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Effects of space environment on structural materials: a preliminary study and development of materials characterization protocols

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A preliminary study of materials exposed in space in a low-earth orbit for nearly 6 years (in the NASA Long-Duration Exposure Facility) has revealed a wide range of micrometeorite or microparticle impact craters ranging in size from 1–100 μm diameter, debris particles from adjacent and distant materials systems, reaction products and other growth features on the specimen surfaces, and related phenomena. The exposed-surface features included fine-grained and nearly amorphous materials as well as single-crystal particles. A replication-type, lift-off technique was developed to remove reaction products and debris from the specimen surfaces in order to isolate them from the background substrate without creating micro-chemical or microstructural artefacts or alterations. This resulted in surface features resting on a carbon support film which was virtually invisible to observation by electron microscopy and non-dispersive X-ray analysis. Characterization of these surface features involved observations by optical metallography, scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray analysis; including an analytical transmission electron microscope with a STEM attachment. The results illustrate a wide variety of materials phenomena which must be addressed in the evaluation of materials exposure in space, and the formidable materials characterization effort which will be necessary to understand these features.

1. Introduction

In the early years of space exploration after *Sputnik*, it was often assumed that the vacuum of near-earth orbits and deeper space would maintain many material surfaces unreactive and unaltered. The incidence of microparticles and micrometeorites as well as other debris and fragments in space were recognized as potential hazards, but again the concerns were minimized in many considerations of materials in space.

More recently, it has been recognized that geosynchronous orbits around the earth have become "contaminated" by residues and debris from orbiting satellites and other "space junk". Degraded and detached coatings including paint fragments now contribute to these orbital environments along with other microparticles and other lesser known species of "atomic" elements and molecules in ground states and excited energy states [1]. Some earth orbits are also known to contain energetic fluxes of electrons and protons. In particular, it has been observed that spacecraft, and more importantly, structural and coating materials are exposed to significant concentrations of atomic oxygen in low-earth orbit which aggressively attacks many of these materials as well as organic polymers [2]. Lightweight structural materials such as graphite–epoxy composites and other composites, may undergo unique oxidation reactions and be subject to unanticipated reaction kinetics.

In the early 1980s, with mounting interest in the development of space platforms and stations as well as the inception of and concerns for the US Strategic Defense Initiative and its space-based detection schemes, NASA and other US agencies and laboratories began the development of a satellite designed to initiate the testing and evaluation of a wide variety of materials exposed to low-earth orbit (LEO) space environments. Called the NASA Long-Duration Exposure Facility (LDEF) and illustrated schematically in Fig. 1, LDEF consisted of a hollow structure containing hundreds of test arrays and panels of the widest variety of materials and materials systems: metals, alloys, ceramics, polymers, semiconductors and a host of simple and complex composites; composing a total of 57 different experiments (shown as trays in Fig. 1). Launched into a non-geosynchronous, LEO from the payload bay of the Space Shuttle Orbiter *Challenger* in April, 1984, LDEF could not be recovered until January 1990 because of the shuttle

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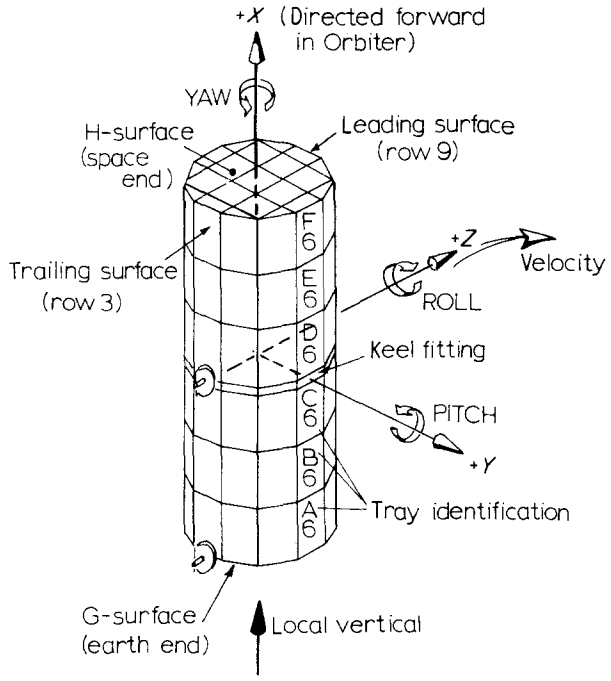

Figure 1 LDEF Orbital orientation model, schematic illustration.

Challenger accident in January 1986, and the cessation of NASA shuttle flights until January 1990; resulting in an exposure period of 5 years and 10 months.

As Fig. 1 illustrates, tray (and sample) locations on LDEF were characterized in regard to leading edge or trailing edge geometries. This is an important distinction because leading edge areas move into orbital debris and materials surfaces are "washed" by atomic oxygen or other orbital species while trailing edge materials are shielded.

Fig. 2a shows a NASA shuttle astronaut photograph during the retrieval of the LDEF satellite while Fig. 2b shows the satellite being unloaded from the shuttle payload bay upon the return of the Shuttle Orbiter *Columbia* on 12 January, 1990 [3]. The arrows in Fig. 2 provide a point of reference for a group of test panels and trays which will be the focus of some preliminary materials characterization to be reported in this paper.

Fig. 3 shows enlarged views of the test section shown in Fig. 2 (arrow) while Fig. 4 illustrates some of the specific panel and test section matrix component materials. The "X" in Figs 3b and 4 indicates a small region on a 6061-T6 aluminium alloy (1 wt % Mg, 0.7% Fe, 0.6% Si), panel which will form the basis for preliminary research to be reported here.

2. Experimental procedure and the development of materials characterization protocols

Although, as illustrated in Figs 3b and 4, there are an enormous range of materials panels to be examined, this paper will deal with some preliminary observations and the development of some simple and effective techniques for the examination and characterization of surface features and surface-related phenomena. We will limit our discussions to the examination of a small section ("X") of an aluminium 6061-T6 test panel (from the leading edge shown in Fig. 1) illustrated in the test array shown in Figs 3b and 4.

