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Low Earth Orbit Environmental Durability of Recently Developed Thermal Control Coatings

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Abstract

The Materials International Space Station Experiment provided a means to expose materials and devices to the low Earth orbit environment on the exterior of the International Space Station. By returning the specimens to Earth after flight, the specimens could be evaluated by comparison with pre-flight measurements. One area of continuing interest is thermal control paints and coatings that are applied to exterior surfaces of spacecraft. Though traditional radiator coatings have been available for decades, recent work has focused on new coatings that offer custom deposition or custom optical properties. The custom deposition of interest is plasma spraying and one type of coating recently developed as part of a Small Business Innovative Research effort was designed to be plasma sprayed onto radiator surfaces. The custom optical properties of interest are opposite to those of a typical radiator coating, having a combination of high solar absorptance and low infrared emittance for solar absorber applications, and achieved in practice via a cermet coating. Selected specimens of the plasma sprayed coatings and the solar absorber coating were flown on Materials International Space Station Experiment 7, and were recently returned to Earth for post-flight analyses. For the plasma sprayed coatings in the ram direction, one specimen increased in solar absorptance and one specimen decreased in solar absorptance, while the plasma sprayed coatings in the wake direction changed very little in solar absorptance. For the cermet coating deployed in both the ram and wake directions, the solar absorptance increased. Interestingly, all coatings showed little change in infrared emittance.

Introduction

Surfaces on the outside of spacecraft are exposed to many environmental threats, which can be harmful to the spacecraft and their operations (Ref. 1). In low Earth orbit these threats include: ultraviolet radiation and solar flare x-rays, electrons and protons, temperature extremes and thermal cycling, micrometeoroid and orbital debris impacts, and atomic oxygen (Ref. 2).

Coatings selected for use on the exterior of a spacecraft to control the temperature of the underlying material are known as thermal control coatings. Some coatings have the combination of low solar absorptance and high infrared emittance for the purpose of rejecting heat, while other coatings have the combination of high solar absorptance and low infrared emittance for the purpose of absorbing heat, from sunlight. The tailored optical properties are achieved in practice by incorporating appropriate materials and material combinations. The thermal control coatings that are tailored to reject waste heat from the spacecraft achieve the combination of low solar absorptance and high infrared emittance by incorporating materials that are reflective in the visible wavelength range and emissive in the infrared wavelength range. Zinc oxide pigment imbedded in a potassium silicate binder serves as one means of achieving the desired optical properties and radiators utilized for heat rejection are coated with such a coating. As a fully oxidized oxide and silicate, the pigment and binder are durable to the atomic oxygen environment in low Earth orbit. It is undesirable for the solar absorptance to increase substantially with time. Some darkening does occur as a result of ultraviolet radiation, because of the formation of color centers at the molecular level after years of service. Hence, spacecraft designers often utilize both beginning-of-life and end-of-life optical property values in determining the design of the spacecraft exterior surface. Though traditional radiator coatings have been available for decades, recent work has focused on new coatings that are applied via custom deposition. One coating recently developed as part of a Small Business Innovative Research (SBIR) effort with Applied Materials Systems Engineering, Inc., was designed to be plasma sprayed onto high temperature carbon-carbon composite radiator surfaces (Refs. 3 and 4). The thermal control coatings that are tailored to absorb heat from the sun often achieve the combination of high solar absorptance and low infrared emittance by utilizing molecular mixtures of ceramic oxides and metals, known as cermets, that are achieved in practice by ion beam sputter deposition. One coating recently developed by Glenn Research Center was designed to absorb solar energy at the hot end of a Stirling convertor (Refs. 5 to 8). Given the importance of controlling the heat flow into the Stirling convertor, it would be undesirable for the solar absorptance to decrease over time. Specimens of both of these new coatings were flown on Materials International Space Station Experiment 7 (MISSE 7) to evaluate their durability to the space environment (Ref. 9).

Early versions of the plasma sprayed coatings were flown on the MISSE 6 Thermal Control Paints Experiment (Ref. 10). These specimens were also developed by Applied Materials Systems Engineering, Inc., including new binder and pigment, and the process of plasma spraying (Ref. 3). Ground-based testing was completed at the Space Combined Effects Primary Test and Research Facility (SCEPTRE) prior to the MISSE 6 flight and the early specimens exhibited acceptable Beginning-of-Life and End-of-Life optical properties to simulated 1 keV, 10 keV, and 4.5 MeV electrons. Exposure to 1.45 yr of the low Earth orbit environment on MISSE 6 validated the early versions of the plasma sprayed coatings (Ref. 4). The final version of the plasma sprayed coating, PS–16, was selected for use on the Gravity Recovery And Interior Laboratory (GRAIL) carbon-carbon composite radiators and was selected for durability evaluation on MISSE 7B.

Cermet coatings have been studied extensively in the past for the purpose of capturing and utilizing the sun’s energy for solar thermal applications (Refs. 5 to 7). The cermet coatings here were deposited utilizing ion beam sputter deposition from an innovative pie-shaped ceramic target on a cylindrical frame. Moving the target in a step-wise fashion while under the ion beam has the effect of varying the individual quantities of oxide and metal being deposited, tailoring the through-thickness composition of the coating. Ideally, the coating is metal-rich at the substrate interface and oxide-rich at the surface. Monte Carlo modeling of the deposition process reveals that as the fraction of metal decreases, islands of metal are formed which are locked into place forming a labyrinth in the ceramic. Light impinging on the surface is trapped within the labyrinth (Ref. 8). The exterior surface being oxide alone provides both high emittance and atomic oxygen durability. Though initially considered for space solar power, recent research suggests that solar thermal energy may prove useful for in-situ resource utilization (Refs. 11 and 12).

