LABORATORY STUDIES OF KAPTON DEGRADATION IN AN OXYGEN ION BEAM

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Results are presented from a preliminary laboratory investigation of the degradation of the widely used polyimide Kapton under oxygen ion bombardment. Recent space shuttle flights have shown that Kapton and some other materials exposed to the apparent "ram" flow of residual atmosphere (at orbital velocity in low Earth orbit) lose mass and change their optical properties. It has been hypothesized that these changes are caused by chemical interaction with atomic oxygen, aided by the 5-eV impact energy of atmospheric oxygen atoms in the ram.

In the laboratory investigation the atomic oxygen flow was simulated by a flow of oxygen ions. The ions were generated by a discharge in a microwave resonant cavity, accelerated and decelerated electrostatically, and impacted on Kapton targets in a high vacuum. Tests were also performed using a non-reactive gas, argon, in place of the reactive oxygen. Oxygen-bombarded samples showed a loss of material and a change in optical properties very similar to those of samples returned by the space shuttle. Scanning electron microscope photographs of the oxygen-ion-bombarded samples also showed structures strongly resembling those of samples from the shuttle. Argon-bombarded samples showed no significant material loss or change of optical properties or surface structure under SEM.

All bombarded samples showed changes in surface composition when examined by low-energy windowless energy difference X-ray analysis (EDAX) and Auger spectroscopy. Oxygen-bombarded samples showed an apparent decrease in surface carbon as compared with pristine samples, whereas argon-bombarded samples showed a variable increase in surface carbon, depending on where the samples were located in the argon ion beam. These changes are attributed to sputtering.

The reaction rate under O+ bombardment seemed to be independent of incident energy over a wide range of energies. Although the flux of thermal ions in this experiment was much greater than the accelerated flux, the observed Kapton degradation was limited to the beam area and ram flow direction. This is consistent with an activation energy above the thermal energies but well below the beam energies.

The results reproduce well the material loss, optical changes, SEM surface structure, and "ram" directionality of the samples returned by the shuttle. These factors, along with the lack of degradation under argon ion bombardment, are convincing evidence for ram flow oxidation as the mechanism of degradation.

INTRODUCTION

Kapton and other materials (such as carbon coatings and paints) undergo weight loss and surface degradation in low Earth orbit (ref. 1). Kapton, a polyimide with wide applications in spacecraft technology, experiences surface roughening on micrometer length scales, a change in surface appearance from a glossy transparency to a milky translucence, a loss in weight, and changes in its optical properties. These changes, first noted on the early space shuttle flights (ref. 1), have important implications for conducting extended operations using Kapton in low Earth orbit. Kapton has been used for thermal control coatings and electrical insulation and has been proposed as a flexible substrate for large solar arrays because of its excellent temperature stability, extremely low surface conductivity, and flexible strength. It is important to know the mechanism for deterioration in low Earth orbit so that Kapton can be modified, coated, or replaced with other materials in critical applications.

It has been suggested that interaction with the residual atomic oxygen atmosphere is the mechanism of degradation (ref. 1). The major atmospheric constituent at shuttle altitudes is atomic oxygen. Each atom of oxygen impacts an orbiting vehicle with an energy of about 8×10^{-19} J (5 eV), equivalent to the impact energy of thermal atoms at about 60 000 K. High-temperature oxidation, about which little is known, may then be the reaction leading to mass loss, change of surface properties, etc.

Although oxidation is a likely hypothesis as the mechanism of degradation, other possibilities exist. The mass loss might be due to low-energy sputtering, for example. It is well known that sputtering thresholds for metals seem to be higher than the impact energies of atoms and molecules in low Earth orbit but such thresholds have never been measured for complex organic materials. Also, chemical reactions with other species abundant in low Earth orbit, such as molecular nitrogen, could not be excluded out of hand.

GOALS AND APPROACH

It is desirable to understand the mechanism of the orbital interaction of Kapton and other materials with atomic oxygen, to see whether the interaction is chemical or sputtering in nature, to determine reaction rates and temperature and energy dependences, to investigate the possibility of interfering with the interaction through the use of protective coatings or other materials, and to develop techniques for testing materials before flight. At Lewis Research Center it was decided to attempt the simulation of conditions in low Earth orbit in order to investigate these matters. Since it is difficult to accelerate neutral atomic species to orbital energies, it was decided to use accelerated ions in the Lewis simulation. It is clear from work on sputtering (ref. 2) that charge exchange with the surface can occur long before the momentum exchange, so that by the time the reaction energy is imparted by the incoming ions, they may be identical to neutral atoms for chemical purposes.