Initial observations of surface effects and surface-related phenomena involved optical microscopy and metallography followed by observations of uncoated specimens of the test area in a scanning electron microscope (SEM) fitted with an energy-dispersive X-ray spectrometer (EDS) attachment.

Initial observations revealed a high density of impact craters which ranged in size from more than 100 μm to less than 1 μm diameter. In addition, the surfaces also exhibited various "debris" particles and

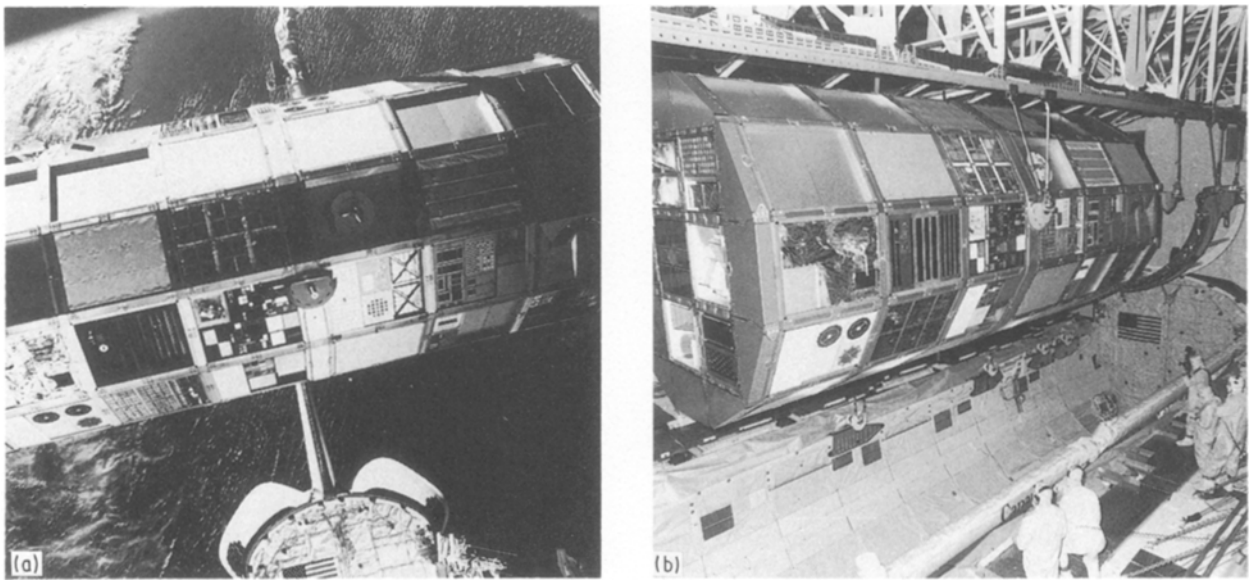

Figure 2 NASA documentary photographs of the LDEF recovery. (a) LDEF was held in the grasp of *Columbia*'s remote manipulator system and rotated repeatedly to accommodate an extensive photo survey. The Atlantic Ocean is in the background. (b) Suspended above the payload bay of the Space Shuttle *Columbia*, the LDEF is monitored by technicians during its move from the Space Shuttle to a transportation canister.

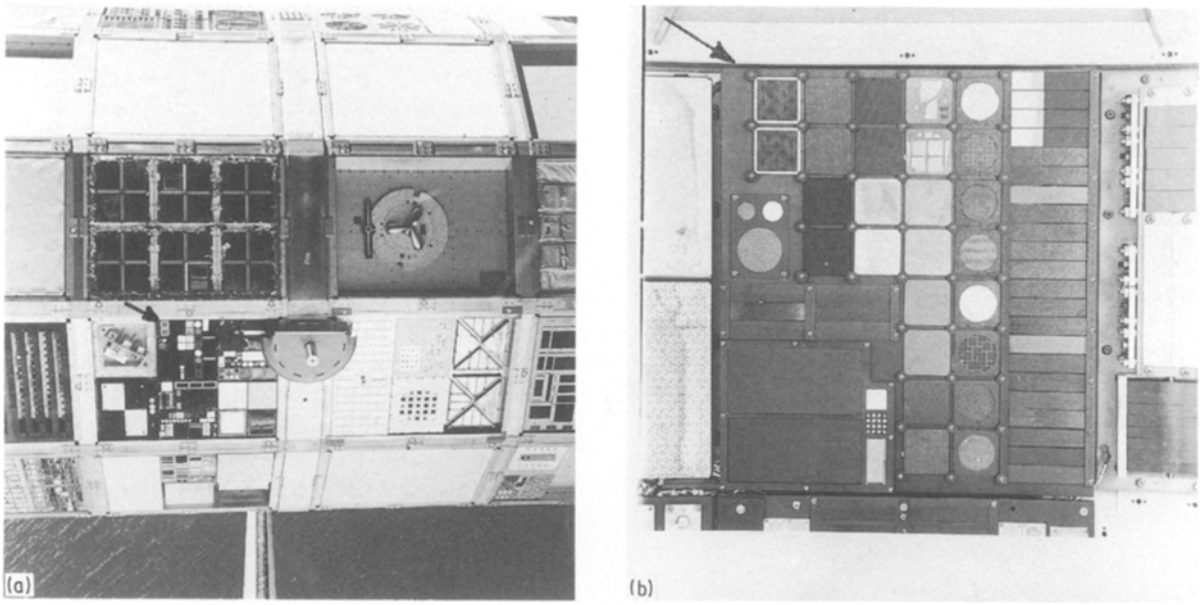

Figure 3 Close-up views of the test panels. (a) Close-up view of Fig. 2a. Arrow marks the tray area of interest. (b) Enlarged view of tray and test panel area. "X" marks the region of interest for analysis to be reported in this paper.

