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PART 1

LDEF MATERIALS: AN OVERVIEW OF THE INTERIM FINDINGS

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SUMMARY

The flight and retrieval of the National Aeronautics and Space Administration's Long Duration Exposure Facility (LDEF) provided an opportunity for the study of the low-Earth orbit (LEO) environment and long-duration space environmental effects (SEE) on materials that is unparalleled in the history of the U.S. space program. The 5.8-year flight of LDEF greatly enhanced the potential value of materials data from LDEF to the international SEE community, compared to that of the original 1-year flight plan. The remarkable flight attitude stability of LDEF enables specific analyses of various individual and combined effects of LEO environmental parameters on identical materials on the same space vehicle. NASA recognized this potential by forming the LDEF Space Environmental Effects on Materials Special Investigation Group (MSIG) to address the greatly expanded materials and LEO space environment parameter analysis opportunities available in the LDEF structure, experiment trays, and corollary measurements, so that the combined value of all LDEF materials data to current and future space missions will be assessed and documented.

This paper provides an overview of the interim LDEF materials findings of the Principal Investigators and the Materials Special Investigation Group. These revelations are based on observations of LEO environmental effects on materials made in-space during LDEF retrieval and during LDEF tray deintegration at the Kennedy Space Center, and on findings of approximately 1.5 years of laboratory analyses of LDEF materials by the LDEF materials scientists. These findings were extensively reviewed and discussed at the MSIG-sponsored LDEF Materials Workshop '91. The results are presented in a format which categorizes the revelations as "clear findings" or "confusing/unexplained findings" and resultant needs for new space materials developments and ground simulation testing/analytical modeling in seven categories: Environmental Parameters and Data Bases; LDEF Contamination; Thermal Control Coatings and Protective Treatments; Polymers and Films; Polymer-Matrix Composites; Metals, Ceramics, and Optical Materials; and Systems-Related Materials. General outlines of findings of the other LDEF Special Investigation Groups (Ionizing Radiation, Meteoroid and Debris, and Systems) are also included.The utilization of LDEF materials data for future low-earth orbit missions is also discussed, concentrating on Space Station Freedom. Some directions for continuing studies of LDEF materials are outlined.

In general, the LDEF data is remarkably consistent; LDEF will provide a "benchmark" for materials design data bases for satellites in low-Earth orbit. Some materials were identified to be encouragingly resistant to LEO SEE for 5.8-years; other "space qualified" materials displayed significant environmental degradation. Molecular contamination was widespread; LDEF offers an unprecedented opportunity to provide a unified perspective of unmanned LEO spacecraft contamination mechanisms. New material development requirements for long-term LEO missions have been identified and current ground simulation testing methods/data for new, durable materials concepts can be validated with LDEF results. LDEF findings are already being integrated into the design of Space Station Freedom.

INTRODUCTION

The National Aeronautics and Space Administration / Strategic Defence Initiative Organization Space Environmental Effects on Materials Workshop, June 1988, identified and prioritized candidate materials spaceflight experiments needed to validate long-term performance of materials on future spacecraft (reference 1). The highest priority identified by all participants of that workshop was virtually unanimous: The return of the NASA Long Duration Exposure Facility (LDEF) safely to earth, followed by a detailed analysis of its materials to compare with data obtained in previous relatively short in-space exposures and to validate, or identify deficiencies in, ground testing and simulation facilities and materials durability analytical models. As the First LDEF Post-Retrieval Symposium proved (ref. 2), the expectations of the NASA/SDIO Workshop were well founded. The initial in-space and experiment deintegration observations of LDEF at the end of its remarkable flight provided to the LDEF investigators an unparalleled opportunity to define space environment parameters and their long-term individual and combined effects on critical properties of materials for spacecraft applications.

The National Aeronautics and Space Administration Long Duration Exposure Facility, ref. 3, was launched into low-Earth orbit (LEO) from the payload bay of the Space Shuttle Orbiter Challenger in April 1984 (figure 1). It was retrieved from orbit by the Columbia in January 1990 (fig. 2). The 57 LDEF experiments covered the fields of materials, coatings, and thermal systems; space science; power and propulsion; and electronics and optics. LDEF was designed to provide a large number of economical opportunities for science and technology experiments that require modest electrical power and data processing while in space and which benefit from post-flight laboratory investigations of the retrieved experiment hardware on Earth. It was also designed to maintain these experiments in a stable orbital attitude to enable determination of directional effects of the space environment parameters. Most of the materials experiments were completely passive; their data must be obtained in post-flight laboratory tests and analyses.

The 5.8-year flight of LDEF greatly enhanced the potential value of most LDEF materials, compared to that of the original 1-year flight plan. NASA recognized this potential by forming the LDEF Space Environmental Effects on Materials Special Investigation Group (MSIG) to address the expanded opportunities available in studies of the LDEF structure and experiment tray material which were not originally considered to be materials experiments, so that the value of all LDEF materials data to current and future space missions would be assessed and documented. Similar Special Investigation Groups were formed for the disciplines of Systems, Ionizing Radiation, and Meteoroids/Debris.

This paper provides an overview of the interim LDEF materials findings of the Principal Investigators and the Materials Special Investigation Group. These revelations are based on observations of LEO environmental effects on materials made in-space during LDEF retrieval and during LDEF tray deintegration at the Kennedy Space Center, and on findings of approximately 1.5 years of laboratory analyses of LDEF materials by the LDEF materials scientists. These findings were extensively reviewed and discussed at the MSIG-sponsored LDEF Materials Workshop '91 (ref. 4). The results are presented herein in a format which categorizes the revelations as "clear findings" or "confusing/unexplained findings" and resultant needs for new space materials developments and ground simulation testing/analytical modeling in seven categories: Environmental Parameters and Data Bases; LDEF Contamination; Thermal Control Coatings and Protective Treatments; Polymers and Films; Polymer-Matrix Composites; Metals, Ceramics, and Optical Materials; and Systems-Related Materials. General outlines of findings of the other LDEF Special Investigation Groups (Ionizing Radiation, Meteoroid and Debris, and Systems) are also included.The utilization of

LDEF materials data for future low-earth orbit missions is also discussed, concentrating on Space Station Freedom. Some directions for continuing studies of LDEF materials are outlined.

Although this overview paper was not presented at the Workshop, it is included in these proceedings for completeness.

THE LDEF MISSION, SCIENCE TEAM, AND MSIG

LDEF was a free-flying,12-sided cylindrical structure, approximately 30-feet long and 14-feet in diameter (ref. 3). It had the capability to accommodate 86 experiment trays, most of which were 50-inches long and 34-inches wide. LDEF had no central power or data systems and no capability to transmit data to Earth while in orbit. Thus, experiments which took data during the flight had power systems (batteries) and data recorders on the inside of their trays, designed for 1-year of operation. Despite the obvious constraints of such arrangements and the much longer flight than planned, these data systems worked exceedingly well in almost all cases. The in-flight data recovered from the data tapes was of high quality. The skeletal structure of LDEF weighed approximately 8000 lb; the combined structure and experiment weight launched into orbit was approximately 21,400 lb. The initial orbit was nearly circular, at 257 nautical miles, with a 32° inclination. General information concerning the flight period, experiments, and participants is shown in Table 1 and further detailed in refs. 2, 3, and 5.

The orientation of the spacecraft with respect to the Earth during the mission is shown in figure 3. Values of key parameters of the low-Earth orbit environment which LDEF encountered are listed in Table 2. This orientation was maintained throughout the flight, from release by the Shuttle Challenger Payload Bay Remote Manipulator System to retrieval by the Columbia Remote Manipulator by precision placement (release) into its orbit, plus a design which included gravity gradient stabilization, careful consideration of mass distribution, and a passive viscous magnetic damper system. The remarkable flight attitude stability of LDEF (within less than 1° of movement in yaw, pitch, or roll) enables specific analyses of various individual and combined effects of LEO environmental parameters on identical materials and systems on the same space vehicle. NASA recognized this potential by forming four LDEF Special Investigation Groups (SIGs) (Table 1) to address the greatly expanded materials and LEO space environment parameter analysis opportunities available in the LDEF structure, experiment trays, and corollary measurements.

The LDEF Science Team management structure is shown in figure 4. Overall responsibility rests with the NASA Office of Aeronautics and Space Technology. The LDEF Science Office is located in the Materials Division of the NASA Langley Research Center; it is responsible for coordination of all LDEF experiment data, supporting data, and data generated by the SIGs.

The LDEF Environmental Effects on Materials Special Investigation Group (MSIG) was chartered to investigate the effects of the long-term LEO exposure on structure and experiment materials which were not originally planned to be test specimens, and to integrate the results of these investigations with data generated by the Principal Investigators of the LDEF experiments into the LDEF Materials Data Base. The LDEF Materials Data Analysis Workshop (ref. 6) addressed the plans resulting from that charter. MSIG membership includes 25 technical experts in the fields of atomic oxygen, radiation, contamination and other space environment effects on materials. Researchers with experimental and analytical experience in chemical, mechanical and physical properties of spacecraft materials and data basing are included. Several members provide liaison with the other LDEF Special Investigation Groups. The members represent technical laboratories and organizations throughout the United States, and laboratories in Canada and Europe. A number of MSIG members are also Principal Investigators of LDEF experiments.

Initial considerations of MSIG related to significant issues concerning space environmental effects on materials and the data potentially available from LDEF analyses to address these issues, as outlined in fig. 5. The general plan for MSIG operations is as follows:

- Systematically examine identical materials in multiple locations around LDEF to establish directionality of atomic oxygen erosion, ultraviolet radiation degradation, contamination, etc.

- Analyze selected samples from LDEF "non-materials" experiments and samples contributed from LDEF materials experiments.

- Establish central materials analysis capability:
    - Standardized, non-contaminating procedures for sampling / shipping / archiving
    - Uniform test / analysis procedures and ground simulation tests
    - Basis for assessment of laboratory-to-laboratory variations in materials data

- Focal point for coordination of all LDEF materials analyses:
    - Sponsor LDEF materials workshops / symposia
    - Generate unified LDEF Materials Data Base, including data from principal investigators, supporting data groups, and special investigation groups

The Boeing Defense and Space Group Laboratories in Seattle and Kent, Washington were selected as the MSIG Central Analysis Laboratory by the MSIG shortly after its formation in 1989.

The LDEF Materials Workshop '91 (ref. 4) was scheduled to elucidate, compare, and assess the results of the initial 1.5 years of observations and laboratory analyses of LDEF materials by the LDEF materials scientists. Figure 6 outlines the Workshop objectives and the materials disciplines addressed. The results in each discipline were extensively discussed and reviewed by technical teams consisting of technologists from the International Space Materials Community, with various degrees of familiarity with LDEF. Their findings are detailed in ref. 4. The next section of this paper (LDEF Materials Findings) includes information presented to and generated during this workshop, plus information based on previous observations of LEO environmental effects on materials made in-space during LDEF retrieval and during LDEF tray deintegration at the Kennedy Space Center in 1990 (see, for example, ref. 2).

LDEF MATERIALS FINDINGS

Environments and Data Bases

In this section the LDEF materials results are presented in a format which categorizes them as "clear findings" or "confusing/unexplained findings." Table 3 is such a listing for the environments encountered by the materials on LDEF and the considerations for LDEF materials data basing. In subsequent sub-sections on polymers and polymer-matrix composites findings from LDEF specimens, the first two "clear findings" of Table 3 will be illustrated; LDEF clearly demonstrated in a long-term flight that LEO atomic oxygen will erode all polymeric materials that are flown, which includes all those commonly used on spacecraft for thermal and electrical insulation, as paint "vehicles," and as composite matrices. Rates of erosion vary in different materials and appear to change with exposure time for some polymers. Thus, results of short-term LEO-exposure tests (e.g.- ref. 7) may not provide data which can readily be extrapolated to predict long-term erosion rates. Fortunately, this erosion was found to be completely preventable with even extremely thin coatings of metals such as aluminum and oxides such as silica; many such coatings also adhered well to the polymer or composite substrate specimen surfaces in spite of thermal cycling during each orbit. Further specimen examination, analysis, and ground simulation testing is required to define atomic oxygen erosion mechanisms and the synergism of the combined atomic oxygen / ultraviolet radiation (and other) parameters of the LEO environment, before these items can be removed from the "confusing/unexplained findings" category.

Extensive molecular and particulate contamination was found on LDEF during post-flight inspections; contamination is addressed in detail in the next sub-section of this paper. While some initial progress has been made in understanding the sources and mechanisms of this contamination, much remains to be done to exploit the immense amount of information that LDEF can contribute to unmanned LEO spacecraft contamination awareness.

MSIG had an important role in defining LDEF mission environments. Figures 7 and 8 summarize the results of calculations of atomic oxygen fluence and equivalent sun hours of UV radiation, respectively, at the end of the mission on each LDEF tray location. Examination of these figures reveals the many combinations of AO/UV exposure conditions available to the SEE analyst on LDEF, because of the remarkable attitude stability during the 5.8-year flight. Fig. 7 shows that the highest AO fluence was 8.81×10^{21} atoms/cm^2, on the LDEF leading edge, about 8.1° off row 9 (towards row 10). Experiment trays on the side rows experienced different AO fluences because of the 8° ram vector angle. The Earth and Space end AO fluences were more than one order of magnitude lower than the ram fluence.The lowest AO fluence on LDEF was 1.13×10^3 atoms/cm^2 between rows 3 and 4. During the LDEF flight, the total fluence for rows 2 through 4 was in the same order of magnitude as the lowest fluence listed in fig. 7. However, during the retrieval mission, after LDEF was safely clamped in the shuttle payload bay, an "anomaly" occurred, when LDEF rows 1 through 3 (which faced out of the bay) were inadvertently subjected to atomic oxygen at the retrieval altitude for approximately 15 minutes. That inadvertent exposure raised AO fluence from the 10^3 to the 10^{17} atoms/cm^2 order-of-magnitude for the experiment trays on those rows.

Fig. 8 shows vacuum ultraviolet radiation fluences on LDEF as a function of row position. The highest VUV fluences were 14500 equivalent sun hours (ESH) on LDEF space-end experiment trays, with intermediate values of 11100 ESH on leading and trailing edge trays and 6500 to 6900 ESH on side trays. The lowest VUV fluence was 4500 ESH, received by the Earth-end trays.

LDEF data presented later in this paper will illustrate another clear finding in Table 3: past atomic oxygen fluence models do not account for atomic oxygen impingement rates at "grazing" angles to the spacecraft. MSIG modified an AO fluence model to account for the thermal velocity distribution of the atomic oxygen atoms in LEO. As shown in fig. 9, this modification predicts orders-of- magnitude higher AO fluences than the previous model (with thermal molecular velocity excluded) at AO incidence angles to LDEF from 95° to 110°, which was verified by LDEF findings.

It has become clear that geometric details of the exposed surfaces in conjunction with their flight attitude are keys to understanding some of the space environmental effects that occurred differently on different parts of experiment trays. Such effects as atomic oxygen atoms which do not "stick" to a surface but deflect onto another surface and react with it, and partial shadowing of atomic oxygen and solar ultraviolet radiation on exposed surfaces will affect fluences of these environmental factors. MSIG is developing analysis schemes to account for these "microenvironments."

MSIG is currently considering options and needs for data basing of the extensive LDEF materials data that has been generated to date and will be in the near future. The LDEF Materials Workshop '91 participants clearly indicated their expectations of two kinds of materials data bases: one for the spacecraft design community and another for the space environmental effects on materials research community. Initial MSIG data basing plans are indicated in figure 10.

LDEF Contamination

The basic contamination control requirement for LDEF was "visibly clean level II" (SN-C-0005) (ref.8a). The provisions for contamination control are stated in the LDEF Experimenter's User Handbook (ref. 8b). General provisions included the following: "Control of contaminants represents a concern for the safe operation of the shuttle system. The shuttle requirements are defined in JSC Specifications SN-C-0005 and SP-R0022A. As applied to an LDEF experiment, these concerns become a requirement for control of particulate contamination, control of stray or trace quantity materials and control of outgassing-sublimation productions. Contamination control represents an element in the materials selection process...". Preflight cleaning procedures were those utilized for any shuttle payload to maintain the cleanliness of the payload bay. Even though these requirements were followed and all materials used on the spacecraft structure and experiments were nominally "space qualified," LDEF carried a significant amount of both particulate and molecular contaminants when it was placed in orbit. Fig. 11 is a general overview of the contamination history of LDEF.

A preliminary report on LDEF contamination is available, ref. 9, which documents initial observations made during the deintegration of LDEF experiments in the SAEF 2 Facility at NASA - KSC from February to April, 1990. Paraphrasing the conclusions of that report, silicones and hydrocarbons are significant contributors to the molecular films accumulated on the LDEF surfaces; the estimated total weight of outgassed material deposited was approximately one pound. The particle cleanliness of LDEF at launch exceeded a MIL STD 1246B level 1000 C. The Shuttle Orbiter Payload Bay is a source of contaminants. The orbital environment creates new particles and distributes particles, even for passive space platforms. Changes in motion of a spacecraft free many loose particles from the vehicle surfaces in orbit. A major redistribution of particles occurred during LDEF reentry, landing at Edwards AFB, California, and ferry flight to NASA - KSC, Florida. Although the cleanliness level of LDEF surfaces during deintegration still exceeded a MIL STD 1246B level 1000 C; an extensive variety of particle types was still present.

