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An Evaluation of Candidate Oxidation Resistant Materials for Space Applications in LEO

Sharon Rutledge and Bruce Banks
Lewis Research Center
Cleveland, Ohio

Frank DiFilippo
Case Western Reserve University
Cleveland, Ohio

Joyce Brady, Therese Dever, and Deborah Hotes
Cleveland State University
Cleveland, Ohio

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AN EVALUATION OF CANDIDATE OXIDATION RESISTANT MATERIALS FOR SPACE APPLICATIONS IN LEO

Sharon Rutledge and Bruce Banks
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

Frank DiFilippo
Case Western Reserve University
Cleveland, Ohio 44106

Joyce Brady, Therese Dever, and Deborah Hotes
Cleveland State University
Cleveland, Ohio 44115

SUMMARY

Ground based testing of materials considered for polyimide (Kapton) solar array blanket protection and graphite-epoxy structural member protection was performed in an RF plasma asher. Protective coatings on Kapton from various commercial sources and from NASA Lewis Research Center were exposed to the air plasma; and mass loss per unit area was measured for each sample. All samples evaluated provided some protection to the underlying surface, but metal oxide-fluoropolymer coatings provided the best protection by exhibiting very little degradation after 47 hr of asher exposure. Mica paint was evaluated as a protective coating for graphite-epoxy structural members. Mica appeared to be resistant to attack by atomic oxygen, but only offered limited protection as a paint. This is believed to be due to the paint vehicle ashing underneath the mica leaving unattached mica flakes lying on the surface. The protective coatings on Kapton evaluated so far are promising but further research on protection of graphite epoxy support structures is needed.

INTRODUCTION

Since the earliest shuttle flights, the durability of materials exposed to the low Earth orbital (LEO) environment has been of great concern (ref. 1). Materials such as polyimides (Kapton), graphite-epoxy, carbon, and some metals are subject to mass loss and surface texturing upon exposure to this environment (refs. 1 to 4). Ultraviolet light from the sun having a wavelength of less than 2430 Å has sufficient energy ($\leq$5.115 eV) to cause oxygen to photodissociate to produce atomic oxygen (ref. 5). The impact of atomic oxygen with a surface may contain enough energy (4.2 to 4.3 eV) to break chemical bonds, leading to oxidation (degradation) of the exposed surface. Mass loss rates documented on shuttle experiments to date are high enough to cause concern for the long term durability of many materials for application on Space Station and other missions in LEO.

Kapton solar array blankets are being considered for Space Station deployable solar arrays. The Kapton would be used as both a structural component, which the cells and interconnects are mounted to, and as a thermal

transfer device to transmit heat from the back side of the solar cells. If the thickness of a 457 cm wide by 0.0051 cm thick array blanket is reduced by approximately 99 percent while the blanket is under a tensile force of 3.34×10^7 dynes, the blanket will experience mechanical failure. If these conditions exist for an array panel on Space Station, it is estimated that structural failure, due to mass loss from atomic oxygen degradation, will occur in approximately 0.43 years in the proposed constant density (ref. 6) Space Station orbit. Prior to this, surface texturing could lead to a decrease in the infrared transmittance resulting in an inability of the solar cells to reject heat from the back side. If Kapton is to be used, coatings are needed which can protect against degradation by atomic oxygen, and allow the underlying Kapton to maintain its optical integrity.

Graphite-epoxy is being considered for use in structural support trusses for Space Station. Protection of truss members is needed, because of the high surface loss rate of graphite-epoxy. One method of protection is to apply to the members a paint in which the filler is comprised of a material, such as mica, which is resistant to attack by atomic oxygen. It is hoped that upon drying, the high aspect ratio mica flakes in the paint will form an interleaving surface which can act as a barrier against atomic oxygen.

This paper presents an overview of various coatings tested for protection of array blankets, and mica paint for protection of graphite-epoxy composite structures.

APPARATUS AND PROCEDURE

Dehydration and Rehydration of Kapton

In order to assess the ability of a coating to protect the Kapton substrate, accurate mass measurements are needed. The mass of Kapton can fluctuate due to the variation in the absorption of water from the environment and in the amount of dehydration in the vacuum of the asher chamber. Two methods which can be used to correct for water in the Kapton are (1) to allow samples to fully rehydrate after exposure in the asher or (2) to fully dehydrate the samples in vacuum prior to making the mass measurement. In order to determine the time for complete dehydration, 0.127 mm (5 mil) and 0.0254 mm (1 mil) thick samples of Kapton HN were allowed to dehydrate in vacuum at a pressure of approximately 30 μm for different lengths of time. Masses were recorded prior to and directly after removal from the vacuum chamber. Sample mass changed rapidly within the first 2 hr of vacuum exposure, and samples experienced complete dehydration after 2 days (figs. 1(a) and (b)). The dehydration rate appears to be similar for 1 mil and 5 mil Kapton samples. Curiously, the presence of a coating on both the top and bottom surfaces also appears to have no effect on the dehydration rate since both mass loss rate curves shown are within the standard deviation of each other (fig. 1(c)).