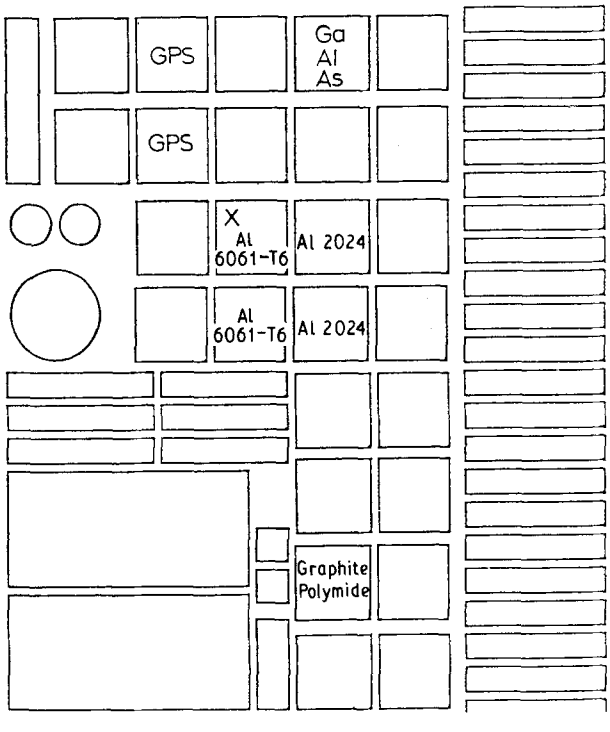

Figure 4 Schematic view of the test panel matrix in Fig. 3b. Specific panels of interest are marked. GPS, graphite polysulphone panels. Ga–Al–As, samples which reside in this panel. Aluminium alloy panels are marked.

what appeared to be growth structures and surface-related reaction products, including "crystals" and non-crystalline-appearing features. These surface features could be examined by EDS in the SEM but the X-ray signals from very small particles were often compromised by X-ray spectra from the supporting aluminium matrix, and it was difficult to elucidate the elemental nature of the particles or to determine anything specific about their internal microstructures or crystal structures.

Unambiguous and detailed examination of surface "debris" and related surfaced features (including reaction products) required the development of a lift-off technique which would allow these features to be selectively removed from the test material surface without creating chemical or microstructural alterations or other artefactual contributions which would compromise or complicate an examination of the isolated products. Utilizing a rather standard surface replication technique illustrated in Fig. 5 [4], a plastic (polymer) film was placed over a selected area of the surface and a standard (3 mm) transmission electron microscope (TEM) copper grid placed on the plastic and allowed to dry. A sticky tape was used to pull the plastic and adhering grid gently from the surface and a carbon support film was then vapour-deposited on to the back side of the plastic support system. The grid, with plastic and carbon support encapsulating the "particles" lifted from the surface, were then placed on a wire screen in a petri dish containing acetone. A hot plate was used to heat the acetone gently creating a vapour in the covered petri dish which dissolves the plastic from the grid-lift-off composite. The final result is a carbon support on the grid, holding the particles removed from the surface.

The carbon support films containing "particles" stripped from the aluminium alloy surface were then examined in an analytical transmission electron microscope or scanning transmission electron microscope (STEM) fitted with an SEM detector and an energy-dispersive X-ray analysis (EDS) attachment. This allowed high-resolution and high-definition microanalysis of surface particles and debris to be examined independent of the surface-related matrix. The carbon support film was essentially "invisible" to the electron probe and contributed only a weak carbon signal to the EDS spectrum [4, 5].

3. Results and discussion

Fig. 6 illustrates the range of impact craters and their

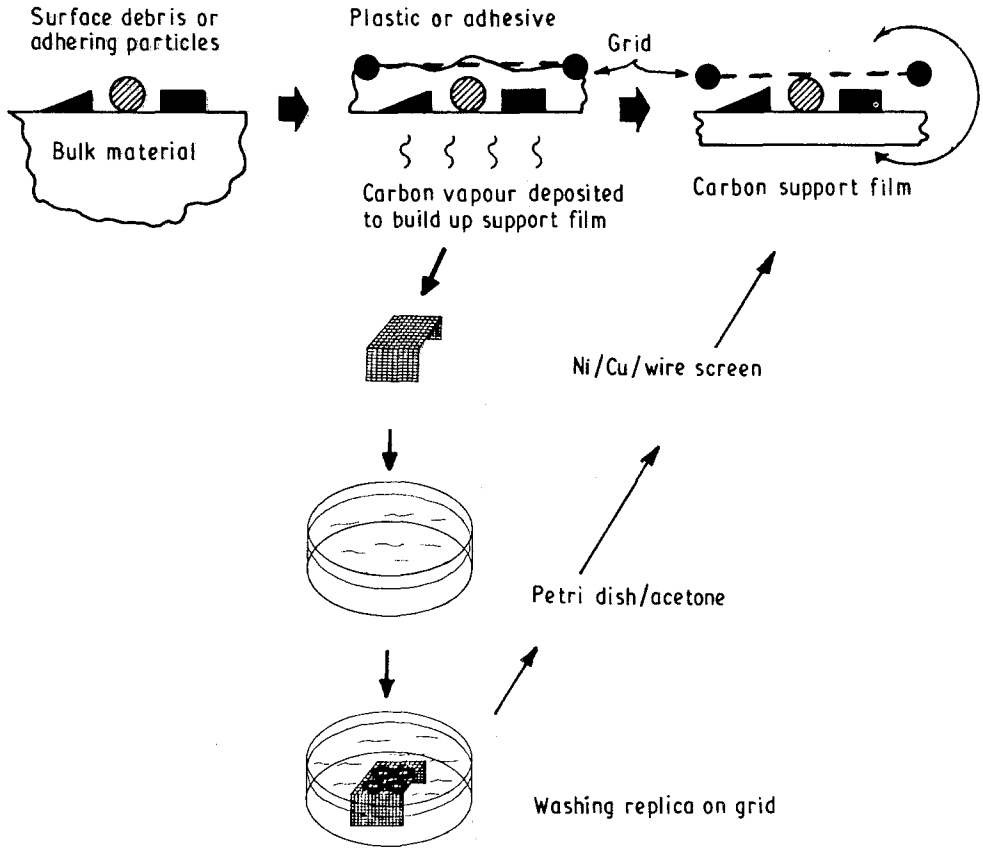

Figure 5 Schematic representation of replication technique adapted for surface lift-off. The process components are separated by arrows. The plastic replica is "washed" in acetone to dissolve the plastic, leaving a carbon support on the copper grid [4, 5].

