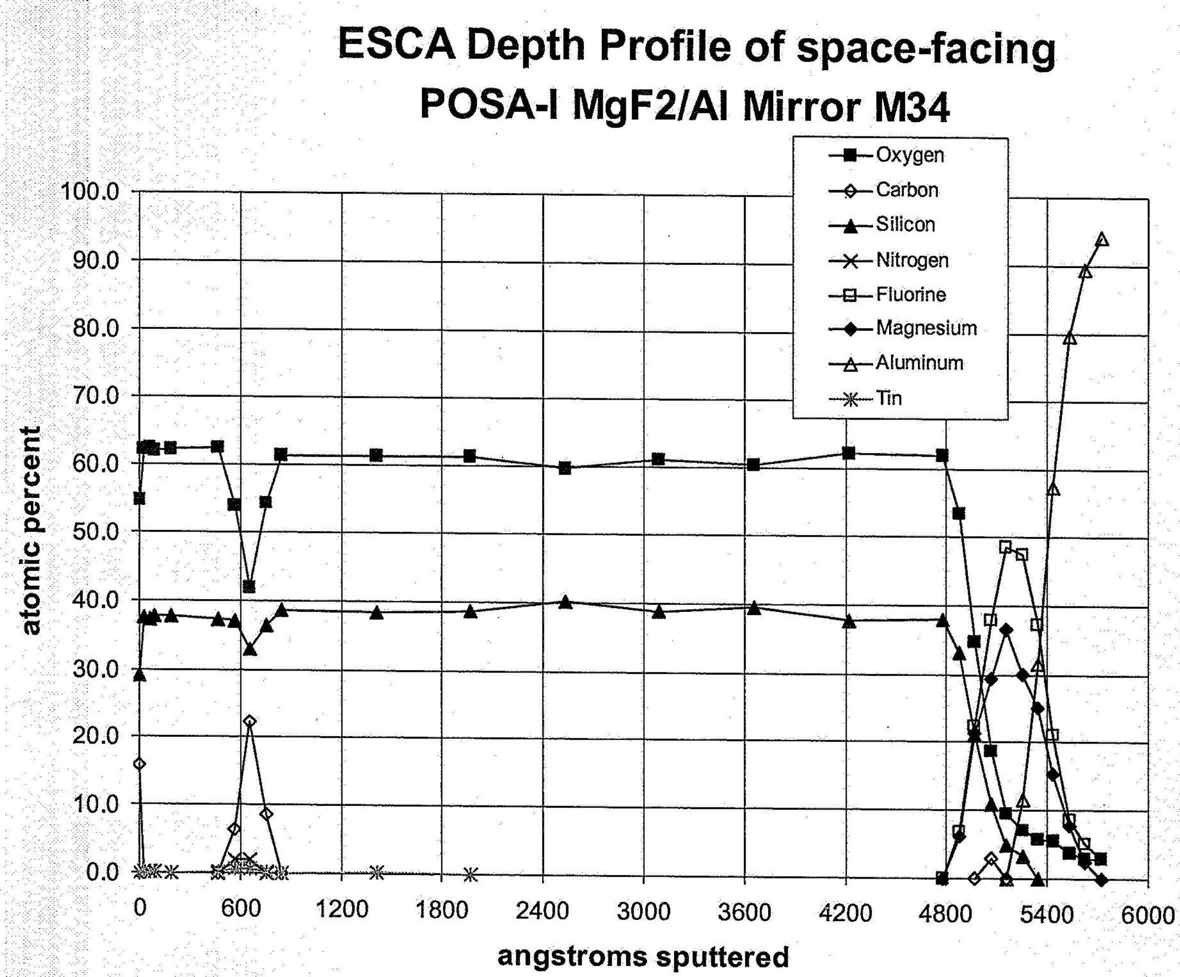
Space Environment Exposures

		AO Fluence (atoms/cm^2)	UV Dose (equivalent sun-hours)
POSA I	Mir-facing	7×10^{19}	413
	Space-facing	Min. 1.2×10^{18}	571
POSA-II	Mir-facing	8×10^{19}	-
	Space-facing	2.1×10^{20}	576
EOIM-III		2.2×10^{20}	31
LDEF A0034 Trailing edge		3.71×10^{3}	11,100
MISSE-2	Ram-facing	$7\text{-}9 \times 10^{21}$	5100-6500