In order to determine the time for complete rehydration, Kapton HN samples were dehydrated fully for 2 days in vacuum then allowed to rehydrate under a relatively constant humidity (55 to 70 percent) environment (fig. 1(d)). Rehydration occurred at a much slower rate than the dehydration. The fraction of initial mass per unit area began to exceed unity with time indicating that the right-hand portion of the curve may move up and down with the environmental humidity. This demonstrates that a controlled humidity environment is needed

if an accurate assessment of when complete rehydration occurs is to be obtained.

Based on these results, it appears that the best method for taking absorbed water into account is to allow the samples to fully dehydrate in vacuum prior to each weighing. The rehydration occurs at a rate slow enough that water absorption upon removal from vacuum should not play a significant role in the error if the mass measurement is made within about 5 min after removal from the vacuum chamber. For evaluation of coated and uncoated Kapton, samples were allowed to fully dehydrate for 2 days in the vacuum of the asher prior to weighing.

Protective Coatings for Kapton

Several commercial coatings on Kapton were supplied by vendors to undergo durability testing to an atomic oxygen environment. Tekmat Corporation supplied Kapton that had been fluorinated to a depth of 200 Å. Andus Corporation supplied magnetron sputter deposited composite coatings on Kapton of 16 percent polytetrafluoroethylene (PTFE)-84 percent silicon dioxide (SiO_2), 8 percent PTFE-92 percent SiO_2, and pure SiO_2 of an average thickness of 500 to 1000 Å. Baltelle supplied a silicone fluoropolymer coating on Kapton that had been plasma polymerized to a thickness of approximately 3000 to 4000 Å. Also evaluated were 8 percent PTFE-92 percent SiO_2 and pure SiO_2 coatings on Kapton HN that had been ion beam sputter deposited in-house at NASA Lewis to thicknesses of approximately 800 to 1000 Å. The uncoated Kapton evaluated was also type HN, Kapton HN will be referred to as Kapton for the remainder of the paper.

Environmental Testing

Environmental durability testing was performed in an SPI Plasma Prep II RF plasma asher. Ambient air, ionized at a frequency of 13.56 MHz at a total chamber pressure of approximately 75 μm was used for all exposure tests performed unless otherwise mentioned.

Plasma ashers are widely used for environmental testing because they can provide a quick, general test of survivability. Materials that survive in LEO usually survive in ashers and those that degrade in LEO always degrade in ashers. The relative rates of degradation between the asher and specific altitudes in LEO differ with the material being exposed. Thus, ashers give a qualitative measure of survivability but not a quantitative one. For all plasma asher exposure tests, air was used as the gas for the plasma. Since the primary specie in the LEO environment is atomic oxygen, there may be some error introduced in survivability determination caused by the reaction of species with the Kapton that are not abundantly present in the LEO environment. Since the prime constituent of air is nitrogen rather than oxygen it is important to know if nitrogen derived species are reacting with the Kapton. In order to determine if this occurred, 5 mil Kapton was ashed both in nitrogen at a total pressure of 160 μm with an air base pressure of approximately 20 μm, and in air at 65 μm. The Kapton samples exposed to the air plasma exhibited a much higher loss in mass as a function of ashing time (fig. 2). The Kapton ashed in nitrogen degraded less than half as fast as the Kapton ashed in air, but still had

a definite mass loss with time. This may be due to the oxygen in the background air present in the asher rather than the nitrogen itself. If the main reacting species are really those that are oxygen derived, then an RF air discharge can be used as a screening technique for material survivability in the LEO environment.

RESULTS AND DISCUSSION

Protection of Kapton

Kapton samples protected commercially by (1) fluorination, (2) sputter deposited metal oxide-fluoropolymer coatings, and (3) plasma polymerized silicone-fluoropolymer coatings, were evaluated for durability to an atomic oxygen environment. Uncoated and untreated Kapton, and ion beam sputter deposited metal oxide-fluoropolymer coated Kapton produced at NASA Lewis were evaluated along with the commercially produced coatings for comparison. Mass loss versus asher exposure time was recorded for all of the samples. If only one side of the Kapton was coated, samples were sandwiched together with double stick Kapton tape so that only the coating was exposed to the plasma environment.