morphological features observed by optical and scanning electron microscopy. These features are interesting because of the symmetry of the impact and the nature of the ejecta. Because the velocity of impacting particles is about $11\ km\ s^{-1}$, they are generally thought to vaporize during impact. However, observations of debris within the impact craters indicate reactions between the impacting particle and the impacted substrate. This is an important feature of the effect of space environments on structural materials because such impact-related reactions could form intermetallic phases or other brittle products. These intermetallic phases could initiate microcracks or cause other deleterious effects, especially if impacting particles or micrometeorites contain iron, nickel, or combinations thereof and impact aluminium or aluminium alloys, as illustrated in Fig. 6.

A further consideration which is currently being examined involves the micrometeorite ejecta shown prominently in Fig. 6c and d. It is of interest to examine the composition as well as the symmetry or asymmetry relative to impact geometry and velocity, and particle shape and composition.

In addition to impact craters shown typically in Fig. 6, the test specimen surface contained numerous debris particles which could be clearly identified as debris. In addition, there were examples of debris which apparently reacted on the surface creating new growths. Examples of these features are illustrated in Figs 7 and 8.

Fig. 7 shows a composite of views of a debris particle consisting of an optical (light) microscope view (Fig. 7a) and a higher magnification view of a portion of the particle viewed in the SEM (Fig. 7b), and a corresponding elemental (EDS) analysis (Fig. 7c) showing GaAlAs. The aluminium peak may be somewhat compromised by the aluminium alloy background, but the particle is unambiguously a piece of a Ga–Al–As semiconductor sample located proximate to the aluminium alloy test panel in the tray matrix illustrated in Figs 3b and 4 (GaAlAs). Such debris may be created by impact damage on the GaAlAs semiconductor similar to that shown in Fig. 6, or some related fragmentation process.

In contrast to Fig. 7, Fig. 8 is an illustration of one of dozens of observations of growth-like surface debris which contain sulphur and silver as shown in the accompanying EDS spectrum. It is believed that the silver originates from a silver-coated polymer film which was located just above the specimen tray indicated by the arrow in Fig. 3a (just above the arrow). This tray was originally covered by silver-coated panels whose recovery exhibits only remnants of the original film around the edges of individual panels. The lower tray area below the arrow (Fig. 3a) exhibits numerous silver-like debris particles covering many test panels. As shown in Fig. 4, the experimental tray pertaining to this research contained test panels of graphite polysulphone, which later were observed to be heavily corroded and eroded by interaction with atomic oxygen as described previously [2]. These features are illustrated in Fig. 9 which shows several typical surface areas from test panels marked "GPS" in Fig. 4. It is possible, therefore, that the silver