EOIM-III MgF2/Al Mirror 3-10



Surface contamination of silicon oxide and carbon
Oxygen throughout magnesium fluoride coating


ESCA Depth Profile of space-facing
POSA-I MgF2/Al Mirror M34
Oxygen
Carbon
Silicon
Nitrogen
Fluorine
Magnesium
Aluminum
Tin
atomic percent
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0
600
1200
1800
2400
3000
3600
4200
4800
5400
6000
angstroms sputtered

Evaluation of Lithium Fluoride Stability with Respect to Atomic Oxygen Exposure

Potential reactions of lithium fluoride and oxygen atoms

$$2LiF + O \rightarrow Li_2O + F_2 \qquad (1)$$
$$2LiF + O \rightarrow Li_2O + 2F \qquad (2)$$
$$LiF + O \rightarrow LiO + F \qquad (3)$$
$$LiF + 2O \rightarrow LiO + OF \qquad (4)$$

Reactions (1), (2), and (3) spontaneous under standard conditions of 1 atmosphere pressure and 298K.

Reaction (2) is even higher energy than reaction (1), but the dissociation energy of F_2.

Pressure changes from 1 atmosphere to on-orbit pressures, and temperature changes from 298K to any temperature between 173K and 423K, only change the Gibbs free energy of reaction very slightly, but do not alter the essential conclusion that these reactions are <u>not</u> spontaneous under the stated conditions.

Reactions of lithium fluoride with oxygen atoms do not occur spontaneously unless additional energy is supplied. (This is what I expect, the calculations will establish if this is true or not, I also expect to do a set of calculations for Thallium fluoride reactions with atomic oxygen, if sufficent thermodynamic data is available.)

Evaluation of Magnesium Fluoride Stability with Respect to Atomic Oxygen Exposure

Potential reactions of magnesium fluoride and oxygen atoms

$$MgF_2 + O \rightarrow MgO + F_2 \quad (1)$$
$$MgF_2 + O \rightarrow MgO + 2F \quad (2)$$
$$MgF_2 + 3O \rightarrow MgO + 2OF \quad (3)$$
$$MgF_2 + O \rightarrow MgOF + F \quad (4)$$
$$2MgF_2 + 2O \rightarrow 2MgOF + F_2 \quad (5)$$

Reactions (1), (2), and (3) are not spontaneous under standard conditions of 1 atmosphere pressure and 298K. Thermodynamic properties of MgOF were not found in the NIST database, but these reactions are not likely to be spontaneous under these conditions because MgOF is an intermediate state between MgF_2 and MgO.

Pressure changes from 1 atmosphere to on-orbit pressures, and temperature changes from 298K to any temperature between 173K and 423K, only change the Gibbs free energy of reaction very slightly, but do not alter the essential conclusion that these reactions are not spontaneous under the stated conditions.

Reactions of magnesium fluoride with Oxygen atoms do not occur spontaneously "in the lab" unless additional energy is supplied.

Evaluation of Magnesium Fluoride Stability with respect to Atomic Oxygen Exposure

The availability of ~5eV collisional energy (on-orbit) changes the conditions sufficiently to allow reactions on the surface of magnesium fluoride exposed in LEO, that do not occur at lower energies.

The dissipation of the collisional energy occurs on/near the surface. Reaction in the bulk is not allowed once the initial collision has occurred.