Thus an attempt was made to simulate the impact conditions in low Earth orbit by acceleration and impact of oxygen and other ions. Then the exposed specimens were analyzed and the results compared with those reported from shuttle flight experiments and other laboratory simulations. Reaction rates

and surface compositions were found. Finally an attempt was made to understand the laboratory results and to see what light they might shed on the flight results and on the reaction mechanism in order to simulate, understand, and suggest ways to control the reaction in low Earth orbit.

EXPERIMENTAL PROCEDURE

For the preliminary results reported herein, a tunable microwave resonant cavity (fig. 1) was used to dissociate and ionize technical grade (99.5 percent) oxygen gas. The gas was leaked into a glass container within the microwave cavity and, after ionization, was accelerated electrostatically to impact samples of Kapton. The experiment was done in vacuum tank 8 of the Electric Propulsion Laboratory at Lewis. Tank 8 is a horizontal circular cylinder about 1 meter in radius and 4 meters in length. Tank pressures were maintained by diffusion pumps at about 1.3×10^{-2} Pa (10^{-4} torr) during beam operation and at about 1.3×10^{-4} Pa (10^{-6} torr) with the beam off. The help of Shigeo Nakanishi of Lewis was invaluable in obtaining the experimental results reported herein.

The microwave cavity used a maximum of 100 W of radiation at a frequency of 2450 MHz. The cavity was electrically biased at a voltage of approximately 800 V, and the accelerating grid (made of molybdenum that was glass coated on one side) was biased to approximately -200 V. The ion beam produced was about 5 cm in diameter and diverged as it traversed the space between source and samples. A typical oxygen flow rate into the microwave cavity was about 4.2×10^{-7} m^3/s (25 standard cm^3/min).

The Kapton samples were supported by a strip heater with attached thermocouples. Source-to-sample distance was 10 cm for some trials and 23 cm for others. The samples were within 5 cm of the axial beam center. The plasma mean free path in all cases was longer than the source-to-sample distance. The beam was decelerated for some samples by biasing the aluminum backing to retarding potentials of up to 1000 V. The heater strip was insulated from the samples by two layers of 2.5×10^{-3}-cm-thick (1-mil) Kapton tape and from the tank wall by a fiberglass mounting beam. All wires in the cavity were covered with Teflon tubing to reduce glow discharges in the tenuous gas.

A retarding potential analyzer (RPA) that could be swung into and out of the beam was used to determine the beam current density. Typical RPA currents were 185 μA, which when divided by the RPA area of 13.4 cm^2 gives an average central beam current density of about 14 $\mu A/cm^2$. The beam was spectroscopically analyzed with a 0.5-m Jarrell-Ash spectrometer with 0.01-nm resolution. The spectrum shows that most of the beam consisted of singly ionized atomic oxygen, although lines of neutral atomic oxygen were prominent near the sample distance because of their greater radiative lifetimes. Equilibrium floating potentials on the heater strip while the beam was in operation were measured on the thermocouple wires to be in the range 400 to 500 V.

While the oxygen beam was operating, a faint white glow extended about 5 mm in front of impacted surfaces. Behind the sample holder a distinct greenish tinge could be seen in the diffuse glow of the beam. The white glow can be attributed to continuum radiation from oxygen recombination at the surface. The green glow appears spectroscopically (ref. 3) to be from the

first negative bands of O_2^+, which one suspects are caused by ionization of the recombined oxygen by the impinging ion beam.

Table I gives the parameters of the Lewis preliminary feasibility studies. Fluxes were calculated from RPA currents and estimated beam divergence and total fluence was calculated from fluxes and exposure times. In each case, the expected thermal flux of neutral oxygen was greater than the ion flux in the beam, and yet degradation occurred only in areas where the beam actually struck the samples. Thus the impact energy must be important to the degradation.