Kapton that had been fluorinated to a depth of 200 Å appeared to offer some initial protection and then degraded at about the same rate as the uncoated Kapton (fig. 3(a)).

Commercially magnetron sputter deposited metal oxide-fluoropolymer coatings offered protection for a longer period of time, but samples with 16 percent PTFE degraded at the same rate as the uncoated Kapton after ashing for 24 hr, which indicated that the protective coating may no longer be present (fig. 3(b)). Lower mass loss rates were observed for those coatings with lower percentages of fluoropolymer. The magnetron sputter deposited coatings were found to not adhere as well to the substrate as the ion beam sputter deposited coatings. This may account for the difference observed in the mass loss with ashing time. Methods are currently being examined by the manufacturer to improve the adherence of these coatings to the Kapton.

Plasma polymerized silicone-fluoropolymer coated Kapton exhibited little to no degradation with ashing time (fig. 3(c)). Slopes were similar to that for ion beam sputter deposited 8 percent PTFE-92 percent SiO_2 on Kapton with a thickness of approximately 800 Å. Ion beam sputter deposited metal oxide-fluoropolymer coatings produced by a similar technique have been flight tested and found to be protecting in the LEO environment.

Overall, coatings of metal oxide-polymer both produced in-house and commercially appear to offer protection to Kapton in asher tests. Figure 4 illustrates the degradation rate for these coatings in comparison to unprotected Kapton. The Space Station goal shown is based on the highest mass loss rate of Kapton that can be tolerated for a 15 year life at the constant density Space Station orbit when scaled to give an equivalent rate in the asher. Assuming that the only loss that occurs from the coated samples is due to the ashing of Kapton rather than the coating, a comparison can be made between this goal and the mass loss rate of the coated samples. This is probably a reasonable assumption since the mass loss rate of metal oxide is so much lower than

that of Kapton in LEO and the metal oxide rate probably does not accelerate as much as the rate for Kapton in an asher. Based on these assumptions, it appears that the plasma polymerized silicone fluoropolymer and ion beam sputter deposited 8 percent PTFE-92 percent SiO_2 offer adequate protection to Kapton. If the adherence of the magnetron sputter deposited coatings could be improved, it is believed that the rates for these could be as low.

Protection of Graphite-Epoxy

Various compositions of mica paint were produced by mixing 4.6, 20.6, and 31.6 percent of number 160 muscovite mica in a water-borne polyurethane based paint (Sancure 847). Percentages of mica higher than 31.6 percent could not be used because the paint became too thick to spread. The mica paint was applied to the top surface of 2.5 cm by 2 cm by 2 mm graphite-epoxy squares, whose edges had been covered with aluminum tape, and allowed to completely dry in air. After drying, the painted graphite-epoxy was exposed in a plasma asher for varying lengths of time.

The samples with larger percentages of mica exhibited longer initial protection of the graphite-epoxy substrate as evidenced by their lower slopes (fig. 5). Eventually, all samples degraded at nearly the same rate as the unprotected graphite-epoxy. Scanning electron microscopy reveals the reason the mica paint does not stay protecting. It appears that the paint medium ashes from between and underneath the mica leaving unattached mica flakes lying on the surface which can easily be removed (figs. 6(a) and (b)). Where a portion of the flakes were removed prior to viewing, exposed and degraded portions of graphite fiber are evidence of ashing of the surface underneath the mica paint (figs. 6(c) and (d)). Varying amounts of water were added to the paint at a fixed mica mass percentage to see if thinning the paint would allow greater and closer interleaving of the mica flakes upon drying. Addition of water up to 70 percent slightly improved the coating protection. At larger percentages the paint became too thin to allow the mica to be spread evenly. Results so far indicate that mica paint offers very limited protection.

The mica paint may not be protecting in the asher because the plasma can approach the sample in all directions giving a greater opportunity for undercutting. Mica paint may protect the substrate from directed flux degradation more effectively because there would be less line of sight between the atomic oxygen and the paint medium (fig. 7). Asher exposure may also yield different results if large air pockets in the paint underneath the mica become ionized in the RF discharge causing the paint to degrade from the inside. Other paint bases and directed flux exposure need to be examined to determine whether mica paint is a practical solution for protecting graphite-epoxy.

CONCLUSION

Adequate protection of Kapton appears feasible based on mass loss results obtained for metal oxide-fluoropolymer coatings on Kapton exposed to an air discharge in a plasma asher. Mass loss rates appear to fall within the desired Space Station goal if the coating material ratios for LEO to asher conversion are similar to or less than that for Kapton. Coatings similar to this have

been flight tested on STS-8 and proved to be protecting. They can also be produced commercially in quantities suitable for fabrication of large scale solar arrays. The results obtained for the protection of graphite-epoxy by using mica paint are not as promising. The paint offers limited protection to the underlying surface. The extent to which the RF plasma exposure technique, as opposed to a directed beam exposure, contributes to the degradation is unknown at present.