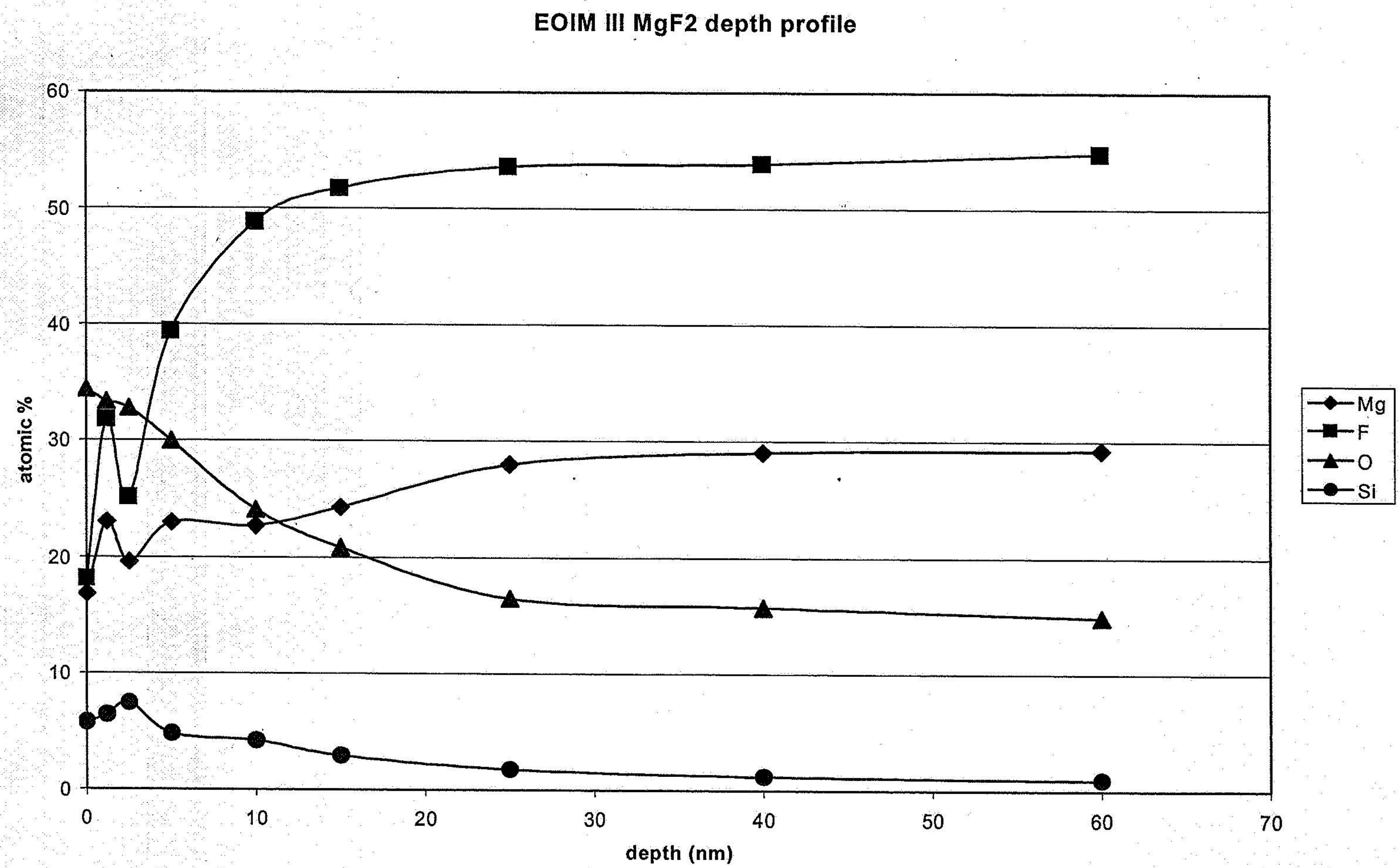
Result is that once a thin layer of MgO is formed, the reaction will essentially stop.