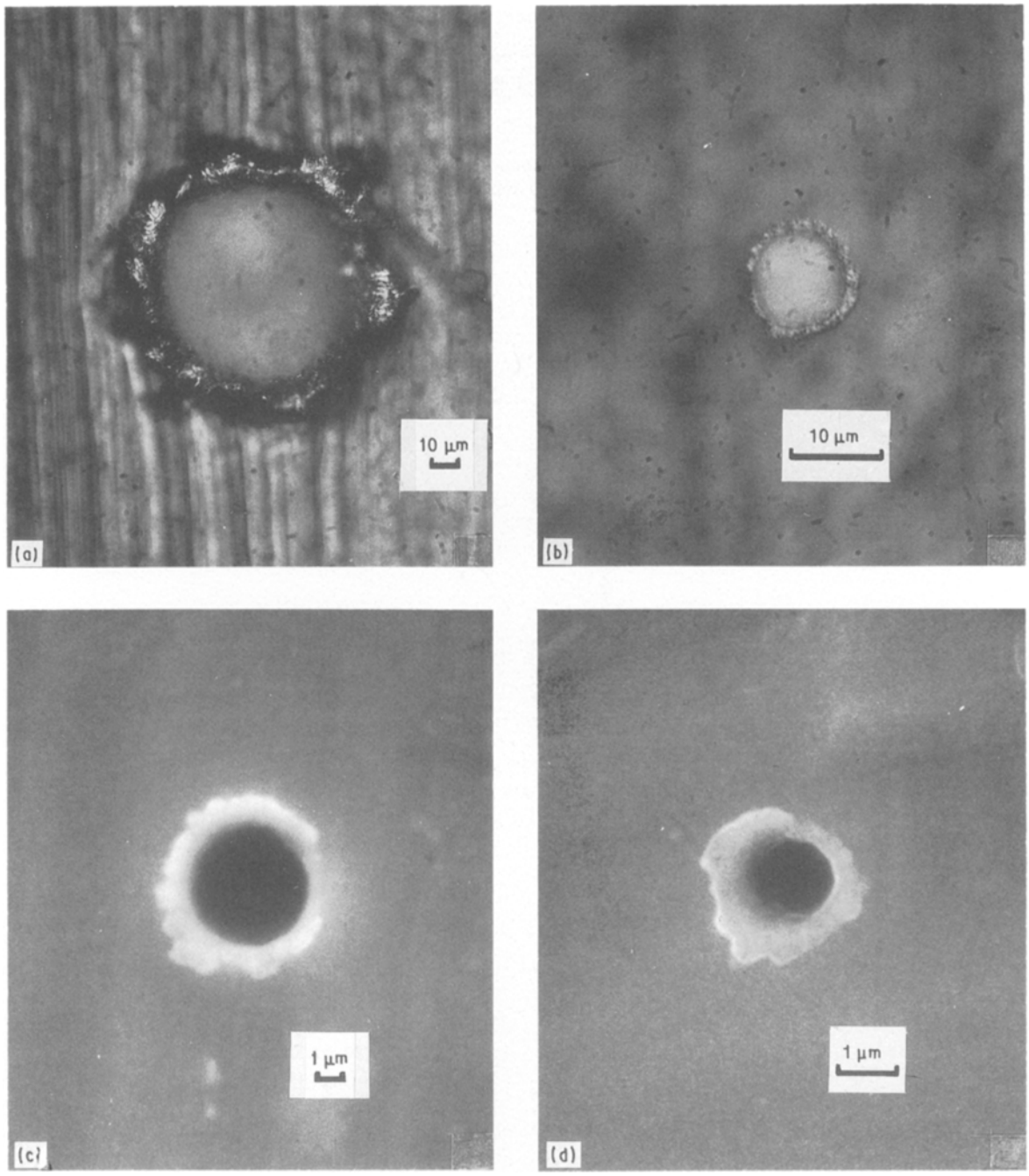

Figure 6 Optical microscope (a, b) and scanning electron microscope (SEM) views (c, d) of micrometeorite impact craters in 6061-T6 aluminium test panel specimen.

available in debris particles from the upper tray reacted with sulphur available through erosion of the graphite–polysulphone by reaction with atomic oxygen, forming AgS_x or even combinations of AgS_x/AgO_x, because oxygen is also present in the EDS spectrum shown in Fig. 8b.

The availability of sulphur due to reactions of atomic oxygen with the polysulphone panels, and other reactions with atomic oxygen apparently also gave rise to other surface reaction products which are illustrated in Fig. 10. Fig. 10a shows what appear to be thin crystals of MgO/MgS complexes as suggested from the associated EDS spectra shown in Fig. 10b, and selected-area electron diffraction patterns obtained for similar crystals lifted from the surface using the replication technique illustrated in Fig. 5 [4, 5].

Of course the aluminium peak in Fig. 10b arises from the aluminium alloy (6061-T6) test sample and some of the magnesium peak may also be background signal. However, by lifting these particles from the surface and performing EDS in the analytical transmission electron microscope, these features can be unambiguously demonstrated. Fig. 11 shows some examples of MgO/MgS particles lifted from the surface which do not contain aluminium in the EDS spectrum (Fig. 11c) and which are also not crystals, at least large crystals as suggested in the SEM images of Figs 10a or 11a. The selected-area electron diffraction (SAD) pattern in Fig. 11b shows a very fine-grain (nearly amorphous) structure well below the crystal morphologies suggested in the SEM image (Fig. 11a) where "crystal" geometries measure 0.5 μm × 2 μm.