Table 4 is a listing of LDEF contamination findings, based on the LDEF experiment deintegration preliminary observations and subsequent studies. The scope of the contamination analyses is indicated in fig. 12 (see refs. 8a and 10). Fig. 13 is a photograph of the LDEF skeleton structure after experiment tray deintegration. The brownish-yellow or amber colored contamination film (which was once described to resemble a "nicotine stain") is clearly present on aluminum alloy structural element surfaces which were exposed directly to the space environment. The lighter regions of those structural elements were covered by experiment tray edges and clamps; thus, the molecular contamination film did not deposit on them. Also visible in this photograph of the aft end of LDEF is the magnetic viscous damper system which was a critical contributor to LDEF's remarkable attitude stability throughout its mission. The LDEF molecular contamination was extensive, apparently a result of multiple sources of organic hydrocarbons and silicones, both internal and external to LDEF (including cross-contamination from the Shuttle). The molecular contamination film detailed studies indicated a temperature dependence during the deposition process. A possible scenario for these observations is as follows: Outgassing products from a variety of silicones and organic materials formed a "contamination cloud" around LDEF during all or most of the mission. Solar ultraviolet radiation and/or atomic oxygen polymerized some of the molecular components of that cloud, increasing molecular weight and, thus, increasing the temperature at which these materials will condense on adjacent surfaces. LDEF surfaces were alternately heated and cooled by the presence or absence of sunlight during the different portions of each 90-minute orbit. In the "mornings" of the orbits, when surfaces are coolest and the solar UV begins to polymerize the "cloud," deposition of a contamination film layer on LDEF surfaces is most probable. Observations of a number of LDEF surfaces indicated that the ubiquitous contamination "stain" had been deposited in numerous layers. In addition to this general contamination film, which was probably on the order of tens of nanometers in thickness, there were a number of localized areas of LDEF which had heavy molecular contamination deposits, such as areas adjacent to some electrical connectors.

There were apparently interactions of the space environment with the contamination films during the LDEF flight. Leading edge deposits were more transparent than those on the sides and trailing edges of LDEF. The effects of atomic oxygen, perhaps combined with the other parameters of the low-Earth orbit space environment, can be postulated to cause such an effect, by changing silicones to silicates, for instance. Some additional aspects of this general molecular contamination are discussed in refs. 9 through 14.

Particulate contamination (table 4) was deposited on and from LDEF surfaces throughout its pre-flight, on-orbit, and post-flight history. An example of a particle which came from a degraded LDEF specimen is shown in fig. 14; it is an orbit-modified carbon fiber composite particle which was found in the Shuttle Orbiter Columbia payload bay on the cradle from which the Syncom satellite was launched during the LDEF retrieval mission. Further information on LDEF particulate contamination is found in refs. 9, 10, 13, and 15.

The right side of table 4 lists the findings related to LDEF contamination that have yet to be explained or quantified, including sources of contaminants, quantitative degradation mechanisms, and the contributions, if any, of chemical derivatives of LDEF materials which resulted from AO interactions. Perhaps the most important of the findings to be definitized are the effects of the LDEF contamination on analyses of materials for other space environmental effects.

At the bottom of table 4 are self-explanatory comments on new materials development requirements for future spacecraft and ground simulation testing requirements which have resulted from the initial LDEF contamination studies.

LDEF provides a unique opportunity to provide a unified perspective on unmanned spacecraft contamination mechanisms in low-Earth orbit. It was the ultimate witness plate for the shuttle orbiter payload bay. It was a molecular film deposition experiment. It provided data for many potential studies of orbital effects on surface contaminants, both molecular and particulate. It provides data for validation of current and future contamination monitoring systems for spacecraft.

Thermal Control Coatings and Protective Treatments

Table 5 outlines the findings of LDEF materials studies on thermal control coatings and protective treatments. One of the most important (and reassuring) findings to spacecraft designers regards the excellent stability of chromic-acid anodized aluminum as a thermal control surface. Fig. 15 summarizes solar absorptance (α_S) and thermal emittance (ε) data, averaged for 228 tray clamps on all areas of the LDEF structure (ref. 16). A slight increase in average values of α_S/ε was noted after the 5.8-year low-Earth orbit exposure, as compared to both ground- and flight-control specimen data; this increase is insignificant from an engineering consideration. However, additional data of this type from other LDEF investigators indicates that this small increase is a real effect which may require consideration for critical components on much longer flights than LDEF experienced.

Fig. 16 illustrates the second clear finding in table 5. The solar absorptance of white thermal control paints on a leading edge LDEF tray was measured before, during, and subsequent to the flight (refs. 17 and 18). The stable emittance behavior of the Z-93 coating is representative of only four of the many thermal control paints flown on LDEF. Many other "space qualified" white paints behaved like the A276 paint, increasing in solar absorptance as the flight progressed (as shown in fig. 16). Fig. 17 shows α_S/ε ratios of A276 paint disks located on many regions of the LDEF external surface. It is obvious that the white paint surfaces facing the front of LDEF (and thus the atomic oxygen fluence) retained the α_S/ε ratios of the control specimen, while those on the rear face of LDEF (where atomic oxygen fluence was low) showed a doubling of α_S, compared to that of the control specimen (ε values were not affected during the flight). Note that the α_S changes occurred at an incidence angle of approximately 100° to 105°, confirming the discussion presented previously in relation to fig. 9. The thermal control property stability of the Z-93 (and similar) thermal control paint coatings is attributed to its high purity potassium silicate binder; organic paint binders such as the polyurethane used in the A276 paint are affected by solar ultraviolet radiation, which darkens their surface (raising α_S). Large fluences of atomic oxygen erode this dark surface layer away, "cleaning" the white paint surface. It is postulated that the A276 ram-facing surfaces on LDEF may actually have darkened during the earlier part of the mission when atomic oxygen flux was relatively low, then were "cleaned up" during the last few weeks of the mission, when atomic oxygen flux was much higher.

As noted in the discussion of table 3, atomic oxygen erosion of FEP Teflon was higher than that predicted on the basis of short-time LEO exposures. Predicted erosion of FEP on leading edge LDEF trays was approximately eight times lower than that measured after the flight.

Fig. 18 illustrates microcracking which occurred in the silver/Inconel layer of silvered Teflon (Ag/FEP) second-surface mirror insulation blankets (ref. 18). Such microcracking has been shown to be preventable by modifying the adhesive-backed Ag/FEP application procedures. This microcracking resulted in bleed-through of adhesive to the base of the FEP during the LDEF flight; when the adhesive in the microcracked areas was affected by solar ultraviolet radiation, it darkened and the solar absorptance of the Ag/FEP substantially increased. Figure 19 illustrates another important finding of the LDEF experiments: clear silicone coatings on some substrates experienced extensive surface "crazing" (ref. 4), which could affect light transmittance for some critical applications.

Atomic oxygen "undercutting" of polymer substrates under protective coatings is a phenomenon that can be a particular concern for space applications of multilayer insulation (ref. 19). The phenomenon is illustrated in fig. 20. The low reaction probability with a polymer such as Kapton at the initial impact of monatomic oxygen causes the atom to scatter with a cosine distribution, so that even for coating defects (i.e.- holes or cracks) facing the atomic oxygen ram direction, the underlying Kapton substrate will be undercut. This effect was measured on LDEF multilayer insulations of aluminized Kapton; the results are shown in fig. 21. Undercut widths range from approximately eight times the defect crack width for small cracks (~0.1μm wide) to approximately three times for larger cracks (~0.6μm wide). Thus the LDEF data gives a good engineering perspective on this phenomenon.

The unexplained findings in table 5 included a fluorescence shift in surfaces of several LDEF coating specimens. Whereas the unexposed coatings fluoresced in the ultraviolet portion of the spectrum when subjected to UV radiation, the exposed coatings fluoresced in the visible portion of the spectrum (ref. 18). Although this phenomenon has been noted previously (see, for instance, ref. 20), the details of the surface chemistry changes for the LDEF specimens have not yet been elucidated. Two important coatings, S-13GLO (ref. 21) and black chromium showed variabilities in their thermal control properties which have not yet been explained. The synergistic roles of UV, electron and proton radiation in the atomic oxygen erosion of certain polymeric materials such as FEP Teflon have not yet been quantitatively defined.

New materials development requirements in thermal control coatings and protective treatments for long-term LEO missions are listed in table 5. Included are thin, transparent silicate overcoats resistant to crazing. In regard to the second listed item, discussions at the LDEF Materials Workshop '91 indicated that some technologists feel that the current U. S. supply of pure potassium silicate paint binder for Z-93 might be questionable in the future, while others were not as concerned. The final item in the new materials category regards the need for a flexible white thermal control coating with demonstrated long-term LEO durability. The PCBT coating developed by the MAP Company in France has shown promise in a 9-month exposure (in a FRECOPA cannister) during the LDEF missions and in another short LEO flight (ref. 22). Ground simulation testing requirements in the coatings category are also listed in table 5.

Polymers and Films

Table 6A outlines the findings of the LDEF materials studies on polymeric materials and polymer films. The first two clear finding are illustrated in figs. 22 through 24. The Teflon surface of Ag/FEP blankets was eroded by atomic oxygen as shown in the scanning electron microscope photomicrograph at the right of fig. 22 for a specimen which saw a high AO fluence (refs. 23 and 24). The small salt crystal on the surface of the Teflon was possibly deposited on the launch pad prior to the LDEF insertion flight; the crystal is highly resistant to atomic oxygen and shielded the Teflon under it from erosion. The height of the "mesa" (and, thus, the depth of erosion) is approximately 0.0012-inch; based on short-term LEO exposure data in LEO (ref. 25), the predicted erosion depth was on the order of 0.00015-inch. This may be an example of AO/UV synergism wherein a threshold of UV exposure is reached after which the erosion is accelerated, as postulated in ref. 26. The morphology of the erosion around the "mesa" is consistent with that seen in many AO-eroded polymer specimens from space and from ground simulation AO beam facilities. The two microscopic profiles on the left of fig. 22 were made using a scanning tunneling microscope on an FEP surface that was shielded from AO and one which had a low AO fluence during the flight. The shielded surface is smooth, even at the hundred-nanometer level; the low AO fluence surface at the lower left (compared to the high fluence surface at the right) shows that the erosion mechanism is similar for both low and high fluence exposures. The post-flight visual appearance of the low-fluence surface was transparent and specular, similar to that of control specimens; the high-fluence surface was quite different, milky and diffuse, leading to supposition that the thermal control properties of this widely used second-surface mirror blanket material had been significantly degraded (fig. 23). Fortunately, that supposition was disproved, as shown in fig. 24, which is a plot of α_S/ε ratios for Ag/FEP samples from a number of LDEF locations. Samples from rows 6 through 11 received much higher AO fluences than those from rows 1 through 5 (fig. 7) but all samples retained the α_S/ε ratio of control specimens excepting one sample from row 8, which had a heavy contamination stain on it (ref. 27). The visual appearance change of the uncontaminated Ag/FEP was entirely due to a change in reflectance type from specular to diffuse, but not in magnitude of total reflectance.

Figs. 25 and 26 illustrate the effect of meteoroid and debris impacts on silvered Teflon thermal blankets: A delaminated area (vapor-deposited silver/Inconel coating delaminated from the FEP Teflon) from a fraction of a centimeter to several centimeters in diameter surrounded the submillimeter-diameter craters made by the impacts (fig. 25). The ability of Ag/FEP to function as a second-surface mirror thermal control blanket is affected. Fig. 26 qualitatively indicates this finding. An Ag/FEP sample flown on LDEF with impact crater and delamination diameters of approximately 0.5mm and 10mm, respectively was photographed on its front face with an infrared camera while transient heating was applied to the rear face with an infrared lamp. The resultant "thermal lag" in the delaminated area is evident; the implication is that thermal energy absorbed by the silver surface from solar heating in LEO will not be readily conducted into the Teflon to be radiated to space from the blanket surface. The LDEF blankets most severely affected by this phenomenon had about 5 percent of the area delaminated; from an engineering point of view, this should not result in significant losses of thermal control capability for Ag/FEP blankets. For much longer LEO flights than LDEF's, however, this phenomenon must be considered.

The effects of the LDEF environment on mechanical properties of FEP film from the Ag/FEP thermal blankets are indicated in fig. 27 (ref. 27), which shows data from films exposed to the space environment and control specimens flown on LDEF which were protected from the environment. Although the Teflon surface was eroded by the atomic oxygen exposure on rows 7 to 11 (and, thus, load carrying capability of the film was reduced), the tensile strength was not affected. However, on LDEF rows 1 to 6, where AO fluence was low, tensile strength was reduced by approximately 30 percent from that of the control specimens. This finding was apparently due to the effects of long-term solar ultraviolet radiation exposure of the FEP film surface; erosion of the affected surface layer by AO resulted in no degradation of the film strength (based on the remaining cross-sectional area, after erosion). Ref. 28 also presents data on this phenomenon. Polyethylene films on LDEF exhibited similar effects.

Some film specimens received 10-month exposures in cannisters which were opened to the LEO environment after LDEF was inserted into its orbital trajectory and were closed 10 months later, protecting the surfaces from further exposure for the balance of the mission (ref. 29). Photographs of four such specimens from experiment A0134 are shown in fig. 28; the experimental siloxane-modified polyimide, PIPSX-6 resisted atomic oxygen erosion much better than other polymers flown on LDEF. Fig. 29 shows the results of the full 5.8-year LDEF exposure on polymer films on the same LDEF leading edge experiment tray which were up to ~0.25-mm thick, sized for the planned 1-year LDEF mission. They were completely eroded by atomic oxygen during the 5.8-year flight (ref. 29).

Other clear findings listed in table 6A include the reçognition of LDEF contamination and the importance of considering contamination effects in the analysis of LDEF polymeric materials' surfaces. The finding that atomic oxygen erosion of Kapton is linearly predictable with AO fluence (ref. 4), based on comparison of LDEF data with data from previous space flights, has important implications for Kapton's use as "witness" specimens in AO ground laboratory exposures which attempt to simulate LEO effects, with LDEF data as the baseline for comparison before extrapolation to other flight conditions is attempted. Other polymeric materials, such as polystyrene and PMMA, exhibited greater erosion than predicted for the LDEF exposure (based on previous flight data), similar to that described above for FEP Teflon. LDEF specimen analyses indicate that the atomic oxygen erosion mechanism involves minimal chemical changes, if any, to the polymer films (ref. 30). Some film specimens appear to have been exposed to extensive heating; this may be another "microenvironment" effect. Carbon films were attacked by atomic oxygen, somewhat more slowly than most of the polymer films, but at a high enough rate to require surface protection for long LEO flights.

The unexplained findings for polymers and polymer films (table 6A) include the erosion findings discussed above, the sources of thermal effects, and the degree of confounding of polymer surface analyses due to the molecular contamination.

Table 6B lists new polymeric material development requirements for durability in long term LEO environments and ground simulation testing requirements, based on LDEF polymers and polymer film analyses thus far. No current polymeric material appears to be completely resistant to atomic oxygen and/or UV attack. If such polymers can be developed, they must have the additional attribute of non-contamination of other materials on a spacecraft due to outgassing, reaction products from AO or other LEO environmental parameter interactions, etc. Ground simulation testing requirements listed in table 6B are largely self-explanatory. The final item listed (definition of thermal "lag") will require tests of specimens of significant size in non-contaminating vacuum chambers.

Polymer-Matrix Composites

One of the important benefits of the attitude stability of LDEF during its entire flight is the capability to examine identical or similar materials from different locations on the LDEF exterior. Fig. 30 shows the location of four classes of graphite-fiber reinforced polymer-matrix composite materials, with examples of several materials for the epoxy- and polyimide-matrix composites. The LDEF location, AO fluence, and vacuum ultraviolet radiation fluence are tabulated for each exposure location and additional environmental parameters are listed. In general, as indicated during the discussions at the LDEF Materials Workshop '91, the data on space environmental effects on these composite materials from various principal investigators studies and the MSIG evaluations was remarkably consistent. Anomalies revealed in those investigations may well be due to "microenvironment" effects, discussed previously.

Table 7 outlines the findings of LDEF materials studies on polymer-matrix composites. The first clear finding, surface degradation of uncoated composites, is illustrated in fig. 31 in scanning electron microscope photomicrographs of a small wedge cut from a 4-ply, $[\pm 45]_s$ specimen of T300/ 5208 (Gr/Ep) composite exposed on LDEF Experiment A0134 (on tray 9B, thus on an LDEF experiment tray closest to the leading edge) (ref. 31). Virtually one ply of composite material (approximately 0.012cm) was eroded away during the 5.8-year exposure. The epoxy matrix eroded somewhat more rapidly than the graphite fibers. An ash-like residue remained on the eroded surface after the flight. Fig. 32 shows a compilation of chemical- and mechanical-property data from specimens on the same experiment tray (9B). The chemical properties (infrared spectra, T_g and molecular weight distribution) are for the polysulfone-matrix P1700 specimens. They show no bulk polymer property changes in the composite due to the exposure; similar findings were found for the other composites. The mechanical property chart of tensile modulus for all composites tested in LDEF Experiment A0134 (lower right), shows good correlations between the 3 types of control specimens and reasonable consistency with the erosion data illustrated in fig. 31.

Fig. 33 illustrates an important LDEF finding to spacecraft designers who require polymeric-matrix composites for critical low-Earth orbit applications, because of the combination of very low coefficient of thermal expansion that can be "tailored" into these composites and their low weight and high specific moduli compared to other candidate spacecraft materials: Very thin inorganic coatings on the surfaces of polymeric composites completely prevent AO erosion (ref. 32). A vapor deposited, 1200Å-thick aluminum coating protected the T300/934 (Gr/Ep) from AO, with negligible weight penalty. No coating delamination from the composite surface was noted after approximately 34000 thermal cycles in LEO. Similar results were found for a variety of inorganic coatings, including Ni and SiO_2.