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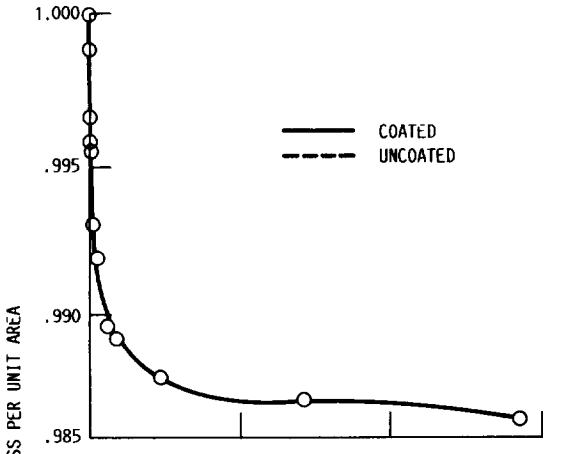
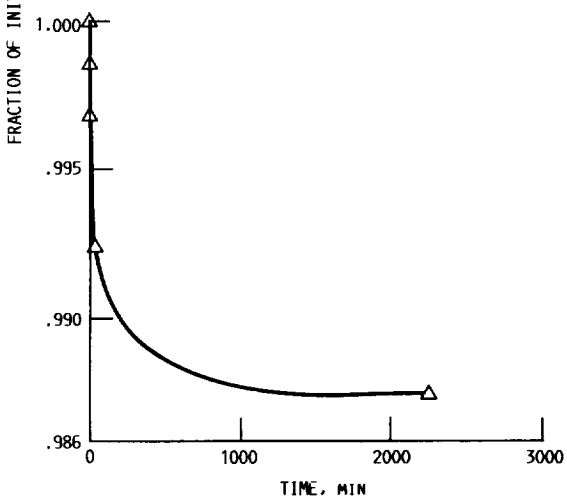
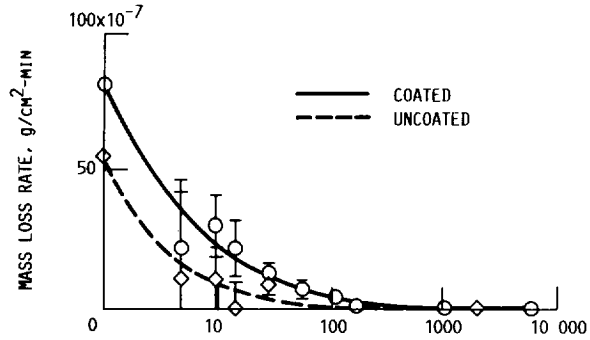


(A) MASS CHANGE OF 5 MIL KAPTON UPON DEHYDRATION UNDER VACUUM AS A FUNCTION OF TIME.

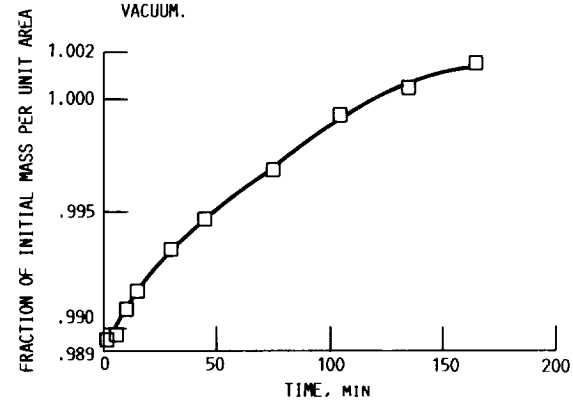


(B) MASS CHANGE OF 1 MIL KAPTON UPON DEHYDRATION UNDER VACUUM AS A FUNCTION OF TIME.

FIGURE 1. - DEHYDRATION AND REHYDRATION OF COATED AND UNCOATED KAPTON OF VARYING THICKNESS.



(C) MASS LOSS RATE OF COATED 1 MIL KAPTON VERSUS UNCOATED 1 MIL KAPTON WITH RESPECT TO TIME IN VACUUM.



(D) MASS CHANGE OF 5 MIL KAPTON UPON DEHYDRATION AS A FUNCTION OF TIME.

FIGURE 1. - CONCLUDED.