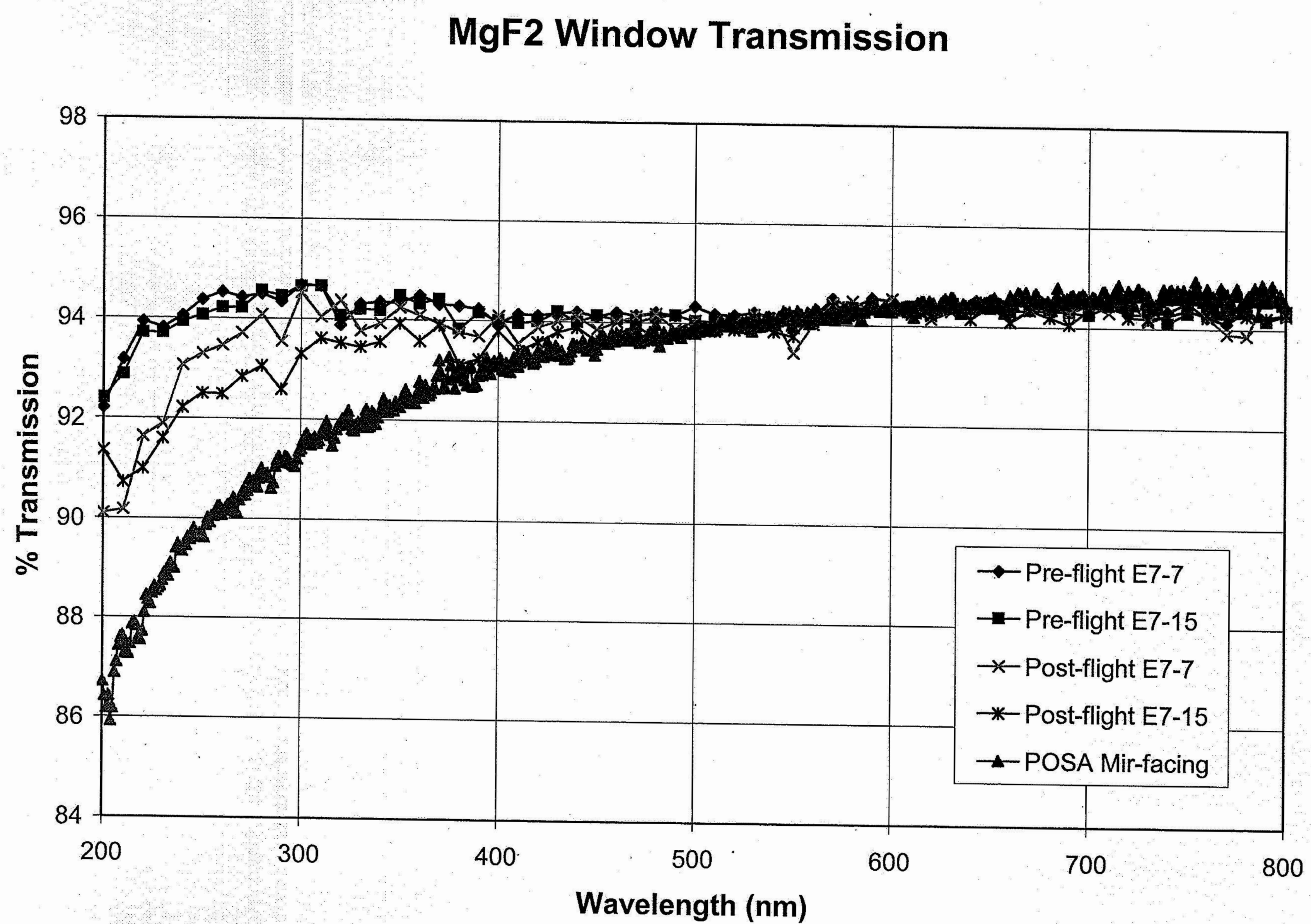
Flight exposures over a range of fluences from ~10^{+20} to >10^{+21} atoms/cm^2 support this conclusion.

MgF_2 coatings and windows have been flown on the EOIM III Space Shuttle experiment, two experiments on the Long Duration Exposure Facility, the Optical Properties Monitor experiment from the Mir-Space Shuttle docking module, and MISSE-1 & 2.

Evaluation of Magnesium Fluoride Stability with Respect to Atomic Oxygen Exposure