The dimensional stability of composite materials after long term exposures in Earth orbit has been a concern of spacecraft designers. LDEF experiment AO180 on tray D12 (90° to the LDEF leading edge) was devoted to this concern and generated excellent data to define the problem, measuring thermal expansion in orbit on a tape recorder, as composite specimens were being thermally cycled during each orbit (ref. 33). Fig. 34 depicts a few of the results. The graph on the right, of microstrain as a function of temperature for a stainless steel calibration tube, illustrates the high quality of the experimental data. The graph in the center of fig. 34 shows that some dimensional changes do occur in a unidirectional graphite/epoxy composite in the longitudinal direction. The graph on the left is for the same composite, in the transverse direction. During the first 40 days in orbit, this transverse specimen shrunk significantly, approximately 500 cm/cm of microstrain. When LDEF returned to Earth, this dimensional instability was found to be completely reversible and to be due almost entirely to moisture desorption in orbit and absorption of moisture from the Earth's atmosphere after return from orbit. Thus, it is possible that preconditioning of composites to remove moisture prior to flight could substantially reduce, if not eliminate, dimensional instability of polymer-matrix composites in orbit.

Other clear findings on LDEF polymer-matrix composite specimens are listed in Table 7, including items related to optical properties, meteoroid and debris impacts and thermal cycling. More information in these areas can be found in ref. 2. The unexplained findings in polymer-matrix composite materials on LDEF include (as for most other materials) the effects of contamination. The second unexplained finding, the differences in AO erosion morphologies of Gr/Ep reinforced with 5-mil tape are depicted in the left side photomicrograph of figure 33. The "ash" residue on AO-eroded composite surfaces appeared to vary with the composite material. The lack of degradation of uncoated composite material mechanical properties may simply be due to the degree of erosion on the fiber and its interface with the matrix.

New materials development requirements in polymer-matrix composites concentrate on scaleup and thermal cycling adherence verification for coatings, plus the development of flexible coatings. Ground simulation testing requirements (Table 7) are similar to those noted for other materials categories, including size of specimens, synergistic effects of simulated space environment parameters, and analytical modelling of such effects.

Metals, Ceramics, and Optical Materials

Table 8 outlines the findings of LDEF materials studies on metals, ceramics, and optical materials. Most of these findings are described in more detail in refs. 2 and 4 . A key clear finding regarded structural metals, aluminum and titanium alloys. Their mechanical properties were unaffected by the LDEF 5.8-year LEO exposure (refs. 34, 35, and 36 and discussions at LDEF Materials Workshop '91), although certain minor surface effects were noted in the highest AO fluence regions (refs. 37 and 38). No coldwelding was found (refs. 39 and 40). Aluminum coated stainless steel was verified to be a very stable mirror/reflector for extended LEO exposures. The molecular contamination on many LDEF surfaces, discussed previously, appeared to be the most prevalent effect on most metallic and ceramic structural materials; it affected the properties of optical materials. The exceptions to this general finding are discussed in the following paragraphs.

As shown in fig. 15, discussed previously, thin anodized coatings on aluminum alloys showed small but measurable increases in the ratio of solar absorptance to thermal emittance as a result of the LDEF exposure. This effect was apparently due to a combination of light contamination and atomic oxygen effects on the surface (ref. 38).

All metallic film coatings excepting tin and platinum showed at least some slight evidence of surface oxidation of the LDEF Leading Edge (ref. 41); silver, osmium, and copper showed heavy oxidation (refs. 41, 42, and 43), as illustrated for a vapor-deposited silver coating on an optical glass substrate in fig. 35.

Both aluminum- and magnesium-matrix composites were exposed on LDEF in experiment AO134. The aluminum metal-matrix composite showed no evidence of degradation due to the 5.8-year exposure. The P100 graphite fiber reinforced magnesium alloy composite was not notably degraded from a structural point of view, but some magnesium oxidation was evident at the specimen edges, where the graphite fibers intersected the surface (fig. 36).

Graphite reinforced borosilicate glass composites with no protective coatings were highly stable during the LDEF flight (ref. 44). The chart on the left of fig. 37 shows the coefficient of thermal expansion (CTE) of this material as a function of temperature for specimens exposed on LDEF leading edge (LE) and trailing edge (TE) trays, compared to that of a control specimen. At the time of the LDEF launch, in 1984, this material was experimental; the CTE values shown are within the material variability. No CTE changes due to the 5.8-year exposure should be inferred. The photograph at the right shows a Gr/Gl exposed LE specimen cross section, with the specimen surface at the top. Only the graphite fibers which were on the specimen surface were eroded by atomic oxygen; even a few μm of glass surrounding the fiber completely prevented AO erosion for the entire flight .

Other clear findings on these classes of materials relate to the LEO stability of ceramics and glasses (unless damaged by meteoroid and debris impacts), effects on optical properties of glass in the ultraviolet regions of the spectrum (probably largely related to molecular contamination), and the increased absorptance of some black coatings, Table 8. Unexplained findings, new materials development requirements, and ground simulation testing requirements are similar to those discussed previously for other material classes.

Systems-Related Materials

This materials category covers lubricants, adhesives, seals, mechanical fasteners, solar cells, and batteries, with materials aspects studies conducted jointly by the LDEF Systems and LDEF Materials Special Investigation Groups; a detailed exposition of findings is presented in ref. 45. In general, LDEF systems functioned well; the system materials met their requirements. Table 9 outlines some specific findings. Clear findings included the need to protect lubricants from direct contact with the LEO environment and to carefully lubricate fasteners to prevent galling during installation, if post-flight disassembly is required. All seals on LDEF were protected from direct exposure to atomic oxygen and electromagnetic/particulate radiation; they functioned well. Some acrylic and RTV adhesives (ref. 35) degraded in one experiment, but silicone adhesives performed well in another (ref. 46).

FINDINGS IN OTHER LDEF DISCIPLINES

As shown in fig. 3, the four LDEF Special Investigation Groups include those involved in the disciplines of ionizing radiation, meteoroid and debris, systems, and materials. The interim findings of the latter have been detailed in the preceding sections of this report. The findings of the other SIGs are detailed in refs. 2, 45, 47, 48, and 49 and are outlined in figs. 38, 39, and 40, which are self-explanatory. Additional information on LDEF thermal and solar illumination environments is presented in refs. 50, 51, and 52.

LDEF MATERIALS CONTRIBUTIONS TO SPACE TECHNOLOGY

As noted in the introduction, the promise that LDEF offered (ref. 1) for providing unparalleled data on long-term space environmental effects on materials in low-Earth orbit is being fulfilled. Fig. 41 is a perspective of LDEF data in comparison to previous sources of ground-simulation and flight-experiment data. Ground-simulation testing is generally limited to simulation of one or simultaneous simulation of two or three, or sequential simulation of the key space environmental parameters which cause material degradation in LEO. However, there are many environmental parameters, both natural and induced, which may become the key parameters for a particular mission or application. Those which have been considered for Space Station Freedom (SSF) Work Package 2 are listed in figs. 42 and 43. Real time flight test data is indispensable to determine whether the ground simulation exposure provides a reasonable simulation of the materials degradation mechanism(s) involved. Thus, ground simulation tests alone are often inadequate for LEO SEE simulation.

Previous flight data from Mir, Solar Max, and Space Shuttle Orbiter Payload Bay experiments (fig.41) have significant limitations in environment definition, specimen material definition and control specimens, and exposure duration. LDEF overcame all these limitations with a relatively long exposure in the proposed SSF orbit (albeit only one-fifth of the proposed life of the SSF structure), well-defined experiments, and the stable orbital attitude which is a key to direct and unambiguous analyses of materials degradation and degradation phenomena.

Fig. 44 lists the variety of NASA and U. S. Department of Defense space mission categories for which LDEF materials data can make important contributions during the planning and design phases. Focusing in on Space Station Freedom, fig. 45 paraphrases a letter from the prime SSF Phase 2 contractor concerning their recent utilization of LDEF materials data (ref. 53). Thermal control materials and coatings data were of particular interest for radiator applications. The verification of long-term stability of absorptance and emittance of anodized aluminum in LEO and the preliminary characterization of contamination were of importance to design considerations for the SSF aluminum alloy truss structure. The revised atomic oxygen fluence model has been utilized to design for materials erosion, particularly in "grazing AO flux" areas. The need for outer layer surface protection for multilayer blanket insulations on SSF for long mission lives was established with LDEF data.

CONTINUING LDEF MATERIALS STUDIES

The LDEF materials studies to date represent approximately 70 percent of the currently planned MSIG observation and data collection activities, ~25% of planned data comparisons with current environmental degradation models and damage theories, ~50% of generation of new environment and damage models, and ~10% of materials data bases and archives development. Given the quantity and quality of archived LDEF materials available, much more than the current plan could be done, but funding limitations have constrained all but the highest priority activities. Another limitation regarding specimen analysis for data collection, especially for polymeric materials, concerns post-exposure effects in Earth storage on surfaces which have been exposed to the LEO environment (refs. 29 and 30). MSIG support for materials analysis on polymeric and metallic materials and on composite materials will decline in 1992 and 1993, with the focus gradually changing to phenomenological understanding, documentation, archiving, and data basing. LDEF specimens and hardware will be archived and will be available to researchers worldwide in the foreseeable future, through the LDEF Science Office and NASA.

Projected MSIG ground-based simulation testing activities (which can now utilize LDEF data as a baseline or "sanity check" on the ability of the ground test to adequately simulate LEO effects and phenomena) are listed for contamination-related tests and LDEF-exposure/ground-exposure effects correlation in fig. 46. Projected MSIG environmental modeling activities are listed for contamination-related modeling, exposure effects modeling, and environmental parameter modeling in fig. 47. Some of these are currently in progress and others have been planned, but some will suffer from lack of funding support. A plan for a detailed study of LDEF contamination mechanisms to provide a unified perspective of large spacecraft contamination for future space missions is outlined in fig. 48; however, implementation of this plan is beyond the scope of current MSIG resources.

CONCLUSIONS

This paper has presented a broad overview of interim findings of materials observations and analyses from ongoing studies of specimens from the National Aeronautics and Space Administration Long Duration Exposure Facility. These findings are summarized in Table 10. The column at the upper left lists materials which demonstrated high resistance to degradation for the entire 5.8-year flight. The column at the upper right lists materials which may be perfectly adequate for flights up to several years in LEO but which, if unprotected, exhibited various degrees of degradation during the LDEF flight. As a result of these findings, new materials development requirements and general ground simulation testing requirements have been identified, as listed in the lower parts of Table 10.

In general, LDEF met or surpassed all of its goals regarding the generation of long-term data on spacecraft materials. The ongoing studies outlined herein indicate LDEF to be the definitive source of long-term exposure verification of low-Earth orbit effects on materials. The quantitative data / micro-environment / mechanistic understanding being developed will strongly contribute to future spacecraft design and new materials development guidelines. LDEF furnishes an unprecedented opportunity to provide a unified perspective of unmanned low-Earth orbit spacecraft contamination mechanisms and interactions. The LDEF materials data bases under development should become the basis of a new family of design guidelines for space environmental effects on materials.

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TABLE 1

LAUNCH:

- April, 1984 (into 255-mile orbit)

RETRIEVAL:

- January, 1990 (from 178-mile orbit)

EXPERIMENTS:

- 57 Technology, Science, and Applications Experiments
- Potential for >25000 test specimens from experiment trays and structure

PARTICIPANTS:

- >200 Principal Investigators from 9 Countries
  - 33 Industry
  - 21 University
  - 7 NASA Centers
  - 4 DoD Laboratories
- 4 Special Investigation Groups, >75 Participants
  - Materials
  - Systems
  - Meteoroid and Debris
  - Ionizing Radiation

Long Duration Exposure Facility information.

TABLE 2

HIGH VACUUM:
- 10^{-6} to 10^{-7} torr

UV RADIATION:
- 100 - 400 nm; 4,500 to 14,500 equivalent sun hours

ELECTRON AND PROTON RADIATION:
- ~2.5 x 10^5 Rads surface fluence

ATOMIC OXYGEN:
- ~10^5 to 8.8 x 10^{21} atoms/cm^2 (wake- to ram-facing)

METEOROID AND DEBRIS IMPACTS:
- >36000 particles from ~0.1 mm to ~2 mm
- High fluence on ram-facing surfaces

COSMIC RADIATION:
- ~6 Rads
- ~20 tracks Thorium and Uranium

THERMAL CYCLING:
- ~34,000 cycles
- [±20°F] to [~ -30°F to ~+190°F]

LDEF exposure conditions.

TABLE 3

Clear Findings	Confusing/Unexplained Findings
• All polymers were attacked by AO	• Sources of contamination
• Metals and oxides protect against AO	• Contamination mechanisms
• LDEF mission environments defined: AO and total solar exposures, contamination history	• AO mechanisms
• "Microenvironment" analysis methodology in development for detailed understanding of SEE	• AO/UV synergism
• AO fluence models must be revised to account for thermal velocity distribution	
• Impacts occur in temporal bursts	
• Widespread contamination occurred	
• Data bases required for both design and research communities	

Environmental parameters and data bases.

TABLE 4

Clear Findings	Confusing/Unexplained Findings
• Molecular contamination was extensive • Multiple sources, external and internal • Surface temperature dependent • Cross-contamination from Shuttle sources • Environmental interactions with AO & UV • Leading edge deposits more transparent • Particulate contamination was deposited pre-flight, in-flight, post-flight; can be differentiated • Opportunity to provide unified perspective of unmanned LEO spacecraft contamination mechanisms	• Sources of silicones/silicates • Deposition mechanisms • Contribution of AO degradation products • Effects on analyses for other space environmental effects

New Materials Development Requirements:
- Alternate, non-silicone materials
- Non-contaminating lubricants, polymers

Ground Simulation Testing Requirements:
- Re-evaluation of current outgassing criteria/tests for long-term missions
- Combined exposure testing and analytical modeling
- System level testing and analytical modeling

LDEF Contamination.

TABLE 5

Clear Findings	Confusing/Unexplained Findings
• Chromic Acid Anodized Aluminum stable • Z-93, YB-71, PCB-Z white TC paints and D-111 black TC paint are stable • A276 affected by AO and UV • Potassium silicate binders are stable; organic binders are not stable • UV accelerates AO erosion of Teflon; FEP erodes more rapidly than predicted • Microcracking in Ag/FEP • Surface crazing of clear silicone coatings • Atomic-oxygen undercutting of polymer substrates under protective coatings	• Fluorescence shift from UV to VIS (under UV rad.) • Black chromium gave variable results • S-13GLO gave variable results • Role of UV, e^-, p^+ in AO erosion of FEP

New Materials Development Requirements

- Thin silicate overcoats for AO protection
- New silicate source for Z-93
- Application process for Ag/FEP
- Durable flexible coating to replace S-13GLO

Ground Simulation Testing Requirements

- Temperature effects on AO, UV degradation
- Single/combined effects data for analytical modeling
- In situ measurement capabilities for AO and UV testing
- Addition of e^- and p^+ to simulation facilities
- Verified accelerated testing and analytical modeling

Thermal Control Coatings and Protective Treatments.

TABLE 6A

Clear Findings	Confusing/Unexplained Findings
• Ag/FEP blankets remained functional, but eroded by AO • No Ag/FEP changes in α/ε; diffuse reflectance increased • Sizeable delaminations of Ag from FEP at meteoroid/debris impacts; thermal "lag" • FEP, polyethylene mechanical properties affected by UV • Siloxane-modified materials resist AO • Non-silicone polymers attacked by AO • Contamination is important effect • AO erosion of Kapton linearly predictable • Greater erosion than predicted for FEP, polystyrene, PMMA • Minimal chemical change from AO exposures • Extensive heating of some films • AO attack on carbon films	• More erosion on some materials than predicted -- UV/AO synergism effects? • Thermal effects • Effects of contamination

Polymers and Films.

TABLE 6B

New Materials Development Requirements:

- Non-contaminating materials resistant to AO attack
- Non-contaminating materials resistant to UV degradation

Ground Simulation Testing Requirements:

- High fluence AO testing (directed beam)
- High fluence UV/VUV testing
- Simultaneous AO/UV exposure testing and analytical modeling
- Verified accelerated testing and analytical modeling
- Large area exposures for mechanical testing
- Thermal cycling
- Temperature effects
- Quantitative definition of thermal "lag" at delaminations in silvered Teflon second-surface-mirror thermal blankets

Polymers and Films (concluded).

TABLE 7

Clear Findings	Confusing/Unexplained Findings
• AO causes surface degradation of uncoated composites; no bulk polymer property changes • Thin inorganic coatings prevent AO erosion • Outgassing dictates dimensional stability of Gr/Ep; other CTE changes minor • Optical properties: No change for Gr PMC except on LDEF LE; fiberglass darkened • Sequential effects of impact/AO erosion • Thermal cycling causes microcracking • No catastrophic failure from impacts	• Effects of contamination on AO erosion rates • Differences in AO erosion morphologies; stripes on T300/934 and T300/5208 with 5-mil tape • Differences in appearance and quantity of "ash" on AO-eroded specimens • No AO degradation of mechanical properties except on LDEF leading edge

New Materials Development Requirements:

- Scale up of coating process to full size parts
- Flexible coatings (for composite springs, etc.)

Ground Simulation Testing Requirements:

- Current capabilities adequate for individual effects
- Capacity and size for AO inadequate
- Synergistic effects (AO, UV, thermal cycling, vacuum, contamination)
- AO simulation on UV degraded LDEF specimens
- Analytical modeling of individual parameter and synergistic effects

Polymer-Matrix Composites.

TABLE 8

Clear Findings	Confusing/Unexplained Findings
• Structural Al and Ti alloys are unaffected • Many surfaces are contaminated • 1000Å Al coating on stainless steel is a very stable mirror/reflector • Thin anodized coatings on Al show small but measurable α/ε increases • Heavy oxidation of Ag and Cu • All metallic films except Sn and Pt show some oxidation • Al-matrix composites are not degraded; Mg-matrix composites oxidize at edges • Gr/glass composites are stable • Ceramics and glasses are generally stable unless damaged by impacts • Optical properties of glasses are affected in UV spectral regions only • Black coatings become more absorbing	• Sources of contamination

New Materials Development Requirements:

- Non-contaminating, craze-resistant clear coatings
- Non-contaminating flexible coatings

Ground Simulation Testing Requirements:

- Synergistic effects (AO, UV, thermal cycling, vacuum, contamination)
- Analytical modeling of synergistic effects

Metals, Ceramics, and Optical Materials.