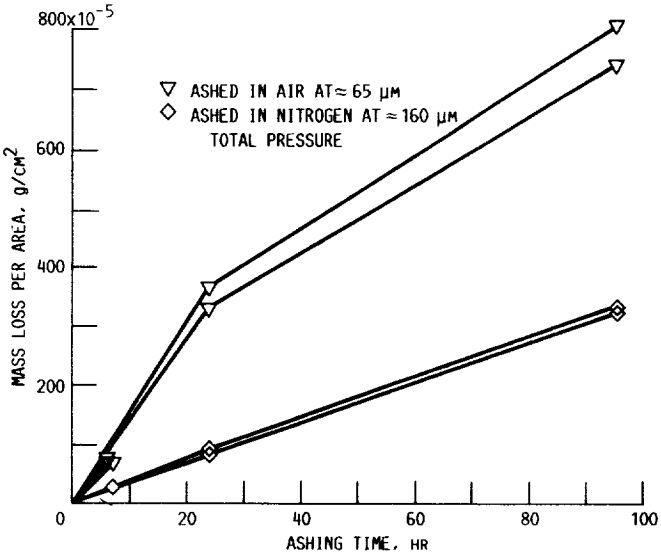
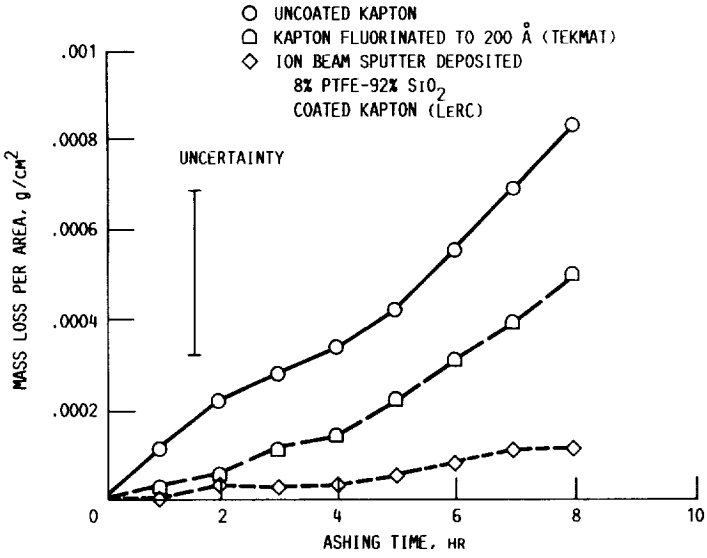
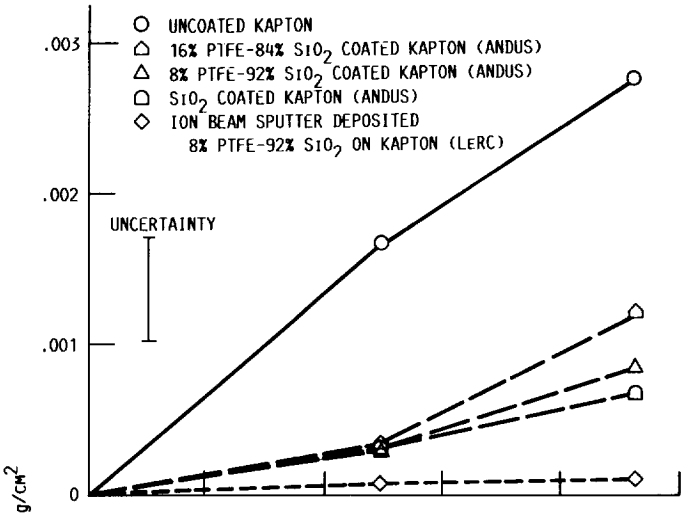


FIGURE 2. - EFFECT OF ASHER PLASMA SPECIES ON MASS LOSS RATE OF 5 MIL KAPTON.

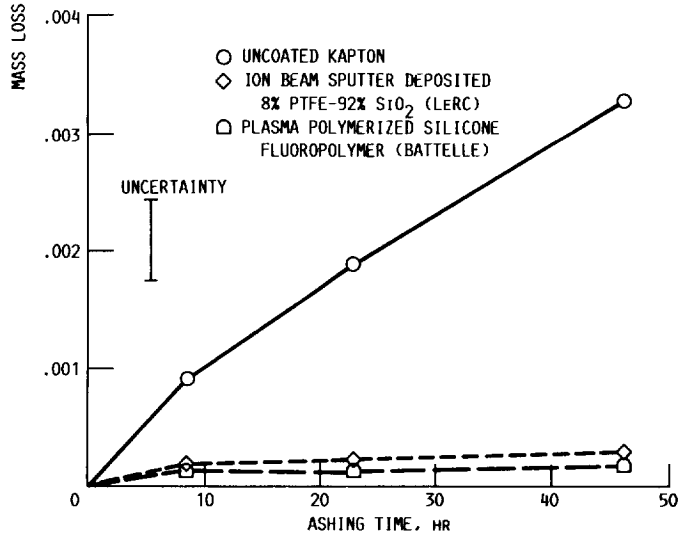


(A) MASS LOSS PER UNIT AREA COMPARISON OF UNCOATED KAPTON, FLUORINATED KAPTON AND ION BEAM SPUTTER COATED KAPTON, AS A FUNCTION OF TIME IN THE ASHER.