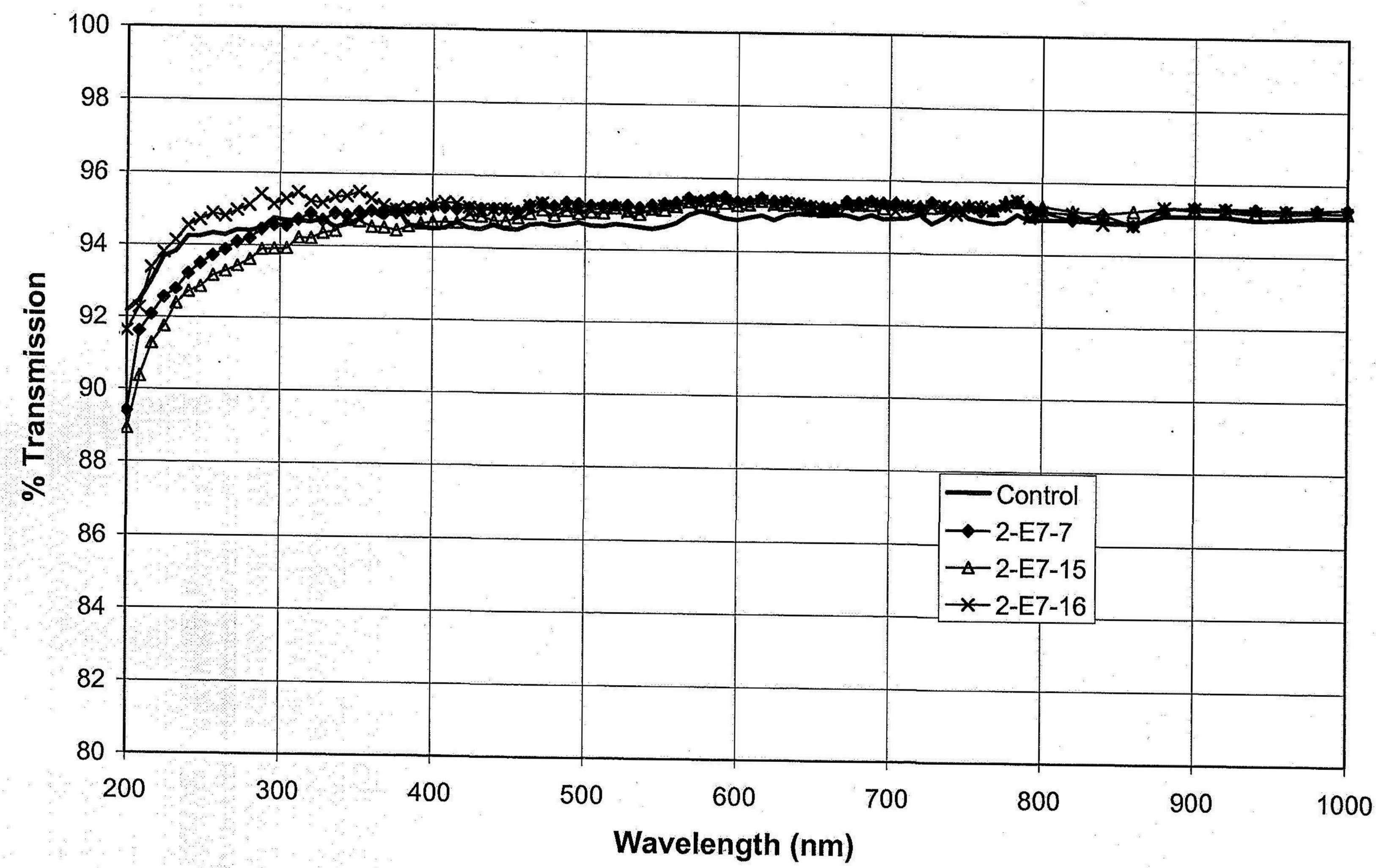
Depth profile for MgF2 specimen from the EOIM III experiment, atomic oxygen fluence ~1E20atoms/cm2