TABLE 9

Clear Findings	Confusing/Unexplained Findings
• Lubricants--OK only when protected • Fasteners--no cold welding failures; galling evident • Seals--no failures (all protected) • Adhesives--a few indications of failure • Solar cells--degradation due to impacts • Batteries--no space-related failures	• Dynamic effects • Solar cells--minor degradation in output, possibly due to contamination, UV, AO

New Materials Development Requirements:

- Non-contaminating dry film lubricants for exposed applications
- Non-contaminating seals for exposed applications

Ground Simulation Testing Requirements:

- Combined thermal vacuum / UV / AO / dynamic testing

Systems-Related Materials.

TABLE 10

Resistant Materials	Degraded Materials
• Chromic acid anodized aluminum alloys • Many metals and Al-matrix composites • Ceramics, glasses, and Gr/glass composites • YB-71, Z-93, PCB-Z, D-111 paints • Inorganic coatings • Some siloxane-based polymers • Al-coated stainless steel reflectors	• Various thermal control coatings • Silicone conformal coatings • Polymers • Polymeric matrix composites • Silver & copper • Ag/FEP second surface mirrors • Exposed lubricants

New Materials Development Requirements:

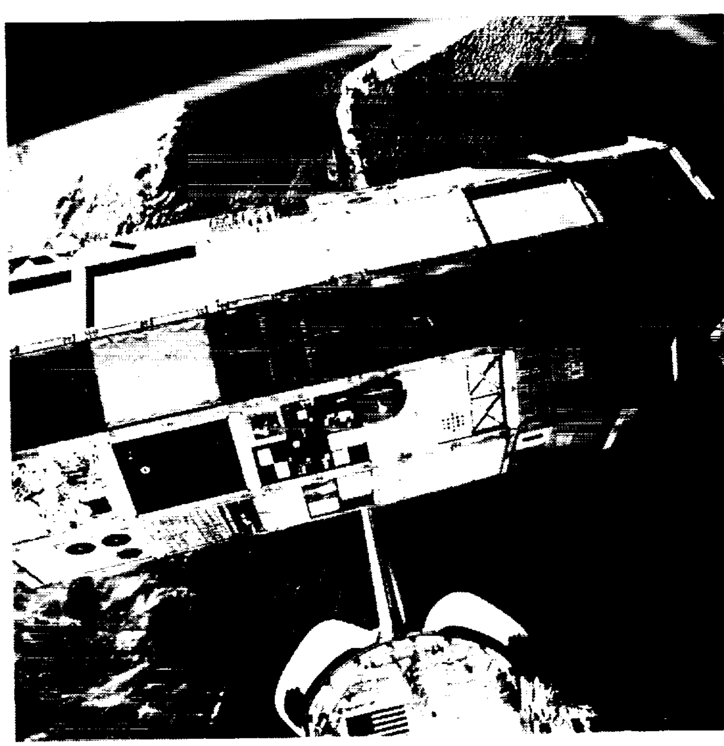
- Non-contaminating, atomic-oxygen-resistant polymers and polymer-matrix composites
- AO-durable flexible polymer for electrical insulation
- Replacement for Ag/FEP with low α_s/ε
- Flexible white paint replacement for S-13GLO
- Non-contaminating lubricants and seals for exposed applications
- Durable transparent coatings
- Efficient concepts for hypervelocity impact resistance

Ground Simulation Testing Requirements:

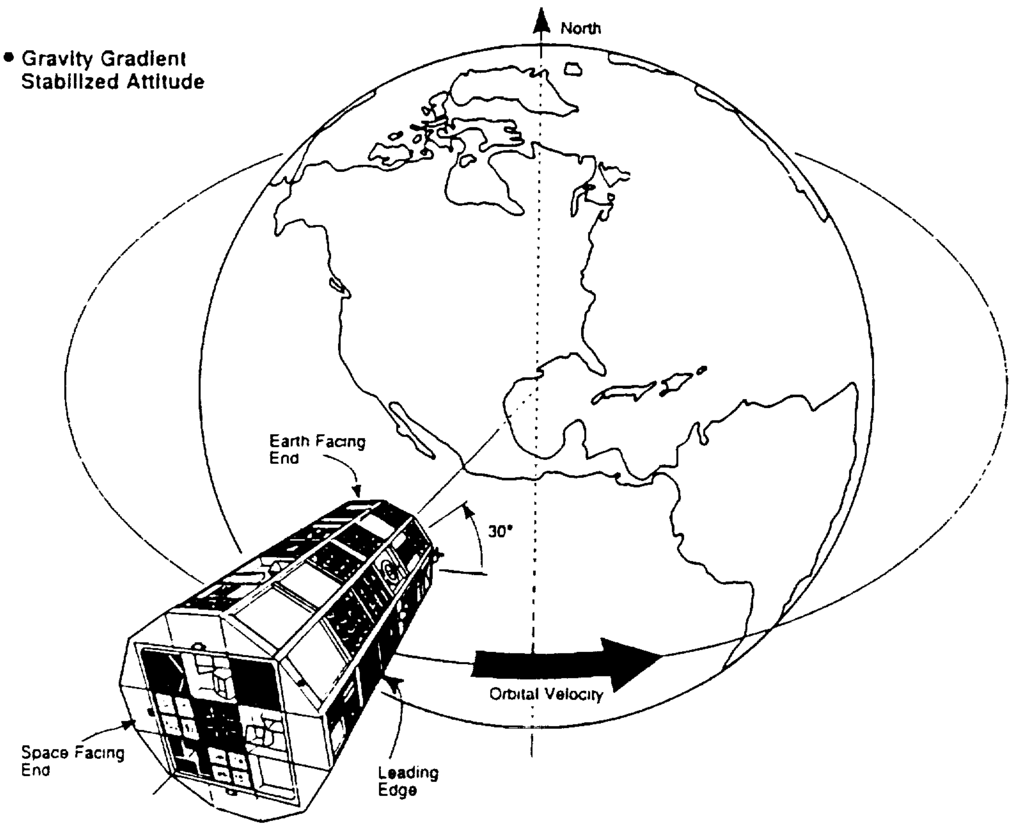
- Synergistic effects testing and analytical modeling
- Validated accelerated tests for combined UV, AO, thermal cycling

Summary of interim findings on LDEF materials.

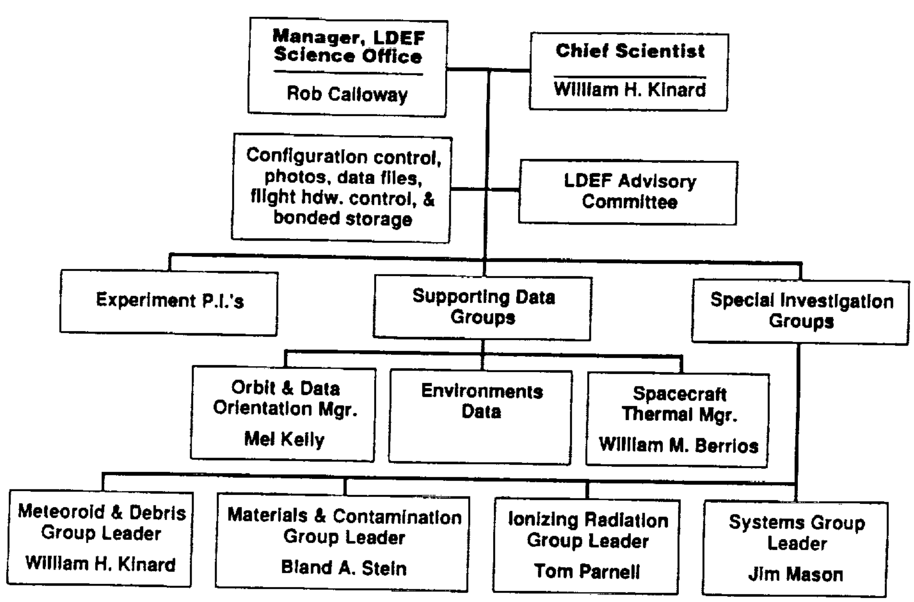
1. LDEF in orbit, April 1984.



2. LDEF retrieval after 5.8 years in low-Earth orbit, January 1990.



3. LDEF orientation.



4. LDEF Science Team.

Materials Issue	Data Available from LDEF
• Stability of Material Properties - Optical - Mechanical - Thermal - Physical - Chemical	• Polymers, Metals, Composites, Ceramics, Glasses, Coatings, Films
• Combined Space Environment Effects Models	• AO, Electrons, Protons, UV, ΔT, M & D, Vacuum • Control Specimens on LDEF and in Ground Storage
• Atomic Oxygen Effects	• Erosion Rates and Mechanisms • Modifications to Fluence Models
• Meteoroid/Debris Impact Effects	• Delamination of Blankets, Composites • Crater/Impact Particle Chemistry
• Contamination	• Molecular & Particulate Levels/Chemistry

5. LDEF data available to address current issues in space environmental effects on materials.

SPONSOR: Long Duration Exposure Facility - Materials Special Investigation Group

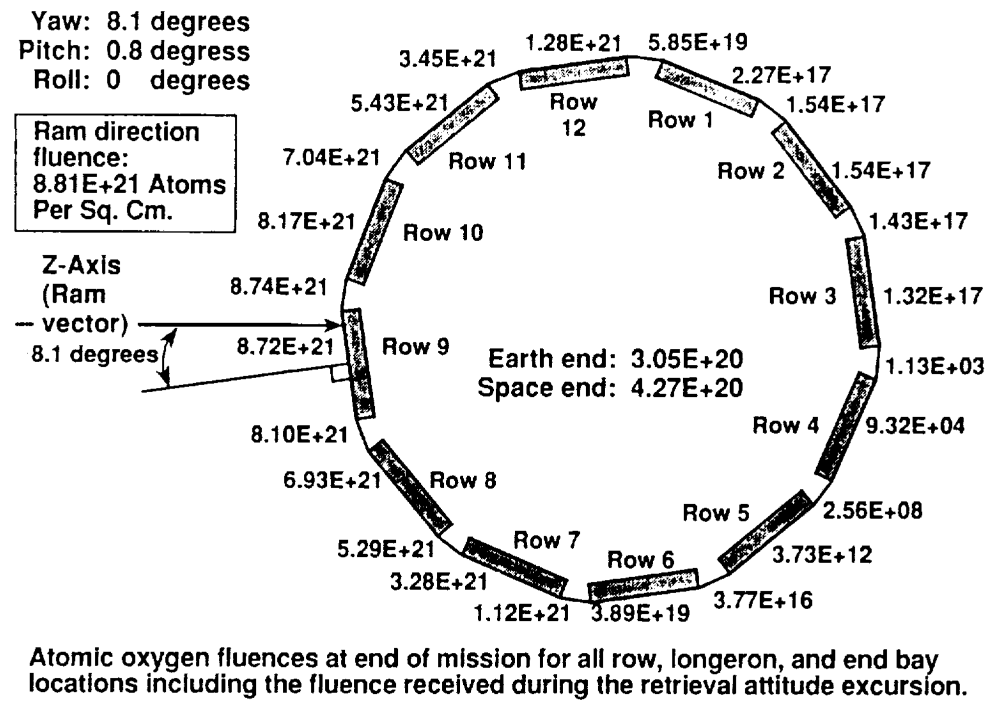
OBJECTIVES:
- In-depth exposition of LDEF Materials Findings from Principal Investigators and MSIG
- Workshop discussions and theme reports on LDEF materials disciplines, data-basing requirements, ground simulation testing and analytical modeling needs, and future flight experiments

TUTORIAL AND WORKSHOP DISCUSSION DISCIPLINES:
- LDEF Materials, Environmental Parameters, and Data Bases
- LDEF Contamination
- Metals, Ceramics, and Optical Materials
- Lubricants, Fasteners, Adhesives, Seals, Solar Cells, and Batteries
- Thermal Control Coatings, Protective Coatings, and Surface Treatments
- Polymers and Films
- Polymer-Matrix Composites

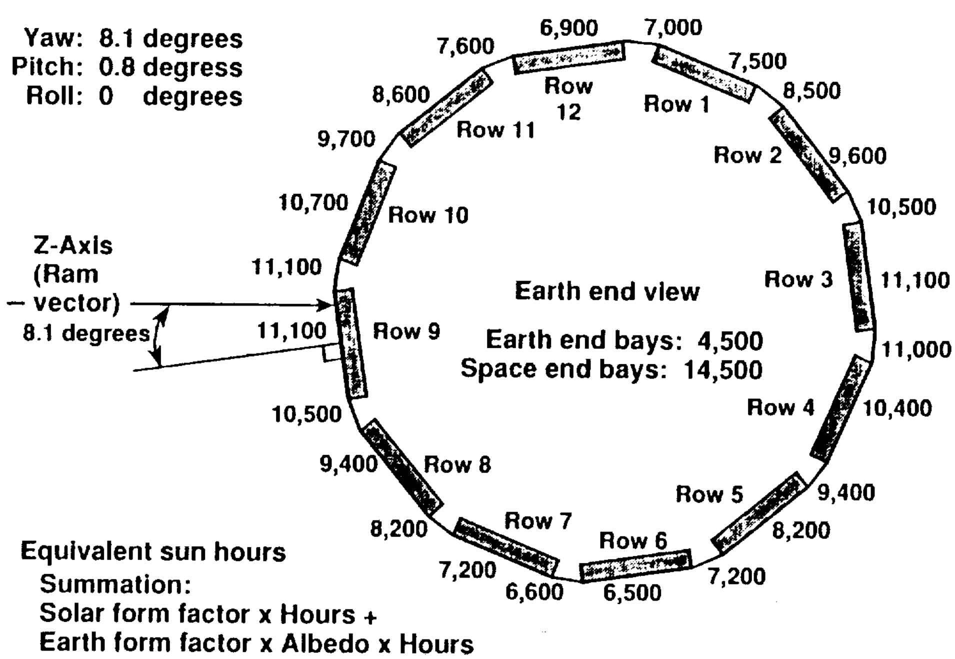
ATTENDANCE:
- ~200 technologists from the International Space Materials Community

REPORT:
- NASA Conference Publication

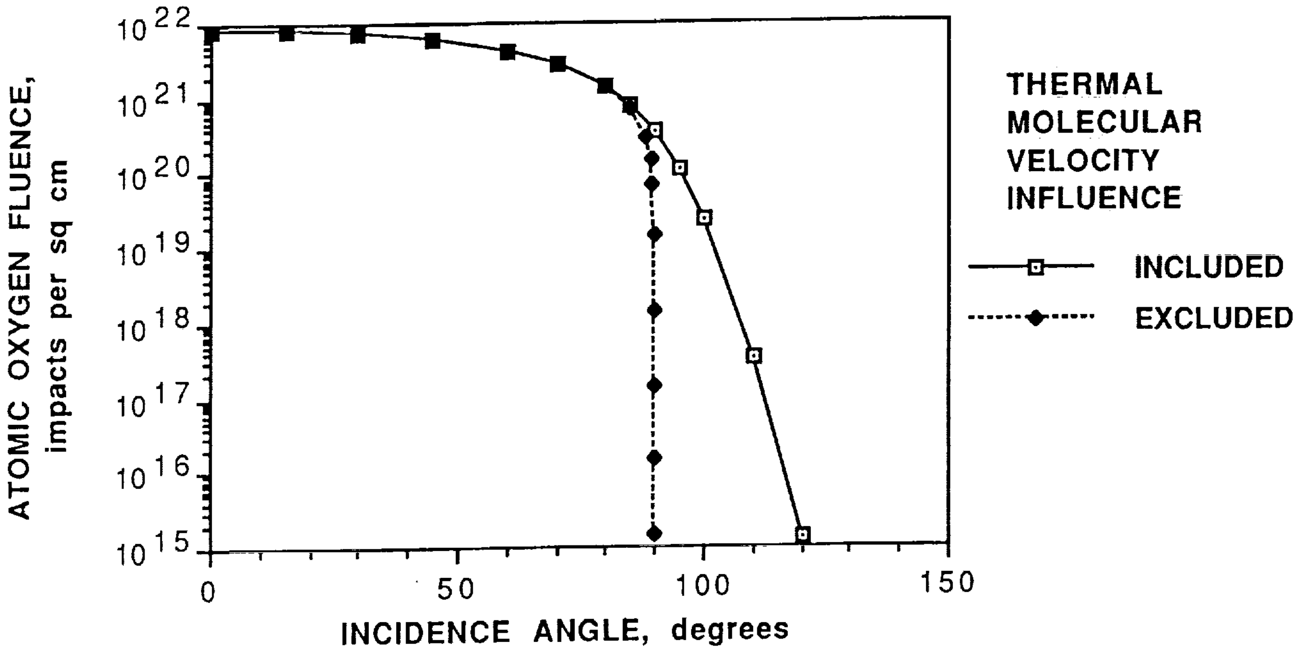
6. LDEF Materials Workshop '91.