FIGURE 3. - AN ASHING RATE COMPARISON OF COATED AND UNCOATED KAPTON.



(B) MASS LOSS PER UNIT AREA COMPARISON OF UNCOATED KAPTON, MAGNETRON SPUTTER COATED, AND ION BEAM SPUTTER COATED KAPTON AS A FUNCTION OF TIME IN THE ASHER.



(C) MASS LOSS PER UNIT AREA COMPARISON OF UNCOATED KAPTON, PLASMA POLYMERIZED, AND ION BEAM SPUTTER COATED KAPTON AS A FUNCTION OF TIME IN THE ASHER.

FIGURE 3. - CONCLUDED.

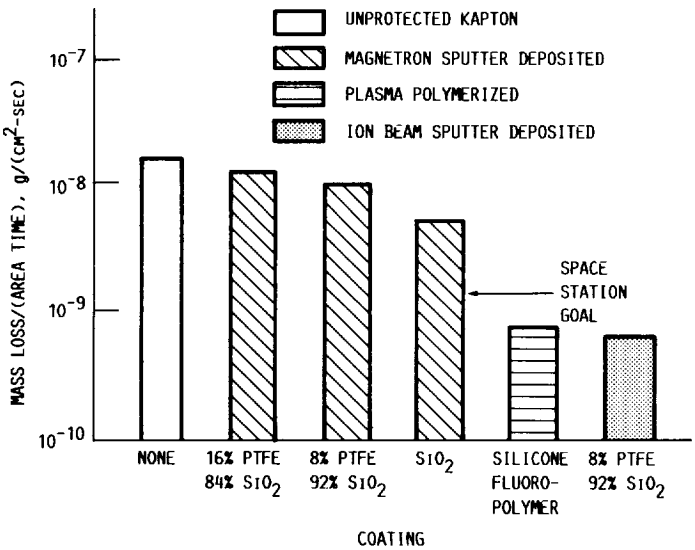


FIGURE 4. - AN ASHING RATE COMPARISON OF METAL OXIDE-FLUOROPOLYMER COATED AND UNCOATED KAPTON.