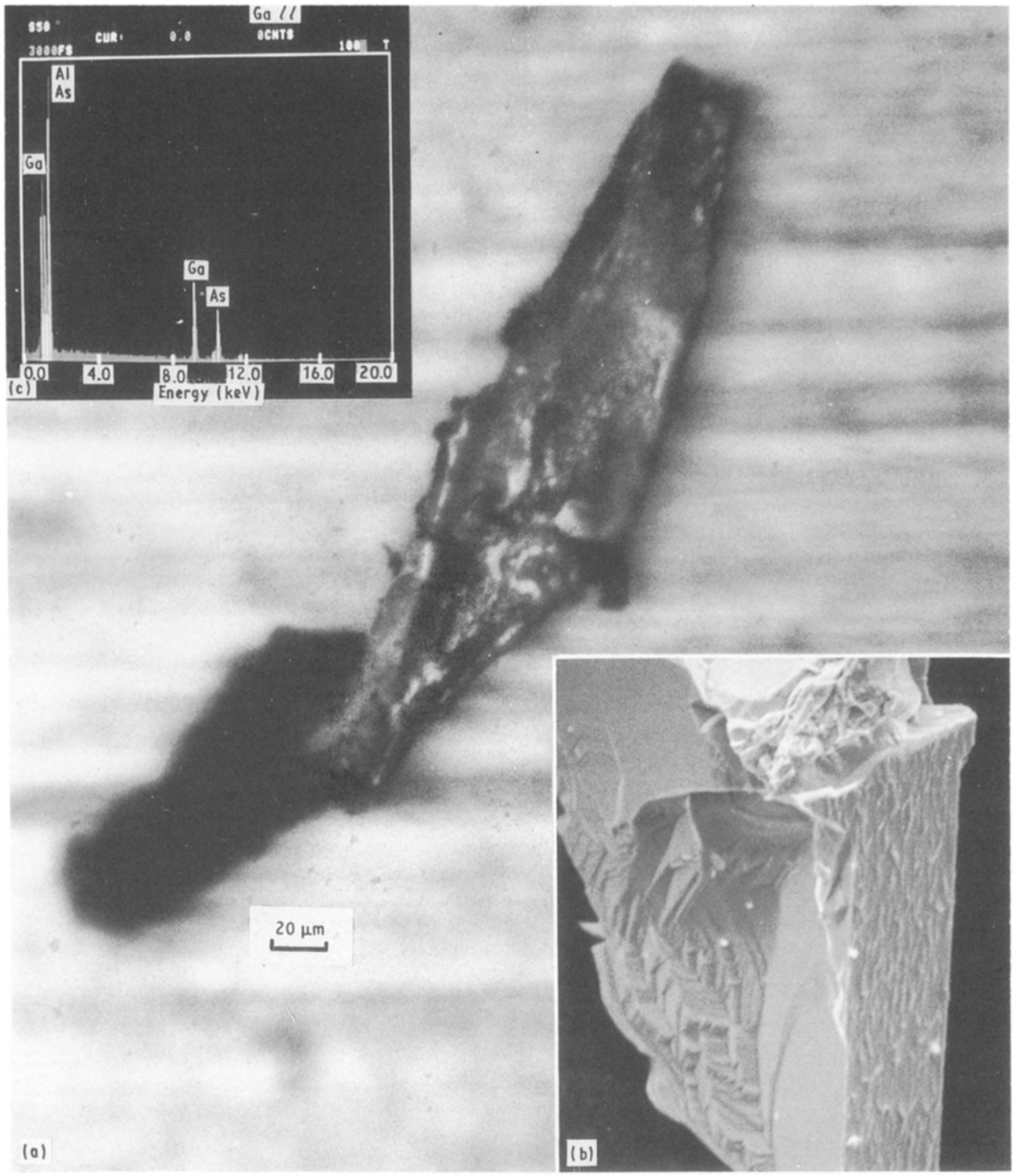

Figure 7 (a) Optical microscope view showing Ga–Al–As debris fragment transferred from neighbouring test panel as illustrated in the matrix of Fig. 4. (b) Surface morphology details, (c) EDS elemental analysis.

Correspondingly, the STEM image shown in Fig. 11d clearly illustrates a "granular" substructure to be characteristic of the particulate mass shown in the SEM image of Fig. 1a [5].

Finally, Fig. 12 shows another example of a different group of crystalline particles lifted from the aluminium alloy surface by the technique shown in Fig. 5. Fig. 12a is a bright-field TEM image while Fig. 12b shows the corresponding SAD pattern. A detailed analysis of these particles has identified them to be a magnesium–iron–aluminium oxide or chlorospinel (cubic crystal structure; $a = 0.819$ nm), and may form by vapour growth from micrometeorite impact with the aluminium alloy (Fig. 6). However, this conclusion must be supported by additional, detailed analysis, including an investigation of the impact craters as shown in Fig. 6.

4. Conclusions

It must be recognized that the results presented in Figs 6–12 represent only a very small sampling of 1 of 57 different trays of experimental/test materials and hundreds of panels of the LDEF Satellite. While these results are neither representative nor conclusive, they do illustrate a wide range of materials issues which will have to be addressed in assessing the effects of space environments on structural and other materials and

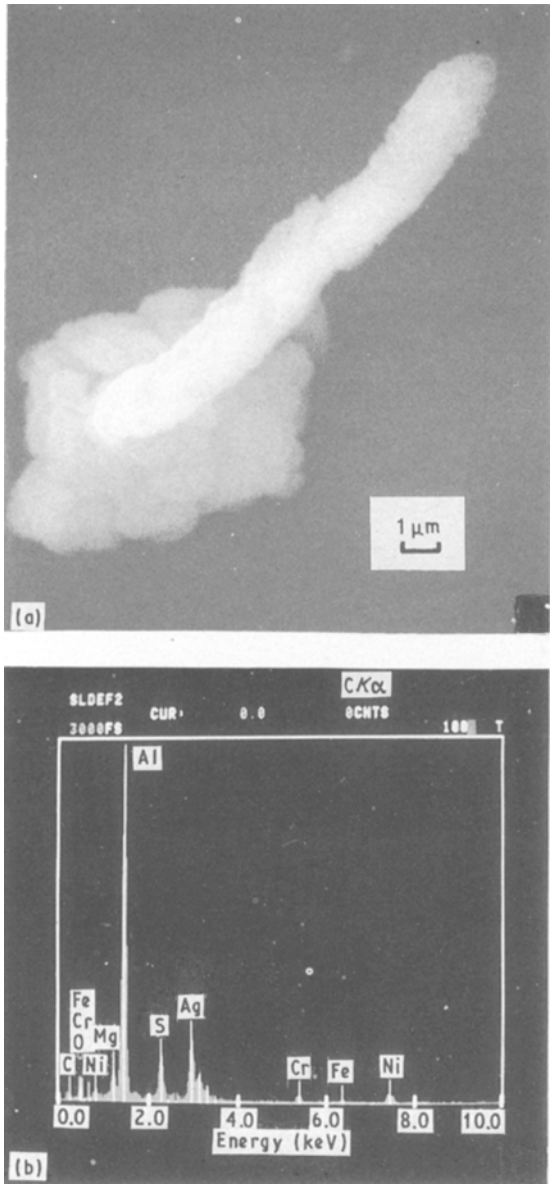

Figure 8 (a) Silver sulphide growth structure observed on the aluminium alloy test panel in the SEM. (b) The EDS elemental analysis spectrum.