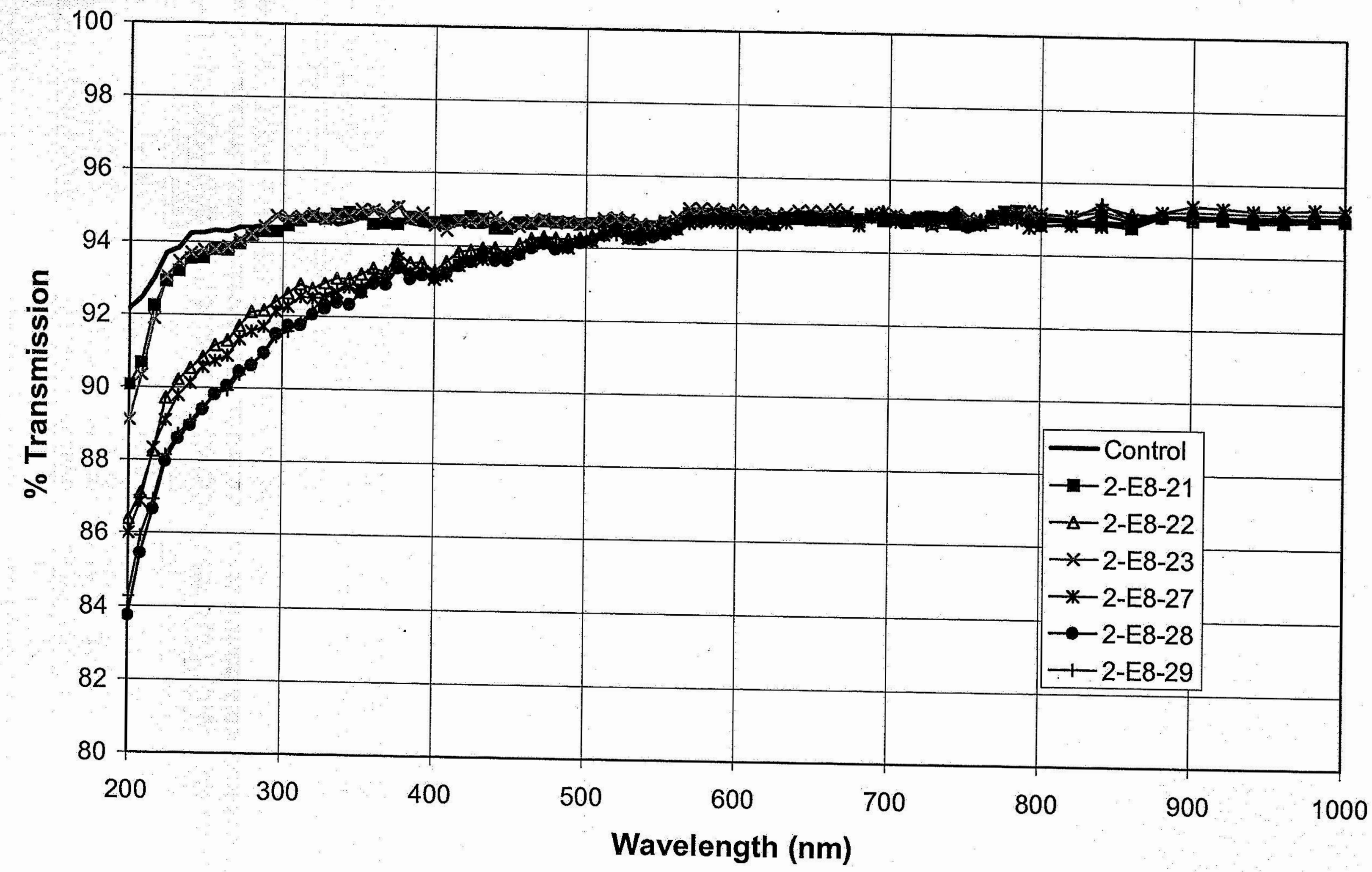


MgF2 Window Transmission
98
96
94
92
90
88
86
84
% Transmission
200
300
400
500
600
700
800
Wavelength (nm)
Pre-flight E7-7
Pre-flight E7-15
Post-flight E7-7
Post-flight E7-15
POSA Mir-facing

MISSE Magnesium Fluoride Windows from Tray E7



MISSE Magnesium Fluoride Windows from Tray E8



Evaluation of Magnesium Fluoride Stability with Respect to Atomic Oxygen Exposure

LDEF MOOO3-4 experiment conclusions

Summary of report conclusions:

"…data would seem to indicate that the MgF2 is mostly intact, but that oxygen may have replaced some of the fluorine in the material. There is no thick layer of oxide formed on the MgF2, as was observed for the ThF2."

The data referred to are Auger measurements on the sample surface showing MgF2 and some MgO peaks.

Quote is from Long Duration Exposure Facility: Preliminary Observations on the Effects of Low Earth Orbit on MgF2, ThF2, and SiO2 optical materials, by P.J. John, U of Dayton Research Institute, A.E. Day, T.W. Haas, and T.M Trumble, Wright Labs

AO114 experiment conducted by NASA MSFC
results indicate slight oxidation on surface of MgF2 thin film

Both AO114 and MOOO3-4 experiments were exposed to >1E21 atoms/cm2 atomic oxygen fluence

Evaluation of Magnesium Fluoride Stability with Respect to Atomic Oxygen Exposure

Conclusions:

- Reaction of atomic oxygen and MgF2 does occur on the surface of exposed MgF2 material.
- Reactions are slow and occur over a substantial time period. LDEF surfaces were not completely converted even after 2100+ days on-orbit and fluences >1E21 atoms/cm2
- Dissipation of collisional energy limits reaction to near surface.
- Thermodynamics (Gibbs free energy of reaction) are not favorable for bulk reaction.
- Several mitigating/competing processes may occur on-orbit
  - Reactions may occur with organic or silicone-based contaminants, essentially scavenging the atomic oxygen.
  - Atomic oxygen that does not react immediately has a finite lifetime on the surface and may leave after some residence time (probably has been "thermallized")
  - Atomic oxygen may inelastically scatter from the surface during the initial collision.
  - Atoms on the surface may recombine with other atoms to from molecular oxygen.