RESULTS AND ANALYSIS

Visual inspection of the bombarded surfaces showed that where the oxygen beam had struck, the smooth, yellow transparent surface of the Kapton had changed to a milky yellow translucence. Argon-bombarded samples at the same low fluence showed no such change, only a thin transparent metallic film that EDAX showed to be molybdenum sputtered from the uncoated side of the accelerator grid. Under oxygen bombardment, shadowed regions of the Kapton tape surrounding the sample holder showed no degradation, nor did areas outside the beam. In one case (11/24/82) the Kapton tape in the center of the beam showed a total loss of Kapton, with only the sticky silicone adhesive remaining. The aluminum back sides of argon-bombarded sample strips were scorched and blackened near the edges. EDAX later showed this to be a thin molybdenum coating, again presumed to be sputtered from the accelerator grid.

Under the scanning electron microscope the oxygen-bombarded samples had a carpetlike texture, with structures about 1 μm and smaller. They looked quite similar to samples returned by STS flights (fig. 2 from ref. 4). In contrast, pristine samples and argon-bombarded samples of Kapton were smooth at all magnifications.

Also, under a scanning electron microscope, an indication was obtained that the surface conductivity of Kapton was changed by ion bombardment. Both oxygen- and argon-bombarded samples retained their surface charge (as made visible by changes in magnification) for much shorter times than did the pristine control sample. It is not clear whether the change in surface conductivity was due to the presence of sputtered contaminants or in part to changes in surface composition.

Low-energy EDAX analysis of the samples was undertaken with the valued assistance of Paul Aron of Lewis. The instrument used had a windowless detector, which allowed very low-energy electrons to be used. Although EDAX at high energies (2.4×10^{-15} J, or 15 keV) showed the presence of aluminum, silicon, and molybdenum in the bombarded samples (presumably sputtered from the accelerator grid and tank wall fixtures) and their absence in the pristine samples, this was of limited usefulness in analyzing the change in surface composition of the Kapton. Pristine Kapton, being an extremely good insulator, will acquire a charge through loss of secondary electrons for incident electron energies above about 2.4×10^{-16} J (1.5 keV). Thus the pristine standard would see EDAX electrons of a different energy than those seen by the more conductive ion-bombarded samples.

Furthermore, electrons of 2.4×10^{-15} J (15 keV) energy have a mean free path in Kapton of about 6.4×10^{-4} cm (0.25 mil), which makes bulk composition and geometrical effects (due to the texture of the oxygen-bombarded surface) important in the analysis. For these reasons EDAX at incident energies of 1.6×10^{-16} J (1.0 keV) was undertaken. At this energy the mean free path of electrons in Kapton should be about 7.6×10^{-5} cm (0.03 mil). This would insure that the true surface composition would be measured, allowing only for shadowing on the X-ray counts from textured surfaces.

By taking mass attenuation coefficients and fluorescence yields from Robinson (ref. 5) and assuming a 3 percent metallic mass fraction from sputtered metals, the relative carbon, nitrogen, and oxygen abundances at the surface could be determined. Table II summarizes of the present results on samples at different EDAX electron energies. The composition measured with the 1.0-keV energy was significantly different from the pristine Kapton used as a calibration for both oxygen and argon-bombarded samples.

These results are insensitive to errors in the total count rate, electron penetration depth, and percentage of metals assumed, largely because the penetration depth is so small that there is less than 20 percent absorption for X-rays from any species. The composition obtained from the EDAX analysis can be compared with that which would occur if pristine Kapton lost 40 percent of its carbon atoms (normalizing to C, N, and O only): 59.4 percent C, 10.1 percent N, and 30.5 percent O. This suggests that the major change in composition of the surface was a severe loss of carbon. Since the electron penetration depths at energies of 4 and 15 keV were so much larger, a loss of carbon only near the surface was also consistent with the measurements made at those energies.

An Auger analysis of other samples done by W. Gordon and R. Hoffman of Case Western Reserve University and communicated to us has confirmed these results for oxygen bombardment (severe loss of carbon) but was quite variable for argon bombardment. It may be concluded that the surfaces of the oxygen-bombarded samples suffered a severe carbon loss, but for the argon-bombarded samples the situation is more complicated. For argon bombardment, composition changes may be due to selective sputtering (ref. 6); for oxygen bombardment, beam deceleration may have made sputtering unlikely. Since chemical interaction was indicated at any rate as the source of surface damage in oxygen bombardment, the major chemical change appeared to be oxidation of carbon on the surface, which then evolved as gaseous carbon monoxide or dioxide, leaving a carbon-depleted surface. This hypothesis is consistent with the reported rapid loss of pure carbon coatings in low Earth orbit (ref. 7).