7. Atomic oxygen fluence for each LDEF tray location.



8. Equivalent sun hours at end of mission for each LDEF tray location.



9. Effect of thermal molecular velocity on atomic oxygen fluence.

- MATERIALS DATA BASE -

GOALS

- DEVELOP COMPREHENSIVE LDEF MATERIALS DATA BASE WITH INPUTS FROM PIs AND SIGs
  - USER FRIENDLY
  - ACCESSIBLE BY INTERNATIONAL COMMUNITY
  - MAINTAINED BY NASA

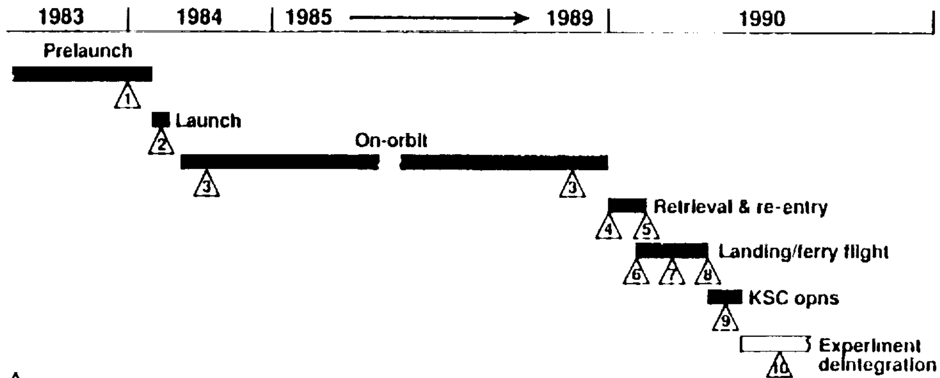
PROCEDURES

- UTILIZE NASA-MSFC MAPTIS DATA BASE METHODOLOGY
- DEFINE REQUIREMENTS
  - MULTI-USER ACCESS
  - MULTI-FILE ACCESS
  - SAMPLE IDENTITY AND LOCATION CODES
- DEFINE, EVALUATE AND STORE DATA
  - NARRATIVE FILES / PHOTOGRAPHIC (STILLS/VIDEOTAPE) FILES / OTHER GRAPHICS FILES
  - COMPARISONS WITH CONTROL SPECIMEN DATA AND DEGRADATION MODELS
  - LABORATORY-TO-LABORATORY DATA VARIABILITY

DELIVERABLES

- "MINI" DATA BASES: 1992 AND 1993
- COMPUTERIZED DATA BASES PLUS HANDBOOK(S) BY 1994

10. MSIG materials data base initial plan.

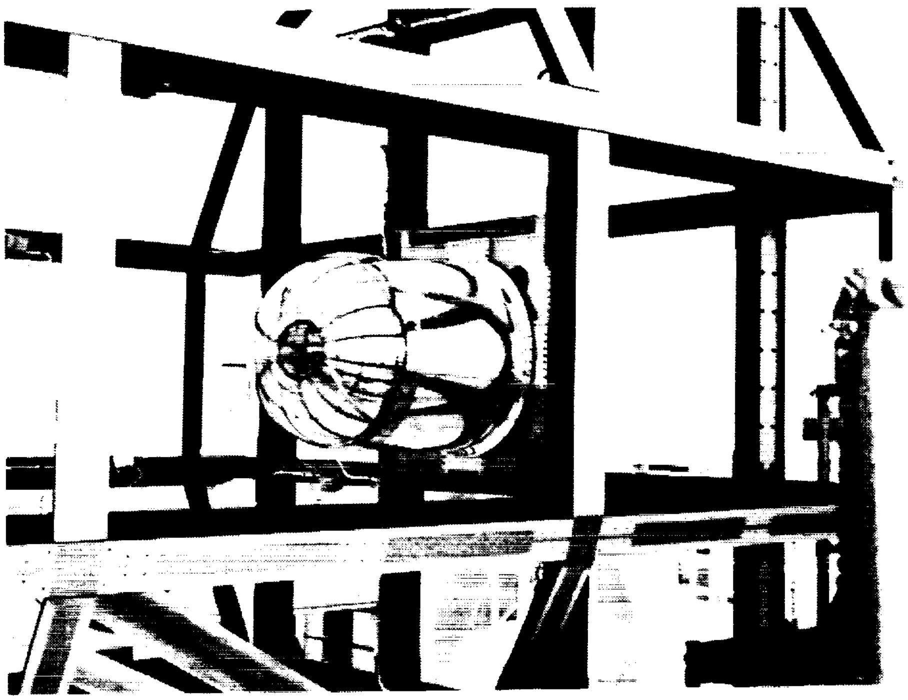


1. **Pre-launch**; Condition of LDEF prior to launch: > MIL STD 1246 level 1000 C for some trays.
2. **Launch**; During launch particulate contaminants are redistributed and Shuttle Bay Debris is added.
3. **On-orbit**; Contaminants are modified and new contaminants are generated in the orbital environment.
4. **Retrieval**; Grappling jars particles and films free, some may have relocated.
5. **Re-entry**; During re-entry particles and molecular contaminants relocate or are created.
6. **Landing**; The Shuttle is exposed to the Edwards Environment, accumulation of natural dusts.
7. **Ferry flight**; High humidity conditions, high velocity flow, thermal and pressure stresses occur.
8. **Ferry flight**; HEPA filter fibers appear on tape lifts after exposure to new filter.
9. **KSC Ground operations**; Ground operations prior to SAEF 2 include many manipulations of LDEF in complex environment.
10. **De-integration**; SAEF 2 exposure.

11. Contamination exposure history of LDEF.

- SAMPLING OF LDEF CONTAMINATION
  - Examined and photographically documented >2000 items of LDEF hardware
  - Collected >200 tapelifts from significant LDEF surfaces
  - Photographic examples shown in poster display
- SURFACE CHEMISTRY: OPTICAL MICROSCOPY, ELECTRON MICROSCOPY, ESCA, SIMS, MICRO FTIR, OPTICAL CRYSTALLOGRAPHY
  - 14 silvered Teflon thermal control blankets
  - Silicon-containing films conspicuously absent from AO-exposed Ag/FEP
  - Particle population on Ag/FEP increases with proximity to edges of trays
  - >90 anodized aluminum tray clamps
  - Impact-penetrated particulate contaminants well documented
- PARTICLE COUNT ANALYSIS
  - Selected areas of 22 trays
  - 24 tapelifts
  - 16 tray clamps
  - Particle counts for large (>100μm) particles higher than expected, based on current models

12. Scope of LDEF contamination analyses.



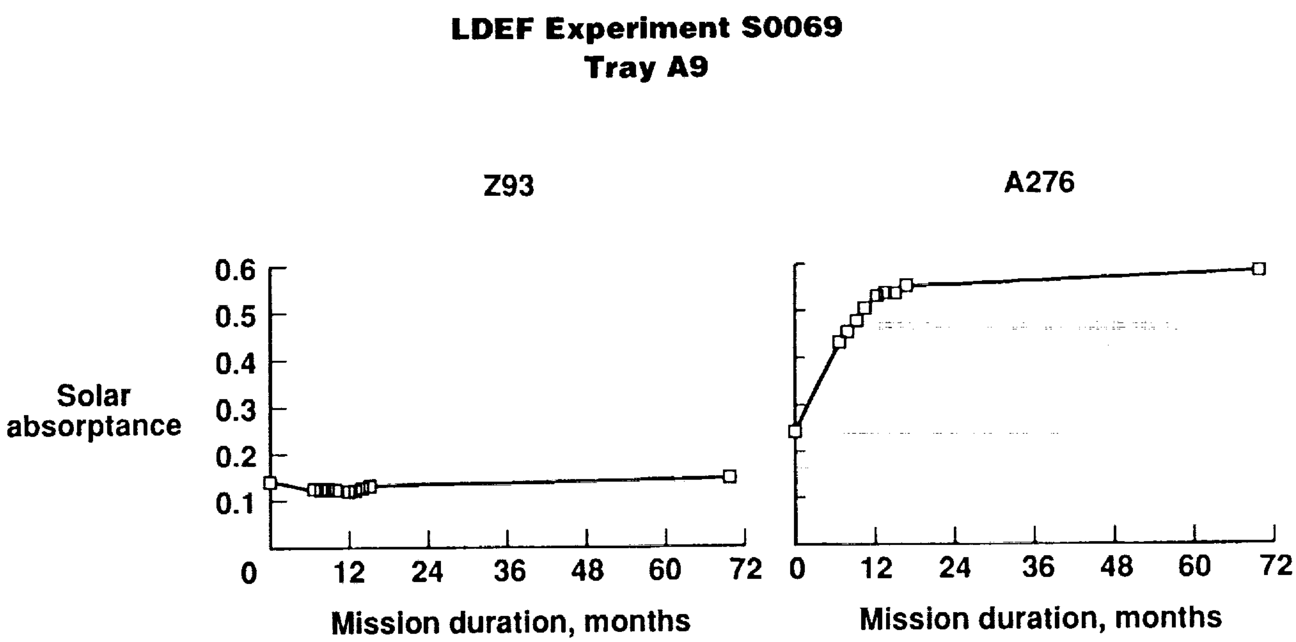
13. Molecular contamination on LDEF aluminum alloy structural elements.

14. Example of particulate contamination: Orbit-modified carbon fiber composite particle. (Magnification 350X)

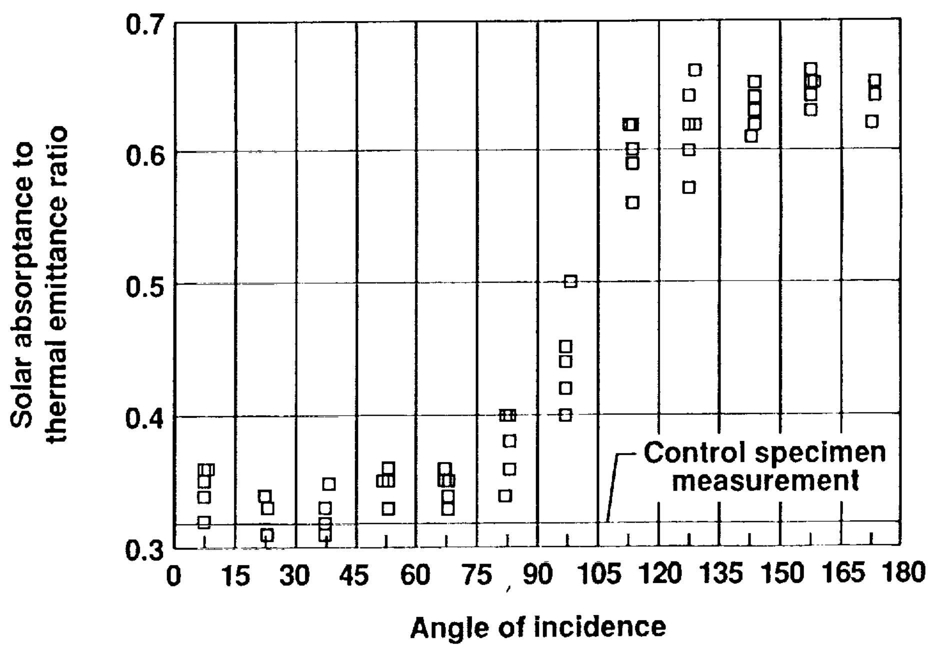
SPECIMENS AND LOCATIONS	α_s	ε	α_s/ε
Exposed Side of Clamps; All Areas of LDEF[1]	0.34	0.15	2.24
Unexposed Side of Clamps; All Areas of LDEF[1]	0.34	0.16	2.12
Control; In Storage on Earth[2]	0.36	0.18	2.00

[1]Average of measurements from 228 clamps, 3 data points per clamp
[2]Average of measurements from 4 control specimen clamps, 3 data points per clamp

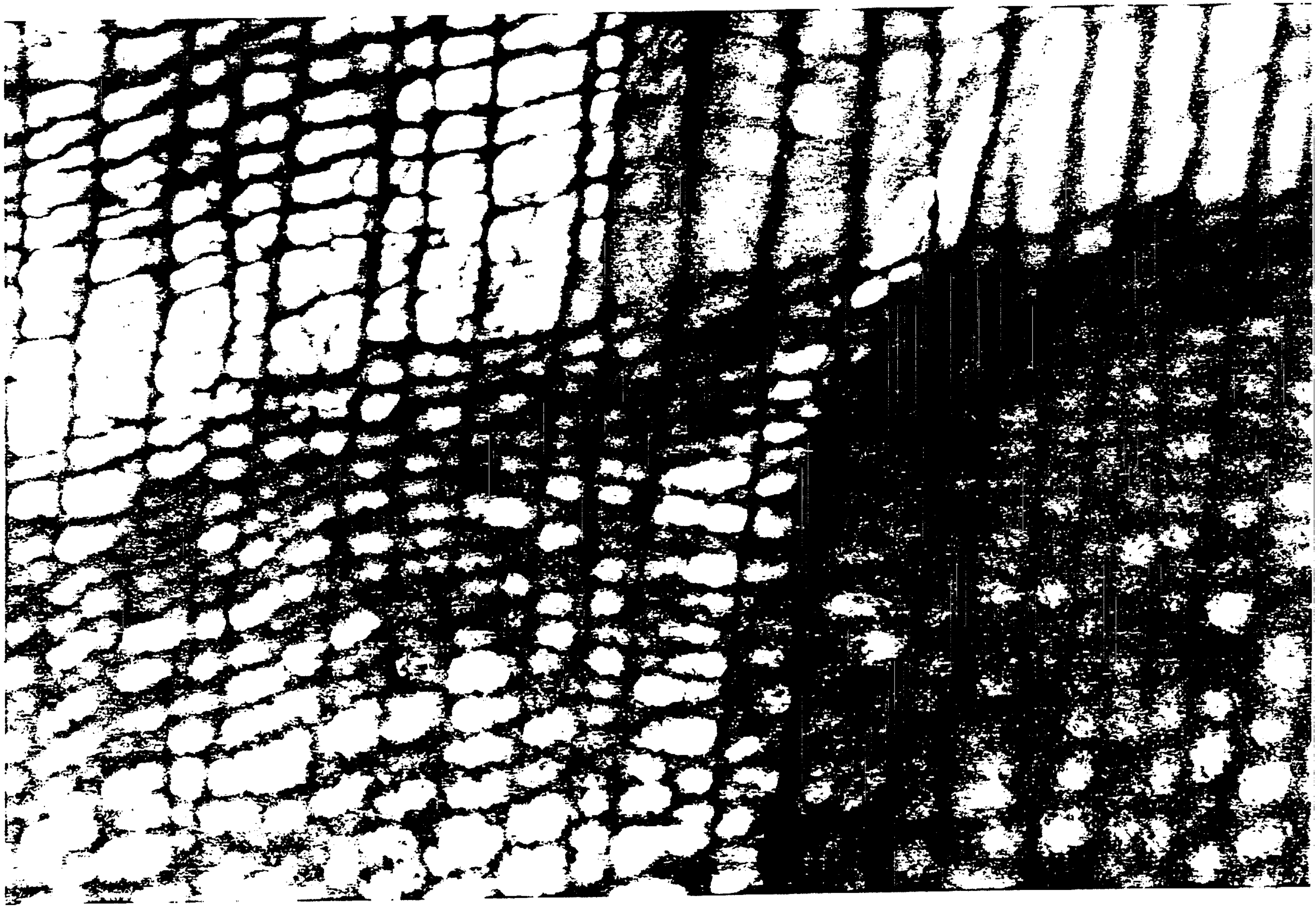
15. Absorptance and emittance properties of anodized aluminum (6061-T6) clamps on LDEF.



16. Solar absorptance of white thermal control paints on LDEF.

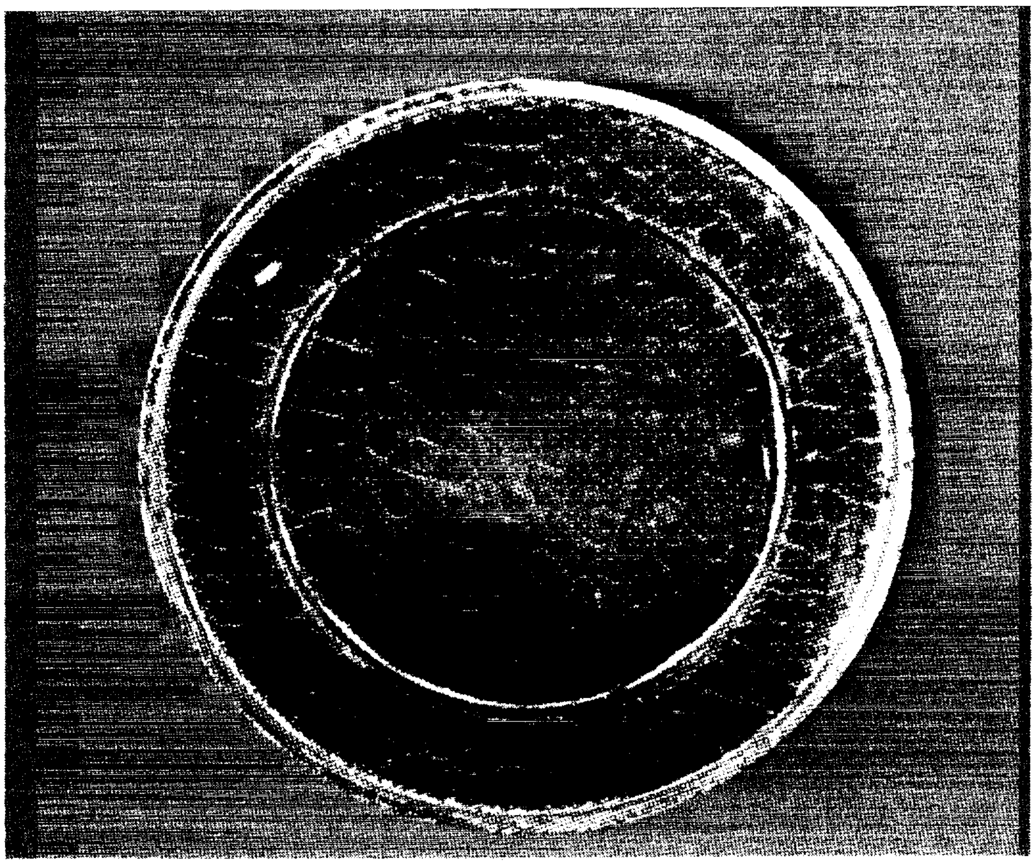


17. Absorptance to emittance ratio versus angle of incidence for A276 paint disks.

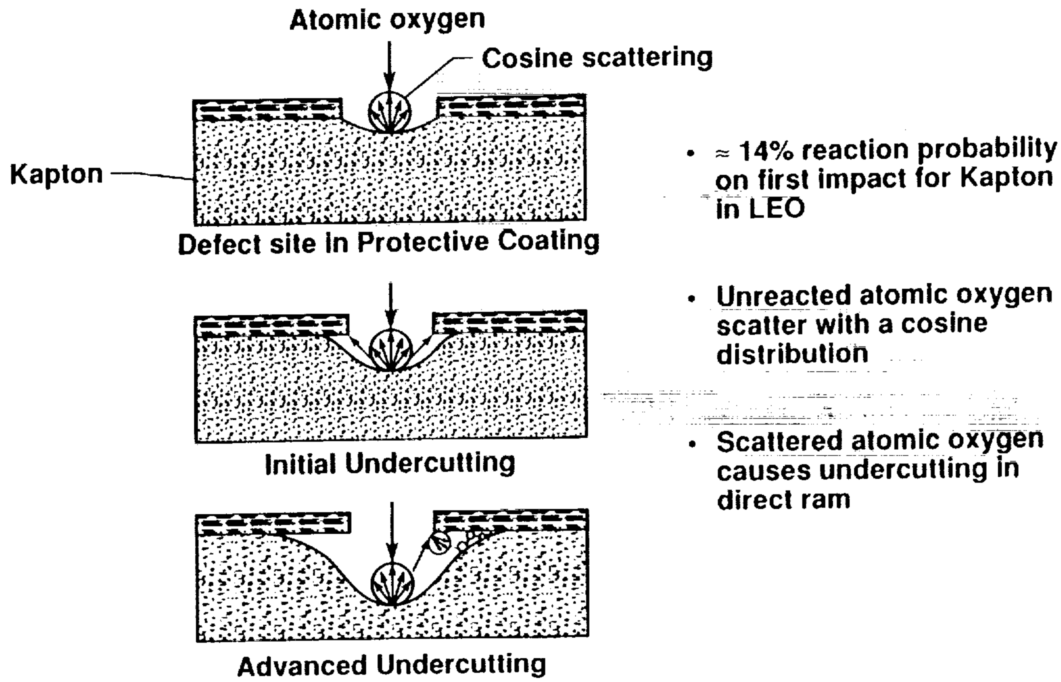


18. Microcracking in silver/Inconel layer and discoloration during of Ag/FEP second-surface mirror thermal blankets during LDEF flight. (Magnification approximately 100X)