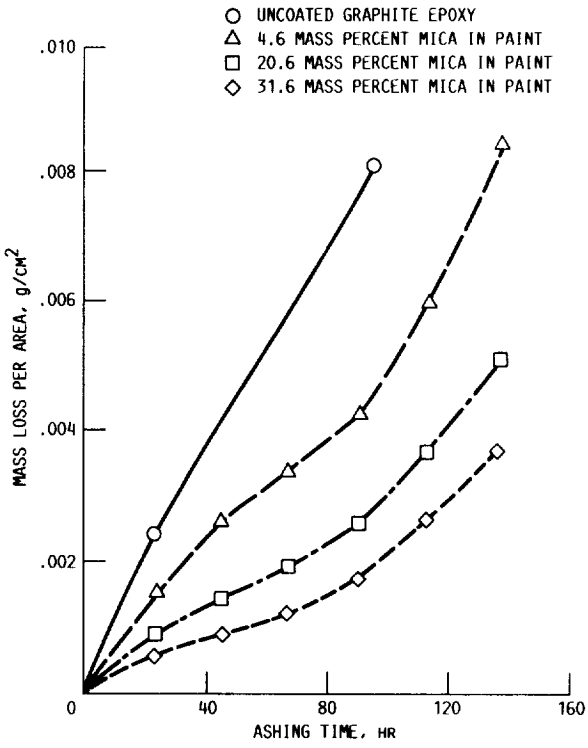
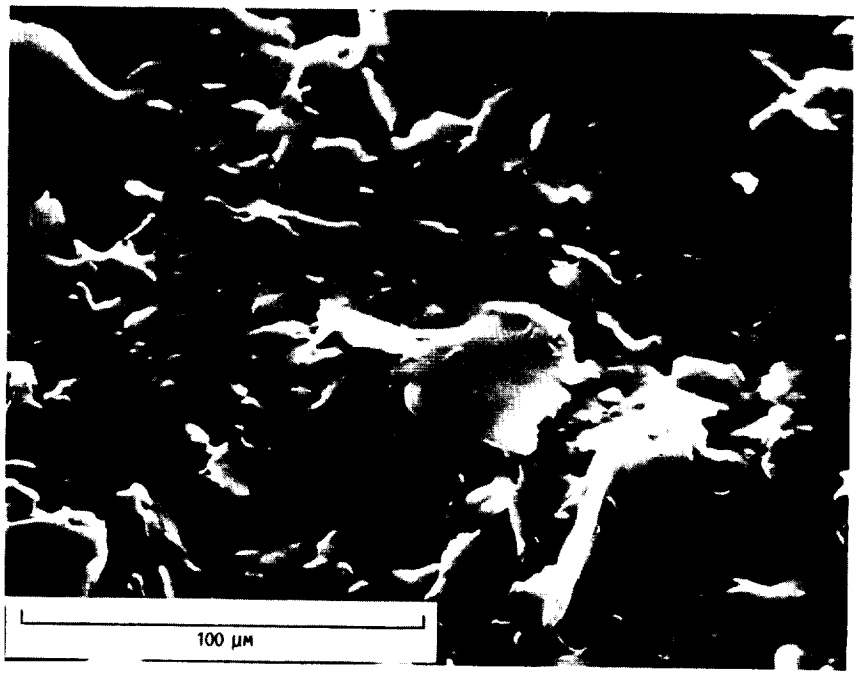
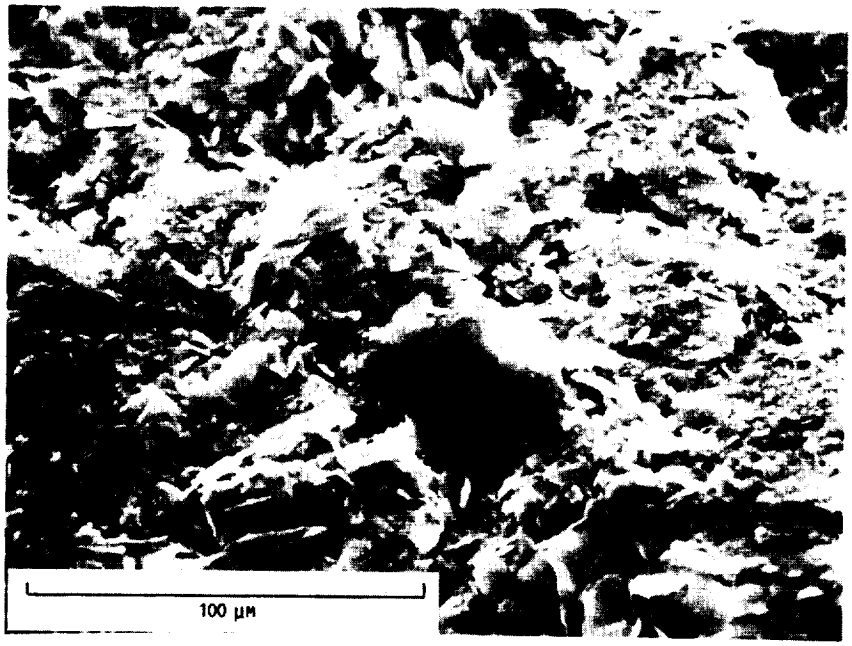


FIGURE 5. - MASS LOSS RATE COMPARISON OF MICA PAINTED GRAPHITE EPOXY OF VARYING MASS PERCENTAGES OF MICA FILL IN SANCURE 847 PAINT.