The surface of the oxygen-bombarded samples became quite soft (easily scratched); abraded sections lost their milky translucence and became yellow and transparent, much like the pristine samples. Because no visible amount of material was left on the scratching implement, the change of optical properties was probably indicative only of a change in surface structure.

The indices of refraction of the samples were measured by ellipsometry. The ellipsometer used a He-Ne laser of wavelength 632.8 nm and had a resolution of ~0.1° in polarizer and analyzer angle. Despite some difficulty in keeping the samples flat, repeatable measurements were obtained, with the following results: although the pristine samples were very similar in optical properties

to their aluminum backing (which proved to be coated by a thin film itself), the ion-bombarded samples were significantly different from their aluminum backing. The real and imaginary parts of the index of refraction are given in table III.

The variation with position on the argon-bombarded sample can be ascribed to variations in the amount of sputtered molybdenum on the surface at different points. Position 2 closely resembled the apparent optical properties of the pristine sample.

Although the samples were aluminum backed, optical measurements were probably not heavily influenced by the aluminum backing because the surfaces of the oxygen-bombarded samples, and in particular of sample 2, were quite opaque. These optical values are probably not intrinsic to oxidized Kapton itself but are indicative of the values as changed by the surface structure, as discussed by Fenstermaker and McCrackin (ref. 8).

At the laser wavelength (632.8 nm) and angle of incidence (70°) used, no specular reflection was observed for sample 2. The observed change in reflectance of the oxidized Kapton may be due to the peculiar surface structure shown in the SEM photographs, which, when disturbed by scratching, reverted to the optical properties of smooth Kapton.

An attempt to calibrate the beam intensity by the changed optical properties of argon-bombarded samples, as described in Mirtich and Sovey (ref. 9), failed because of the thin, sputtered molybdenum film deposited in the present experiment.

Mass loss from the Kapton films was evident from the complete loss of material in the beam center in one trial. An estimate, from the depth of material removed and the measured beam fluxes, of the mass loss rate from two trials is given in table IV. The apparent mass loss rates were much higher than those ($\sim 3.72 \times 10^{-24}$ g/O atom) from shuttle experiments (ref. 10). This may be due to reactions in the tank with thermal oxygen atoms and molecules, which had a much greater flux against the sample than did the ion beam. The absence of reactions outside the beam area can be explained if the activation energy for the reactions is assumed to be supplied only by the energetic ions in the beam. Table V gives calculated reaction rates per thermal collision in the tank, assuming the ideal-gas law and pure oxygen at the tank pressure. These rates are consistent with those found on the shuttle and lend further credence to the hypothesis that the laboratory reaction is the same as that occurring in orbit.

SUMMARY AND INTERPRETATION OF RESULTS

The following aspects of the shuttle-returned samples were reproduced in the Lewis ion beam experiments:

(1) Visual appearance
(2) SEM surface structure
(3) Change from specular to diffuse reflection
(4) Directionality (ram dependence)

In addition, the mass loss would have been consistent with rates seen in orbit if ambient thermal gas in the experiment could share in the activation energy supplied by the beam.

The following findings were new to this experiment and suggest further tests on the shuttle samples:

(1) Reduced scratch resistance of surface
(2) Loss of carbon from surfaces
(3) Enhanced surface conductivity
(4) Confirmation that chemistry is involved in surface structure changes

The structures seen on O^+-bombarded Kapton surfaces seemed to be responsible for the change in specular reflectivity. In addition, the loss of carbon suggested that these surface structures may have been produced by oxygen preferentially attacking certain bonds in the polymer. The bonds that are probably attacked most readily are the C-N bond (E = 3.2 eV), the C-O bond (E = 3.7 eV), and the C-C bond (E = 3.8 eV) (ref. 11), all with energies below the apparent impact energy of atomic oxygen in low Earth orbit. Breaking the C-N and C-O bonds breaks the polymer chain, weakening the material and allowing penetration of succeeding oxygen atoms deeper into the plastic. Furthermore, succeeding breaks of the C-C bonds can allow oxidation of the dangling carbon, leading to a volatile product and mass loss.