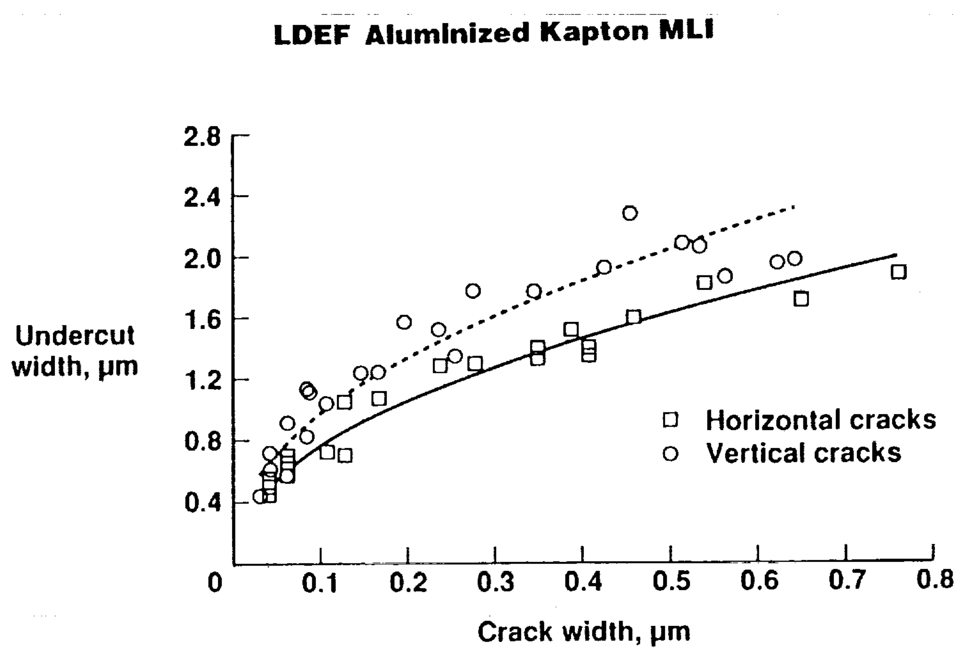
ORIGINAL PAGE
BLACK AND WHITE PHOTOGRAPH



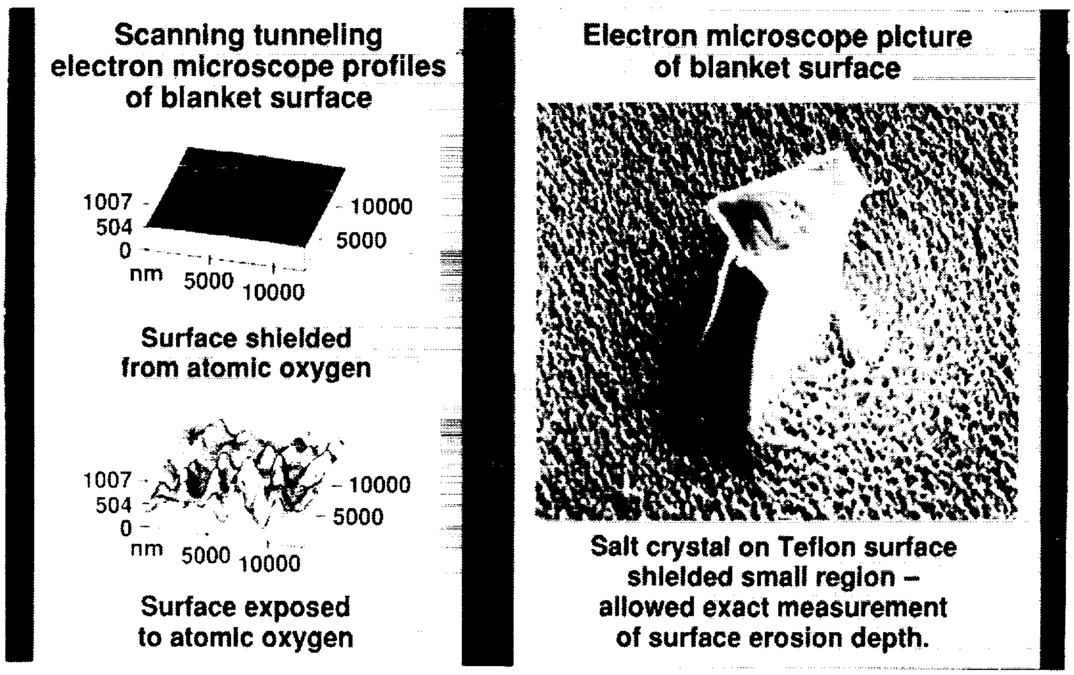
19. Surface crazing of clear silicone coating during LDEF flight.



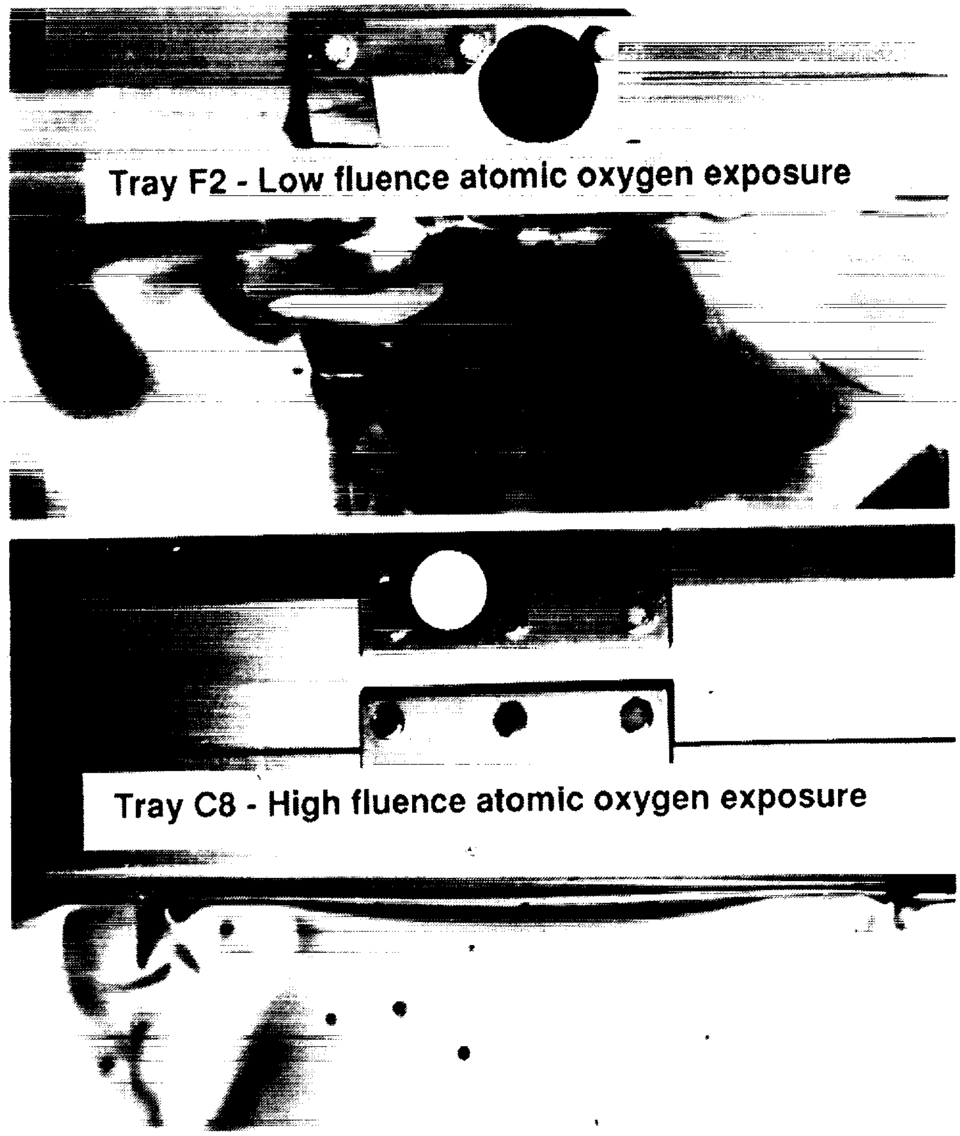
20. Atomic oxygen undercutting of coated polymeric materials on LDEF.



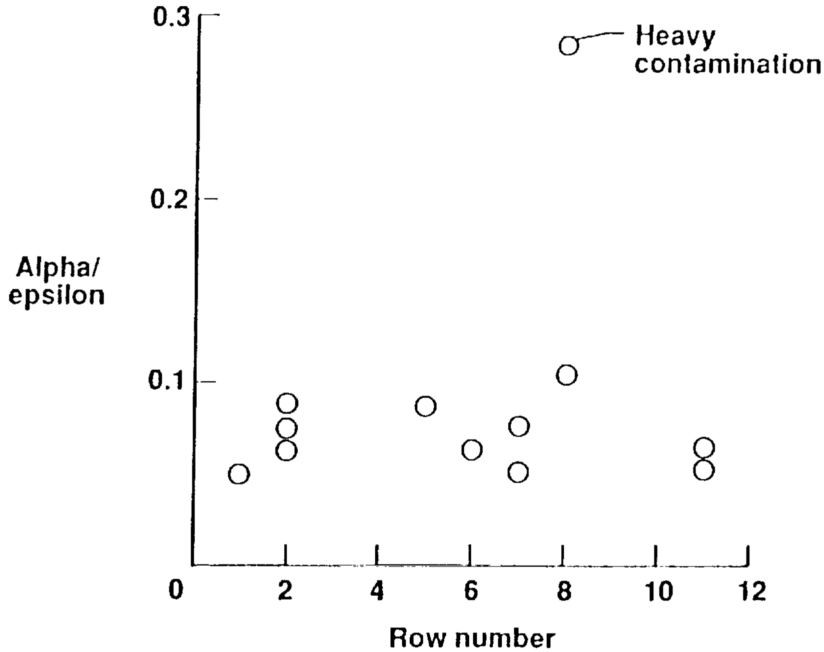
21. Atomic oxygen undercut widths in cracked multilayer insulations.



22. Atomic oxygen erosion of FEP Teflon on LDEF.

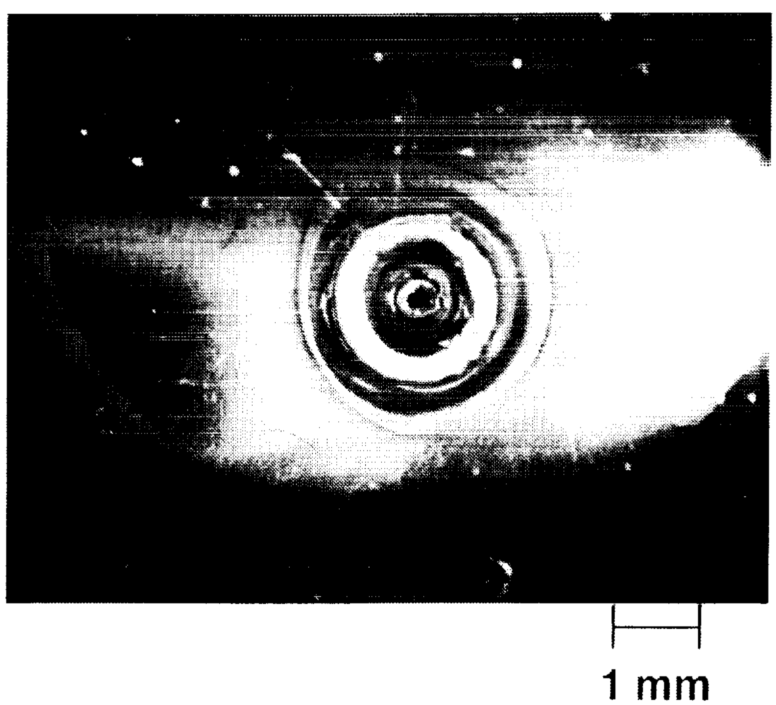


23. LDEF silver/Teflon second surface mirror thermal blankets.



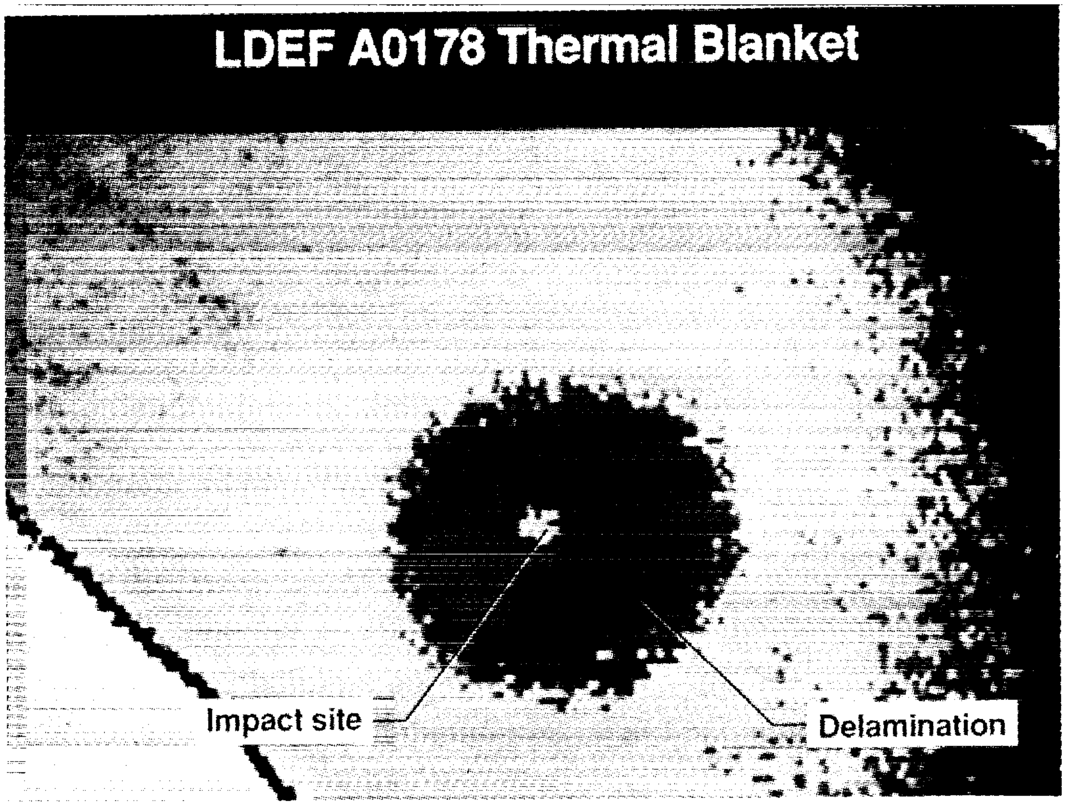
24. Absorptance/emittance ratios for silvered Teflon (FEP) blankets on LDEF.