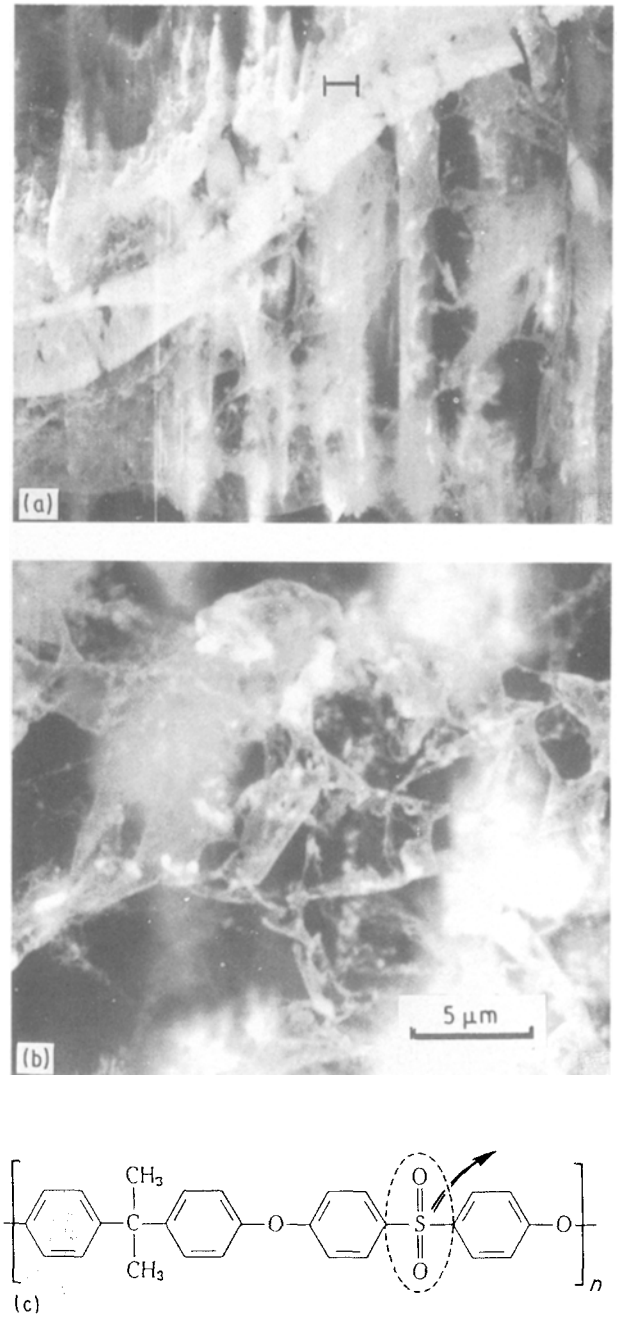

Figure 9 Examples of graphite polysulphone (GPS in Fig. 4) reaction and erosion by atomic oxygen reaction. (a) Linear erosion features (scale bar = 5 μm). (b) Nearly complete obliteration of polymer matrix. (c) Polysulphone repeating (*n*) chemical structural unit. The sulphone linkage is shown dotted and the arrow indicates the probable sulphur release.

materials systems. We have demonstrated that it will be necessary to isolate surface debris and reaction products from materials exposed in space and that replication techniques originally designed for electron microscopy examination of surfaces [4, 5] can be applied to lift off and isolate such surface features. This study has examined debris and reaction products by a variety of analytical techniques associated with analytical transmission electron microscopy; including the surface morphology by SEM, internal microstructures by STEM and TEM, EDS, and SAD [5].

While the results presented in Figs 7–12 are preliminary, they illustrate the role that atomic oxygen and micrometeorites play in surface alteration and reaction in LEO space environments, as well as the role of debris created from other proximate materials. The prospects for the growth of new and even different phases and materials chemistries from those reported on earth, and the possibilities for impact-related reactions and materials interactions provokes the necessity to address a broad range of space-related materials issues and the development of expedient and carefully planned analytical protocols.

The variety of effects suggested in the analytical results illustrated in Figs 7–12 attest to the new frontiers in space materials research which have been opened up for materials requirements for space structures and space craft.

Finally, the large number of micrometeorite impacts (Fig. 6) coupled with the prospects for surface debris (Figs 7 and 8) and related reaction products forming on materials surfaces as shown in Figs 9–12, raise a spectre of problems and concerns for optical

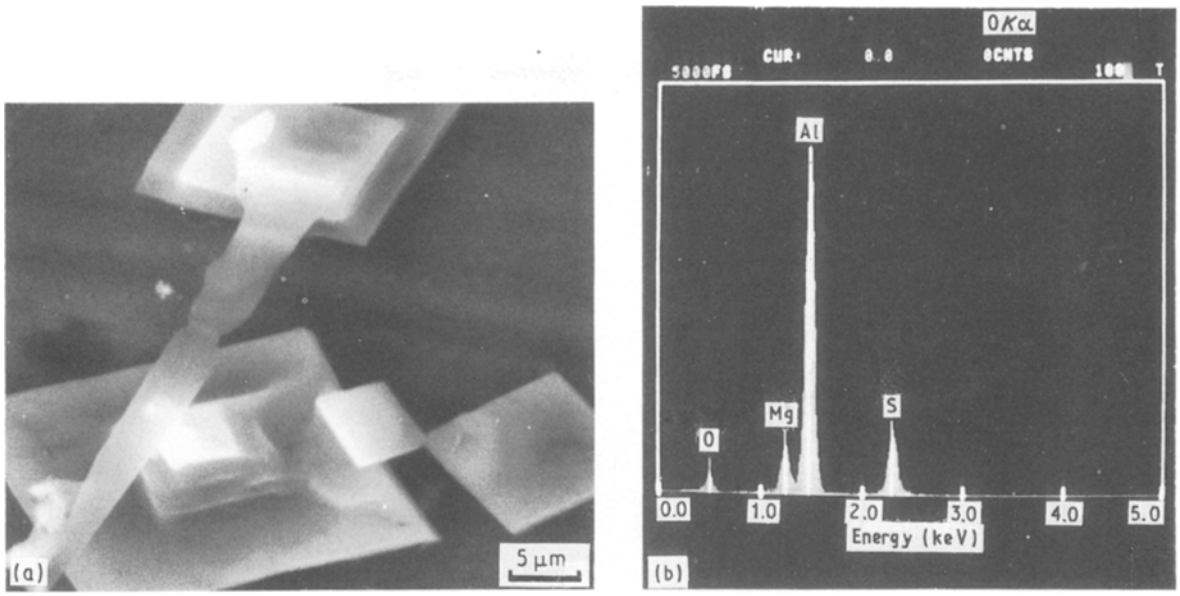

Figure 10 Mg–S–O crystals observed on the aluminium alloy test panel surface. (a) SEM view showing thin cubic crystal geometry, (b) EDS analysis. The aluminium peak represents the panel background.