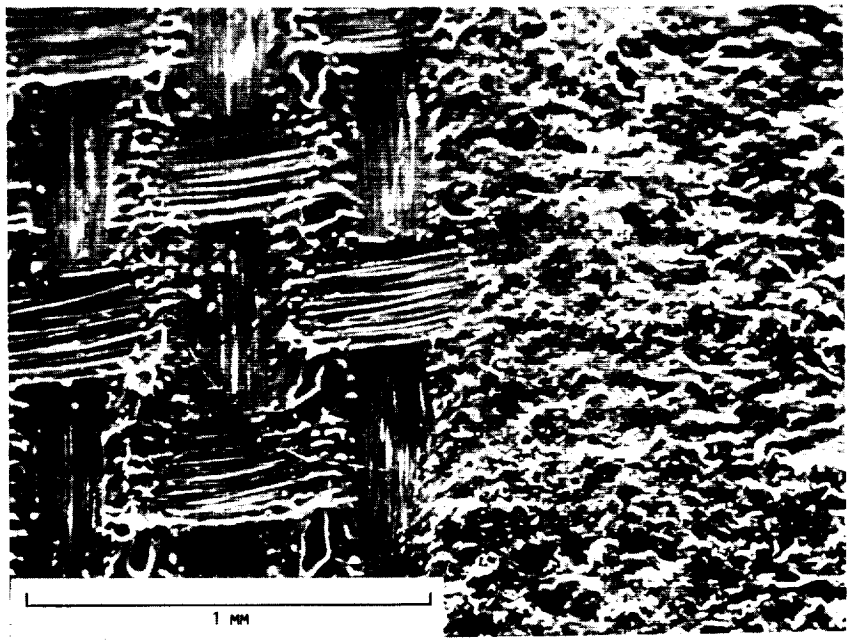


(A) 20.6 MASS PERCENT MICA PAINT ON GRAPHITE EPOXY.

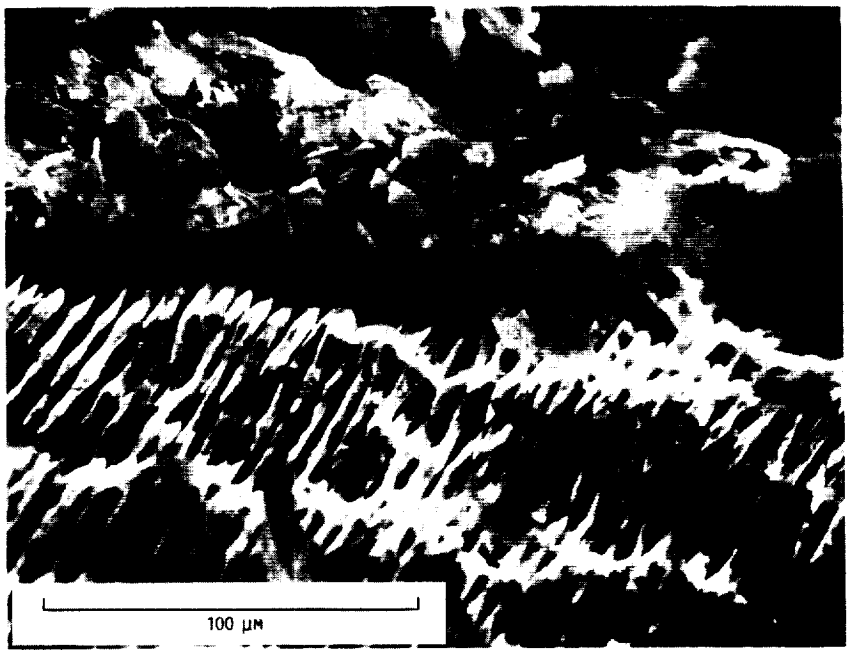


(B) 20.6 MASS PERCENT MICA PAINT ON GRAPHITE EPOXY AFTER APPROXIMATELY 22 HR EXPOSURE IN AN ASHER.

FIGURE 6. - A COMPARISON OF MICA PAINT COATED GRAPHITE EPOXY PRIOR TO AND AFTER ASHING.

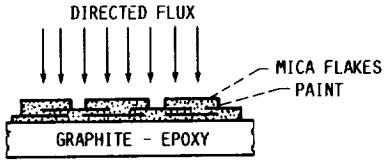


(C) GRAPHITE EPOXY WITH THE RIGHT HALF OF THE SAMPLE COATED WITH 20.6 MASS PERCENT MICA PAINT.

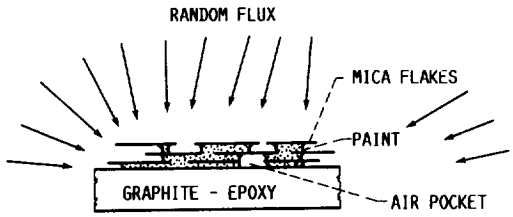


(D) 20.6 MASS PERCENT MICA PAINT ON GRAPHITE EPOXY AFTER 228 HR OF EXPOSURE IN AN ASHER. BOTTOM PORTION SHOWS UNDERLYING GRAPHITE EPOXY SUBSTRATE AFTER MICA FLAKES HAVE BEEN REMOVED.

FIGURE 6. - CONCLUDED.



(A) POSSIBLE APPEARANCE OF MICA PAINTED SURFACE WHEN EXPOSED TO A DIRECTED FLUX WITH MINIMAL SIDE SCATTER.



(B) POSSIBLE APPEARANCE OF MICA PAINTED SURFACE WHEN EXPOSED TO A RANDOM FLUX SUCH AS EXISTS IN THE ASHER.

FIGURE 7. - POSSIBLE MICA PAINT CONFIGURATIONS WHEN EXPOSED TO DIFFERENT FLUX ORIENTATIONS.

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16. Abstract

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