Low magnification (x16)



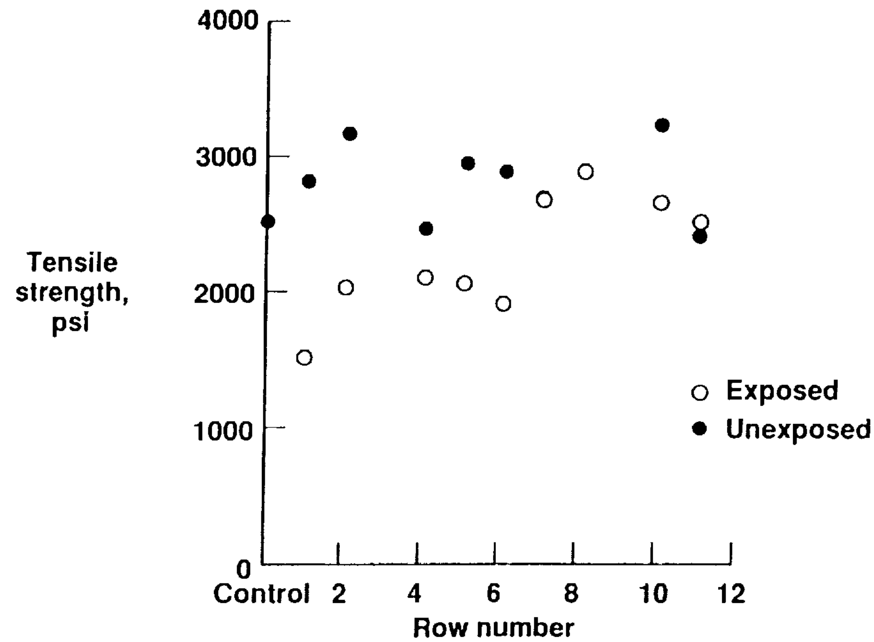
25. Photomicrograph of micrometeoroid impact on LDEF silvered Teflon thermal blanket.

ORIGINAL PAGE
BLACK AND WHITE PHOTOGRAPH

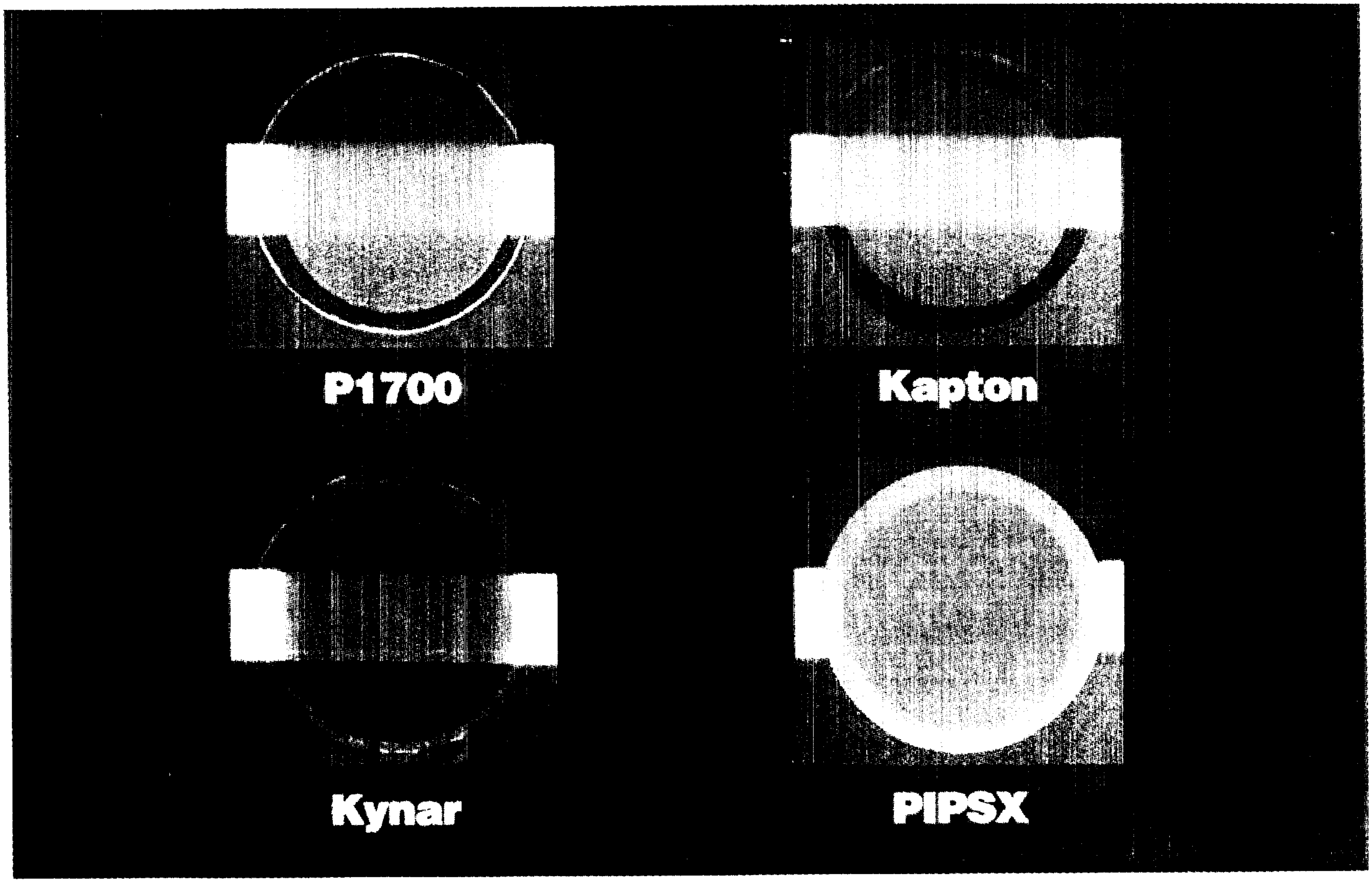


- Impact diameter ~0.5mm
- Delamination diameter ~10mm
- Infrared camera photograph
- Transient heating in air

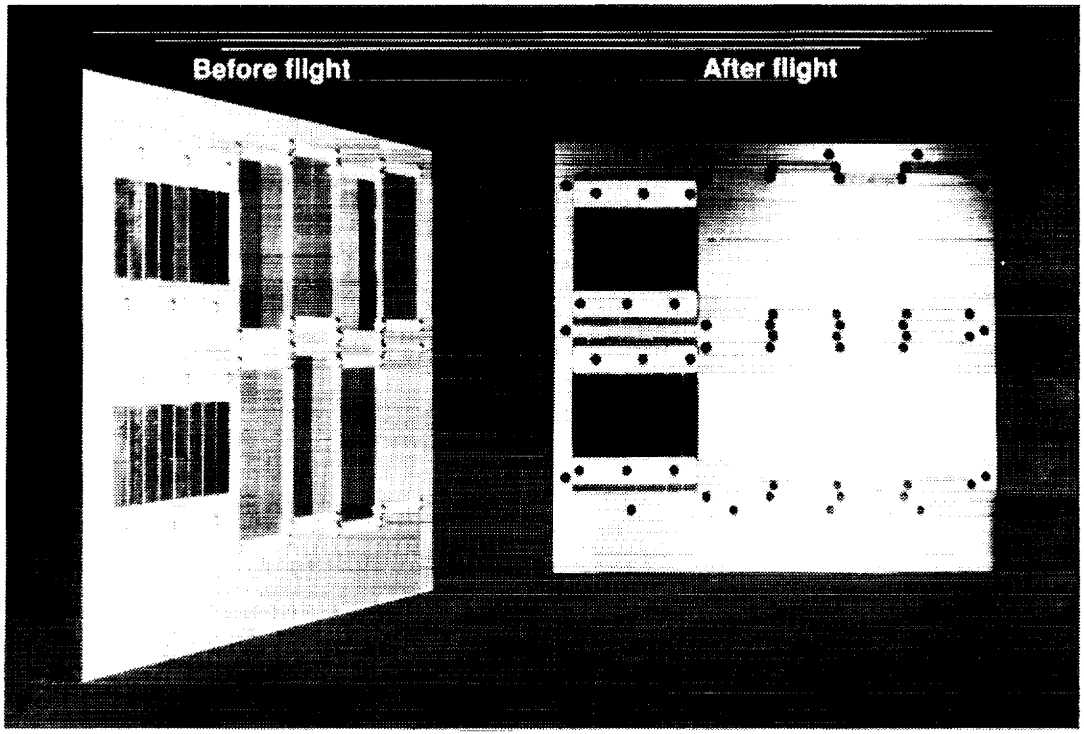
26. Thermal lag in delaminated silvered Teflon.



27. Tensile strength of FEP film from silverized Teflon blankets on LDEF as a function of row number.



28. Effect of 10-month LDEF exposure on four polymer films on LDEF experiment tray B9.



29. Langley polymer film experiment; 5.8-year exposure on LDEF tray B9.

Row no.	Angle off RAM (°)	AO fluence (10^{21} a/cm^2)	VUV (ESH x 10^3)	Epoxy				Polyimide		Bismaleimide	Polysulfone
				934/T300	934/P75	CE339/GY70	5208/T300	PMR/C6000	LARC/C6000	F178A/T300	P1700/T300
9	8	8.72	11.1	✓	✓	✓	✓	✓			✓
8	-38	6.93	9.4	✓	✓	✓	✓	✓			
7	-68	3.28	7.2					✓		✓	
12	82	1.28	6.9	✓			✓				
1	112	0.0002	7.5	✓					✓		✓
3	172	0.0001	11.1	✓	✓	✓	✓	✓			

Additional Environmental Parameters

Thermal Cycles: ~34,000 (-20 to 160°F,±20°)

Particulate Radiation:

e- and p+: 2.5 x 10^5 rad

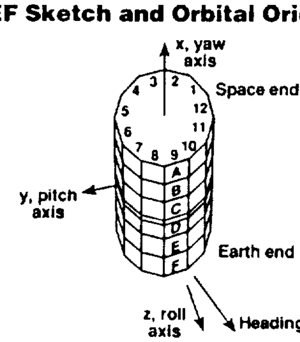
Cosmic: <10 rad

Vacuum: 10^{-6} - 10^{-7} torr

Micrometeoroid and Debris: 34,336 impacts (0.5mm - 5.25mm)

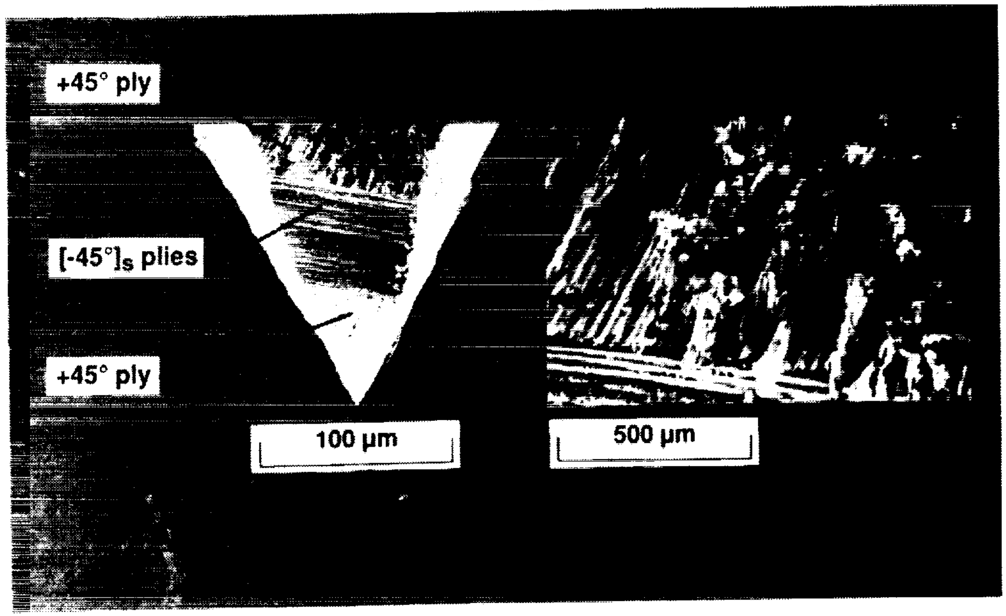
Altitude/Orbital Inclination: 255-180 nm/28.5°

LDEF Sketch and Orbital Orientation



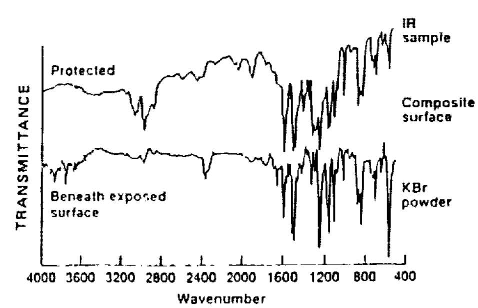
30. Selected LDEF-exposed composite materials.

SEM OF LDEF EXPOSED 5208/T300 COMPOSITE
$[\pm 45]_s$



31. Scanning electron microscope photomicrographs of LDEF-exposed T300/5208 (Gr/Ep) composite.

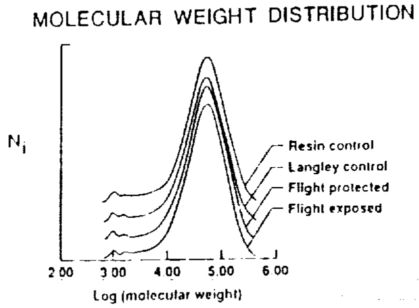
INFRARED SPECTRA



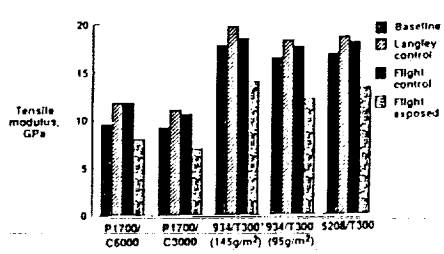
GLASS TRANSITION TEMPERATURE

Sample	Tg (°C)	Contacted side
Langley Control	167° 167° 170° 166°	Random
Flight Protected	164° 166°	Side A Side B
Flight Exposed	170° 171°	Exposed side
	169° 171°	Nonexposed side