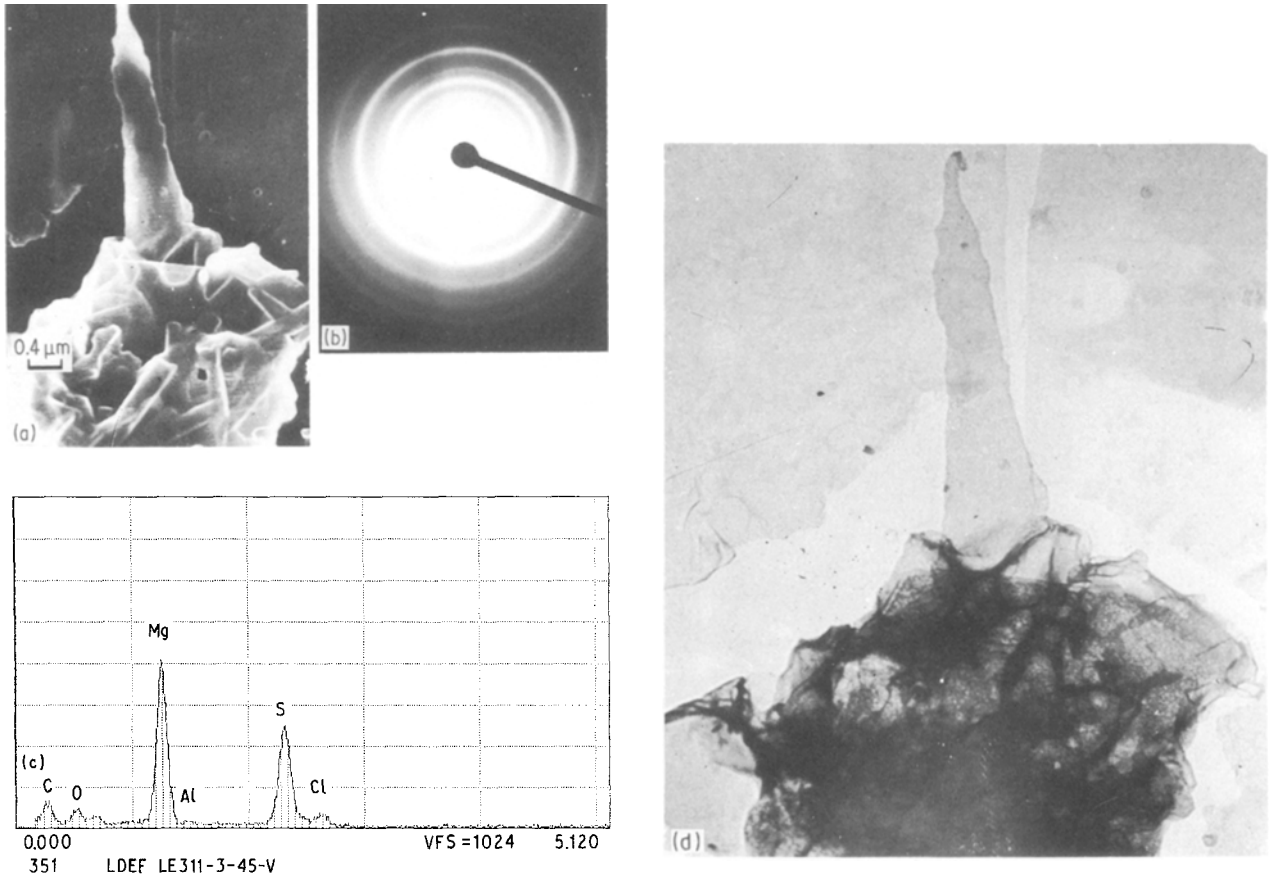

Figure 11 Mg–S–O particles embedded in carbon support film which have been lifted from the aluminium alloy test panel surface and examined in the analytical TEM. (a) SEM view of particle cluster. (b) SAD pattern of (a) showing nearly amorphous rings. (c) EDS spectrum. Note absence of an aluminium peak in comparison to Fig. 10b. Note also reduced oxygen peak due to higher excitation potential (200 kV), and carbon peak due to support. (d) STEM image of (a) showing internal structure.

materials and coatings, optical systems, and space optics. The Hubble telescope and similar space optics systems will be susceptible to a variety of these materials concerns which may compromise the high level of precision required in these optical systems.

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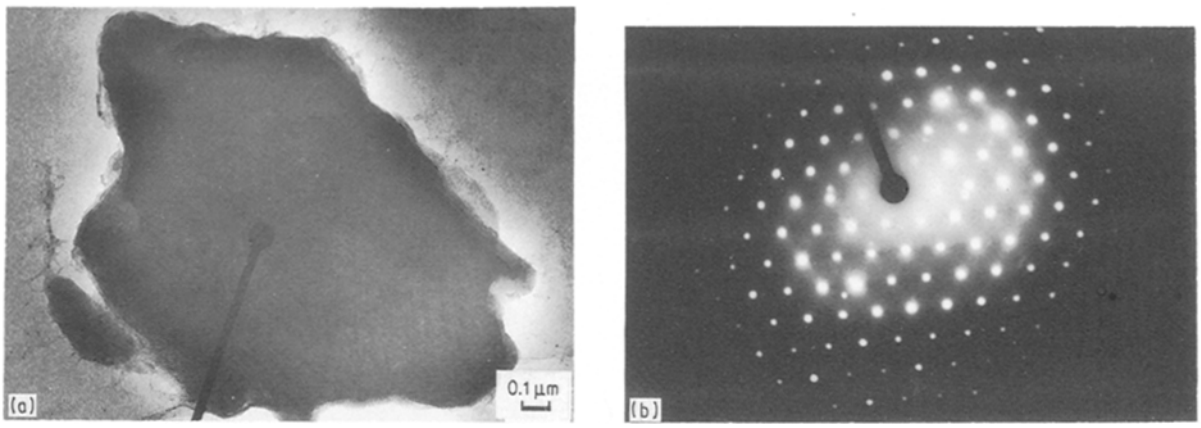

Figure 12 Chlorospinel-type single-crystal particles on carbon support film after being lifted from the aluminium alloy test panel surface. (a) TEM image, (b) SAD pattern of (a).

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