CONCLUSIONS

It is encouraging that this simulation of low-Earth-orbit conditions using O^+ ion beams succeeded in qualitatively reproducing all of the observed characteristics of the interaction of Kapton with the Earth's atmosphere in space shuttle flights. Oxidation is undoubtedly responsible, as opposed to sputtering or reaction with other species, since simulation with O^+ was successful and high-energy impact by an inert gas did not produce the observed characteristics of samples returned from orbit. It may be possible to test a variety of materials for reactivity and quantitative mass loss rates by using O^+ ion beams in the laboratory.

Regardless of the specific chemical reaction involved, it has already been found that other materials are minimally reactive or nonreactive. It may be possible to retain the desirable characteristics (radiation resistance, electrical resistance, strength, flexibility, and high-temperature stability) of Kapton for use as a substrate by coating it with less reactive films. Oxygen ion beam bombardment is a feasible method of testing such new materials before using them in space. Much work remains to be done at Lewis and elsewhere in testing materials and clarifying the reactions that take place.

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TABLE I. - PARAMETERS OF PRELIMINARY FEASIBILITY STUDIES

Date	Thickness, mils	Material	Ion	Flux $cm^{-2}s^{-1}$	Fluence, cm^{-2}	Impact energy		Sample temperature		Pressure	
						J	eV	K	°F	Pa	torr
11/24/82	1	Kapton tape	O+	$(6\text{-}12)\times10^{14}$	1.3×10^{18}	$(0\text{-}1300)\times10^{-19}$	0-800	450-500	350-440	1.7×10^{-2}	1.3×10^{-4}
12/08/82	1/2, 1, 3, and 5	Al-backed Kapton	O+	$(2\text{-}3)\times10^{13}$	2.1×10^{17}	$(0\text{-}80)\times10^{-19}$	0-50	304-309	88-96	1.2×10^{-2}	9.2×10^{-5}
12/09/82	1/2, 1, 3, and 5	Al-backed Kapton	O+	$(2\text{-}3)\times10^{13}$	2.4×10^{17}	$(<50)\times10^{-19}$	<30	344	160	1.6×10^{-2}	1.2×10^{-4}
12/22/82	1/2, 1, 3, and 5	Al-backed Kapton	Ar+	$(3\text{-}4)\times10^{13}$	5.2×10^{17}	$(1704)\times10^{-19}$	1065	311-347	100-165	5.6×10^{-3}	4.2×10^{-5}

TABLE II. - PERCENTAGE BY WEIGHT OF ELEMENTS C, N, AND O

[Assumes 3 percent metals, normalized to C + N + O = 100.0.]

(a) Argon bombardment ($E \approx 1.6\times10^{-16}$ J, or 1000 eV)

Electron energy		Element	Element content, wt %	Pure Kapton content, wt %
J	keV			
1.6×10^{-16}	1.0	C	58.1	71.1
		N	8.5	7.2
		O	33.4	21.6
6.4×10^{-16}	4.0	C	66.9	71.1
		N	6.5	7.2
		O	26.5	21.6
2.4×10^{-15}	15.0	C	72.8	71.1
		N	6.6	7.2
		O	20.6	21.6

(b) Oxygen bombardment ($E \lesssim 4.8\times10^{-18}$ J, or 30 eV)

1.6×10^{-16}	1.0	C	61.2	71.1
		N	7.0	7.2
		O	31.8	21.6
6.4×10^{-16}	4.0	C	70.4	71.1
		N	7.1	7.2
		O	22.4	21.6
2.4×10^{-15}	15.0	C	66.8	71.1
		N	8.6	7.2
		O	24.6	21.6

TABLE III. - COMPLEX INDICES OF REFRACTION FROM ELLIPSOMETRY

Ion	Sample	n (real)	K (imaginary)
O^+	1	1.16	[a]-0.22
O^+	2	2.72	-0.34
Ar^+	1(position 1)	2.4±0.4	-0.8±0.6
Ar^+	1(position 2)	1.0±0.3	2.2±0.1
Pristine		0.5±0.2	1.9±0.1

[a]Errors for the oxygen-bombarded samples are <0.1 in both parts of the index of refraction.