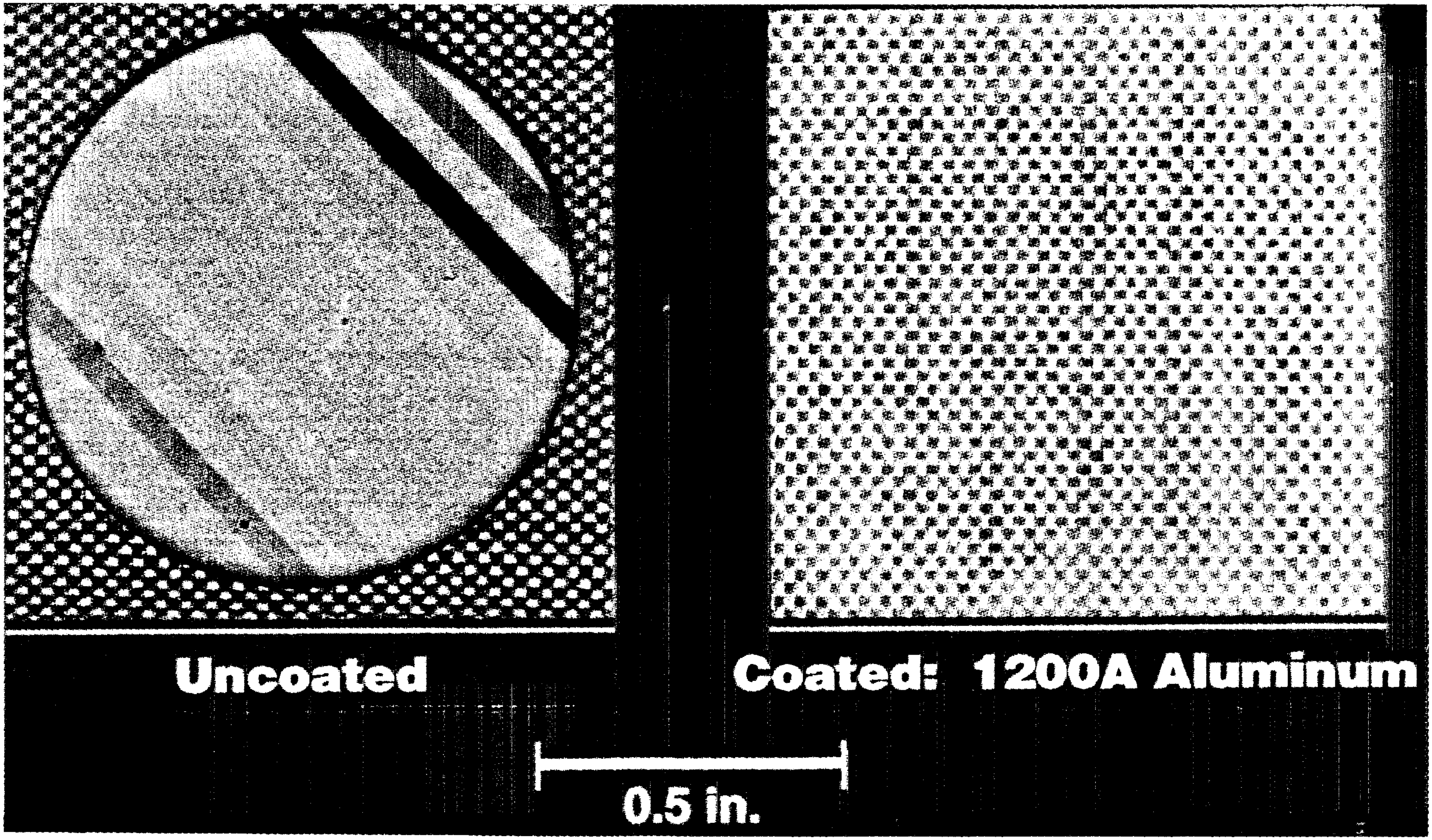
MOLECULAR WEIGHT DISTRIBUTION



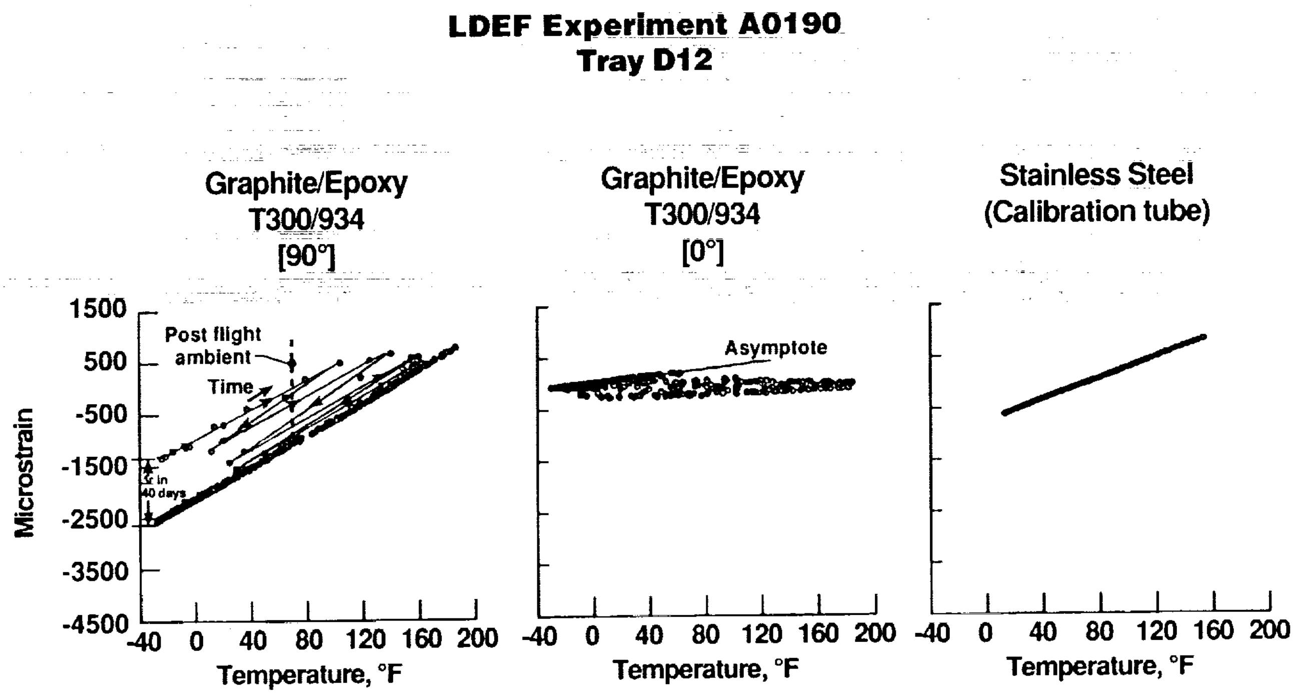
MECHANICAL PROPERTIES



32. Chemical and mechanical properties of LDEF-exposed composite materials.

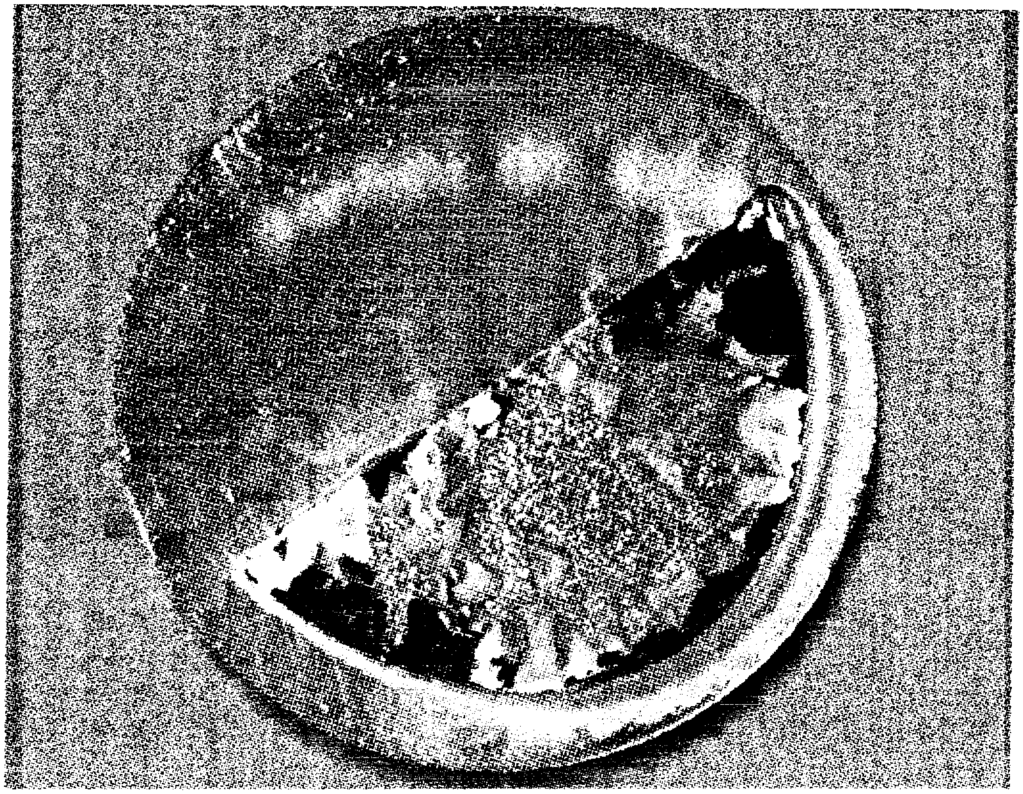


33. Comparison of coated and uncoated T300/934 (Gr/Ep) composite after 5.8-year LEO exposure on LDEF.



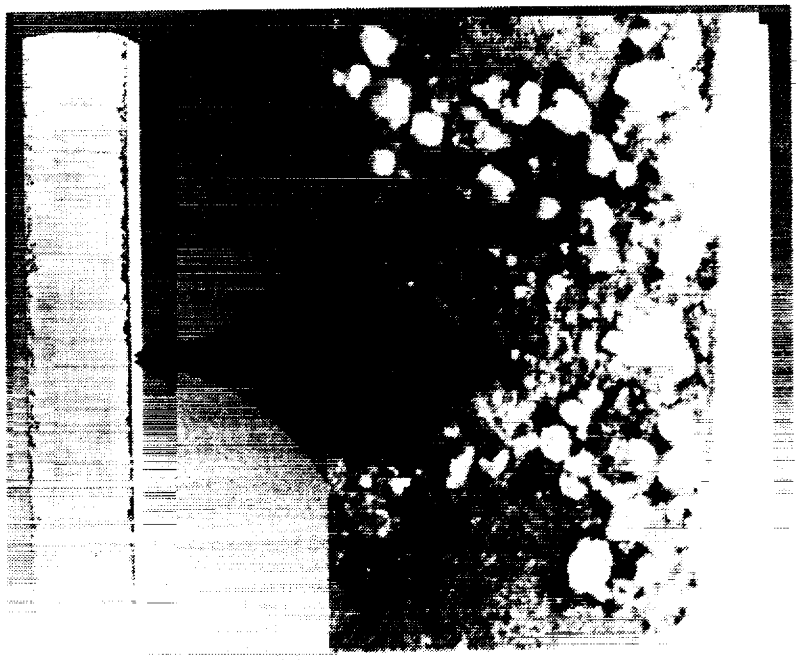
34. Dimensional stability of composites and metals on LDEF.

Optical Glass Substrate

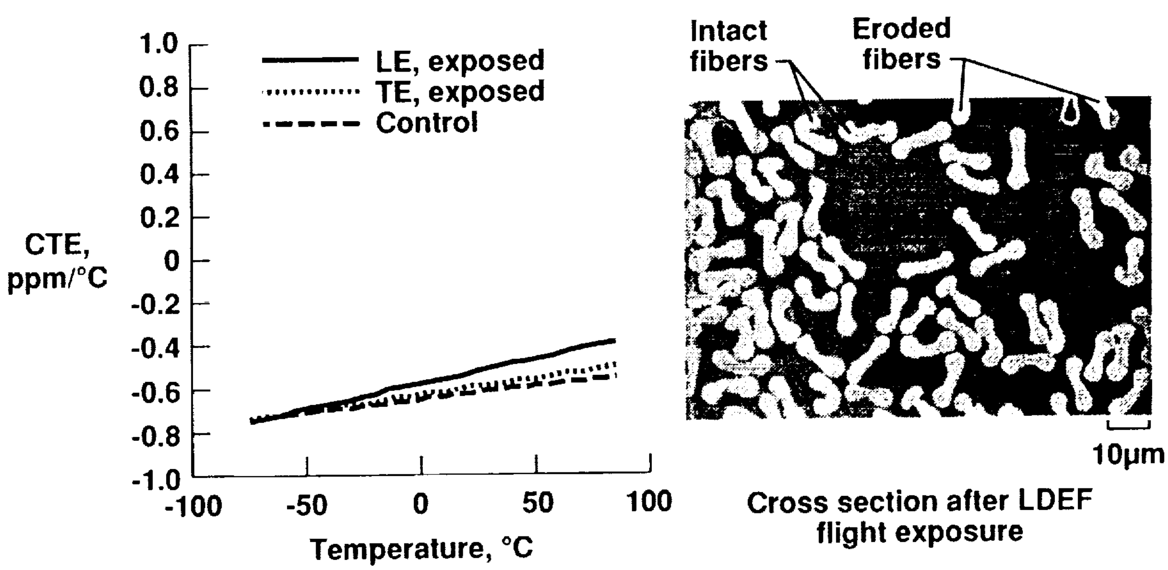


LDEF Experiment A0114
Tray C9

35. Oxidation of silver coating during LDEF flight.



36. Oxide growth on graphite fiber reinforced magnesium alloy metal-matrix composite specimen on LDEF.



37. Long-term durability of graphite/glass composites on LDEF.

- Directionality of trapped protons important to stabilized spacecraft
  - Current proton environment model gives factor of 3 errors
- Crew in Space Station Freedom flying above 400 Km will exceed 1-year dose limits in many locations
- Maximum radiation doses for SSF electronics specified from LDEF data
- Induced radioactivity not a significant radiation hazard for SSF
- Neutrons are significant secondary particles
  - Neutrons and cosmic rays produce measurable radioactivity
- ^{7}Be discovered on leading surfaces of LDEF
  - Inspired new atmospheric science investigations
- Fe nuclei observed with energies between galactic and anomalous cosmic rays (Partially ionized solar flare particles?)
- Activation measurements provide data base for environmental modeling
- Heavily ionizing recoil nuclei measured with good statistics
  - Short range, high-LET particles significant in electronic/biological damage

38. LDEF ionizing radiation findings.

- Unmelted meteoroids can be captured for origin/evolution studies
- Impact events are not random; affected by meteor showers, space operations
- Impacting particles have heterogeneous structure and composition
  - Chondritic compositions, silicates, sulfides identified
  - Beta micrometeoroids (blown away from the sun) identified
- Debris particles include metal and paint flakes
- Damage at impact sites affected by combined LEO environment parameters
- Thin plastic bumper sheets are effective in protecting against impacting particles
- SP-8013 Meteoroid Model requires modification
  - Premature meteoroid flux "roll-off" in model
  - Surface degradation greater than model predicts
  - Anisotropic meteoroid distribution, velocity, and directionality incorrect
- Current debris models require modification
  - underestimate debris in elliptical orbits
- SP-8042 cratering and penetration equations require modification

39. LDEF meteoroid and debris findings.

- No LDEF systems-level failures attributed to the natural LEO environment
- No bulk metallurgical changes in aluminum and titanium alloys
- Viscous damper passive stability concept worked well
  - Viable attitude control concept for SSF
- Uncoated hard optical materials, seals, batteries, heat pipes, wiring harnesses, radiometers, calorimeters, reflectometers, semiconductor diode lasers, LEDs, and adhesives generally performed well
  - A few acrylic adhesive joints failed
  - Some outgassing/contamination from connectors
- No evidence of cold welding; fastener galling observed
  - High quality fasteners / lubrication required for extended LEO missions
- Electromechanical relays continue to be a problem
- Contamination and drifting of conductive materials are hazards
- Solar cells were degraded by meteoroid/debris impact, UV / AO, contamination
- Lubricants showed some degradation where directly exposed to LEO environment
- Uncoated soft optical materials (e.g.- KRS-5 and KRS-6) were degraded
- Thermal cycling delaminated some dielectric and metallic coatings
- Preliminary optical materials data base generated

40. LDEF systems findings.

PRE-LDEF

- GROUND TESTS: Inadequate for LEO simulation
- SOVIET MIR DATA: Limited Value; environment poorly defined
- SOLAR MAX: 2-year mission; no designed materials experiments
- SHUTTLE PAYLOAD BAY DATA: Short, accelerated exposures

LDEF

- 5.8-year LEO exposure; mostly in Space Station Freedom orbit
- Well-defined materials, systems, and science experiments
  - State-of-the art materials
  - Ground and flight control specimens
- Stable orbital attitude
  - Broad range of exposure fluences for key environmental parameters (AO, UV, thermal cycles, etc.)
  - Real-time synergism of environmental effects

41. LDEF generated unique, high-quality, long-term data on space environmental effects on materials in low-Earth orbit.

NATURAL ENVIRONMENTS

ENVIRONMENT
- Orbital Atmosphere: Density and Composition
- Plasma
- Charged Particle and Electromagnetic Radiation
- Meteoroids and Space Debris
- Magnetic and Gravitational Fields
- Thermal
- Physical Constants
- Atomic Oxygen
- Ultraviolet Radiation
- Humidity

MISSION PHASES
- Ground Handling
- Launch
- Landing
- On-Orbit: External
- On-Orbit: Internal

* From McDonnell Douglas Space Systems Company Environmental Criteria Document 1F01920 for SSF Work Package 2

42. Space environmental effects considerations for Space Station Freedom: Natural environments.

INDUCED ENVIRONMENTS

ENVIRONMENT
- Electromagnetic
- Electrostatic
- Vibration
- Acoustics
- Shock
- Linear and Angular Acceleration
- Pressure
- Low Velocity Impact
- Thermal
- Internal Contamination
- External Contamination
- Plasma
- Radiation
- Plume Impingement
- Forces and Moments
- Spacecraft Glow
- Oxygen Concentration

MISSION PHASES
- Ground Handling
- Launch
- Landing
- On-Orbit: External
- On-Orbit: Internal

* From McDonnell Douglas Space Systems Company Environmental Criteria Document 1F01920 for SSF Work Package 2

43. Space environmental effects considerations for Space Station Freedom: Induced environments.

- Space Station Freedom
- Long-term Earth observation satellites
  - Platforms
  - Optical benches
  - System components
- Deep-space observatories in LEO
  - Precision reflectors
  - Electromagnetic sensors
- Space transportation systems
  - Earth-to-orbit
  - Orbital transfer
- Communications satellites
- Surveillance satellites
- Active defense systems
  - Long-term inactivity in LEO
  - Electronics protection

44. LDEF materials data applies to a variety of NASA and Department of Defense missions.

- Data on atomic oxygen erosion of Silvered Teflon
  - Used to define predictive erosion models for SSF radiator coating
- Long-term stability of Z-93 white thermal control coating was verified
  - Z-93 selected for large thermal radiators on SSF
- Anodized aluminum alloy long-term durability in LEO was verified
  - Anodized Al selected for SSF truss structure
- Most other thermal control coatings were degraded by LDEF exposure
  - Confirmed ground-based simulation test results
- Contamination distribution on LDEF was characterized
  - Used in thermal model development for SSF truss structure
- Revised atomic oxygen fluence model generated for orbiting spacecraft
  - Used to design for material erosion on SSF
- MLI blanket surfaces degraded during LDEF mission
  - MLI will require outer layer surface protection for SSF applications

45. Utilization of LDEF materials data in Space Station Freedom design.

CONTAMINATION-RELATED TESTS

- Evaluate potential molecular contamination precursors in UV exposures
- Investigate adequacy of current outgassing tests / criteria for spacecraft materials
- Determine the role of silicon-containing contamination on AO erosion rates
- Investigate the migration of silicone species on spacecraft surfaces

LDEF-EXPOSURE / GROUND-EXPOSURE EFFECTS CORRELATION

- Expose LDEF polymer films, composites, and coatings to AO / UV / tensile loads, individually and simultaneously, and evaluate effects
- Expose specimens of LDEF external surfaces and thermal control paints to elevated temperatures (which could be reached by contact with very high α/ε materials) and evaluate effects

46. Projected LDEF MSIG ground-based simulation testing activities.

CONTAMINATION-RELATED MODELING

- Develop an LDEF molecular contamination model
- Integrate models for contamination + UV + AO effects on surface chemistry

EXPOSURE EFFECTS MODELING

- Correlate observed equivalent dose effects of UV and/or AO in ground base facilities with LDEF data
- Assess potential post-retrieval effects on LDEF materials
    - Radical / reactive chemistry
    - Interaction between specimens and storage containers
    - Oxygen bleaching
    - Artificial light
    - Temperature and humidity

ENVIRONMENTAL PARAMETER MODELING

- Develop models for LDEF "micro-environments"
    - Shadowing due to scuff plates, trunnions, support beam
    - Indirect scattering from scuff plate on tray A4 thermal blanket
    - Gaps between trays

47. Projected LDEF MSIG environmental parameter modeling activities.

OBJECTIVE: Detailed study of LDEF contamination mechanisms to provide a unified perspective of spacecraft contamination

BACKGROUND: MSIG Preliminary study of LDEF contamination; supporting data for LDEF PIs

APPROACH:
- Detailed chemical/morphological characterization of contaminants on LDEF structure, experiment trays, and systems
  - Molecular contamination
  - Particulate contamination
- Identify source(s) of contaminants
- Document features indicative of orbital exposure and define contamination mechanisms consistent with LDEF flight parameters and the LEO environment
- Model the internal and external "LDEF atmosphere" from launch to retrieval
- Characterize the LDEF mission in terms of contamination
  - Sources, mechanisms, and resultant effects
  - Lessons learned

TESTS AND ANALYSES:
- Analytical light microscopy
- Automated image analysis
- Fourier Transform infrared spectroscopy
- Microchemical techniques
- Electron beam techniques

DELIVERABLES: Report and data base on LDEF contamination with implications for future space missions

48. Plan for detailed study of LDEF contamination.

LDEF Materials, Environmental Parameters, and Data Bases

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