TABLE IV. - DERIVED RATES OF REACTION ASSUMING ONLY OXYGEN ION BEAM REACTION

Date	O^+ fluence, cm^{-2}	Rate, g/O^+ ion	Method
11/24/82	1.3×10^{18}	$>2.8\times10^{-22}$	Total loss of 1-mil layer
12/09/82	2.4×10^{17}	$\geq5\times10^{-22}$	SEM photographs

TABLE V. - DERIVED REACTION RATES ASSUMING AMBIENT OXYGEN REACTIONS

Date	Thermal fluence	Reaction rate, g/collision
11/24/82	$\sim1.9\times10^{21}$	$>2\times10^{-25}$
12/09/82	$\sim9.4\times10^{20}$	$\geq1\times10^{-25}$

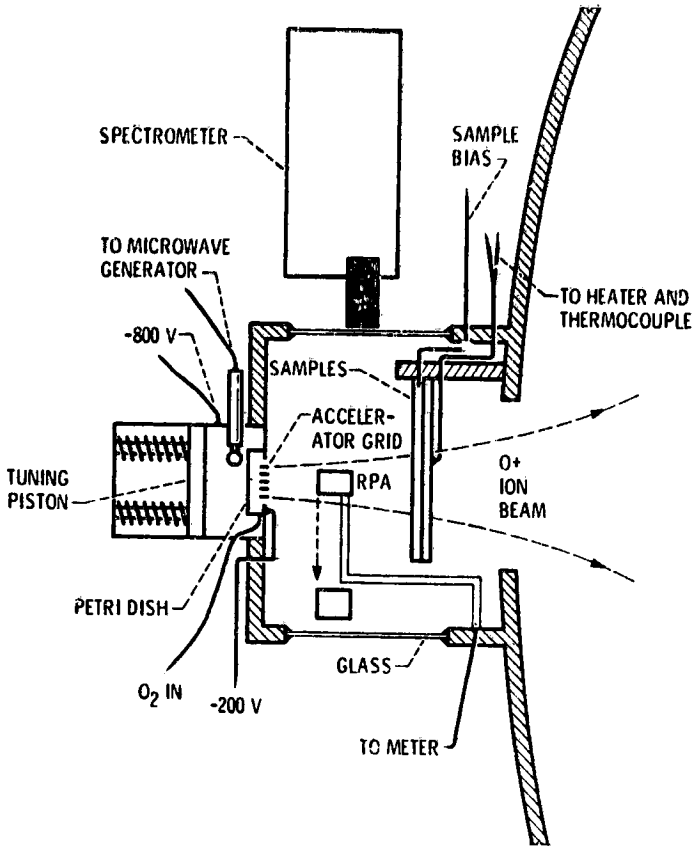
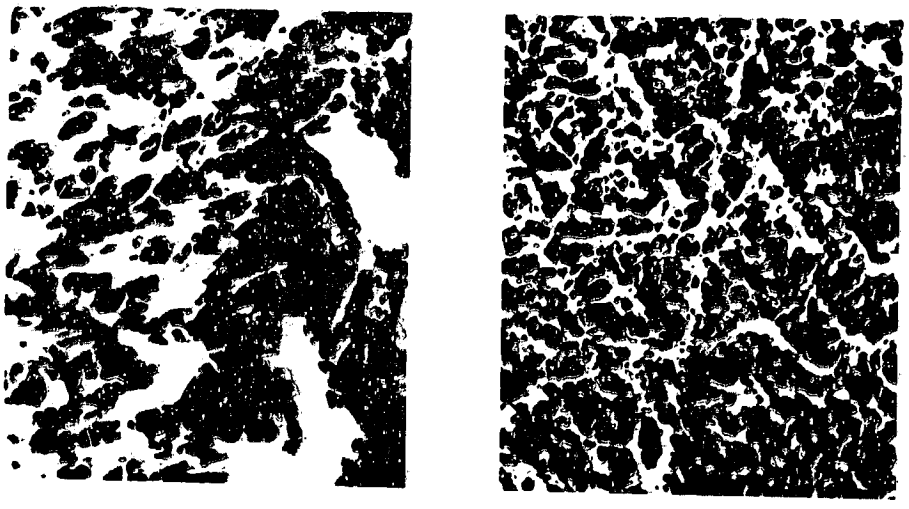


Figure 1 - The experimental setup.



(a) Lewis Research Center O^+ beam exposure.

(b) STS-2 orbital exposure.

Figure 2. - Surface structure of exposed samples. SEM magnification 10,000 X.