Cermet coatings derived from a combination of titanium and aluminum oxide have been identified as having excellent durability to the space environment, by testing coatings in ground-based exposure facilities including facilities that simulate such threats as atomic oxygen, vacuum ultraviolet radiation, and high temperature thermal cycling exposure. Based on these tests, the titanium-aluminum oxide cermet coating was selected for long-term durability evaluation on MISSE 7B.

Methods and Materials

MISSE, was a collaborative effort between NASA, the Department of Defense, industry, and academia, and was a series of materials flight experiments consisting of trays called Passive Experiment Containers (PECs) that were exposed to the space environment on the exterior of the International Space Station.

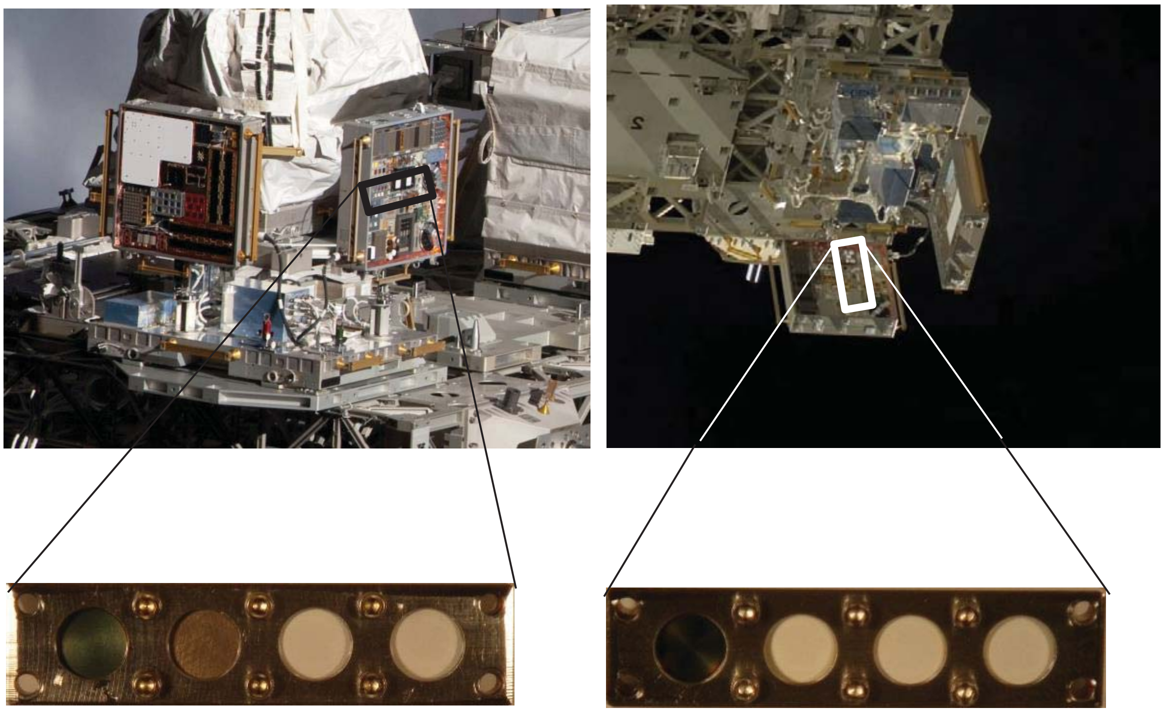

Figure 1.—Post-flight photographs of the ram-facing Thermal Control Paints Experiment tray on the left and the wake-facing tray on the right. The cermet coating is located in the left-most position in both trays. The plasma sprayed coatings are located in the 2nd (wake only), 3rd, and 4th positions. A bare nickel surface completes the ram-facing tray.

For MISSE 7, the PECs were positioned in either a zenith/nadir (7A) or ram/wake (7B) orientation. MISSE 7 was launched on STS–129, placed on the exterior of the International Space Station on 11/23/2009, on the EXPRESS Logistics Carrier 2 (ELC 2). MISSE 7 was retrieved on 5/20/2011 during STS–134. Hence, the duration of low Earth exposure was 1.49 yr. Power and data connections were provided at ELC 2, enabling data collection via telemetry. For the MISSE 7B Thermal Control Paints Experiment, four specimens were flown in the ram facing direction and four specimens were flown in the wake facing direction, each equipped with individual temperature sensors bonded to the back of the sample disk. A post-flight photograph of each tray is shown in Figure 1. Temperature data were processed for the first 80 days of the mission, spanning a range of beta angle values with respect to the sun.

The hardware used to hold the two groups of four specimens was based on the design of a similar specimen holder that was flown on MISSE 6. Each specimen consisted of the coating of interest applied to the front of a 1.27 cm diameter nickel disk and a temperature sensor bonded with epoxy to the back. The specimens were somewhat thermally isolated from each other and from the holder by utilizing four thin polyimide sheets, two around each edge and held in a groove on the nickel disks. In this way, the specimens were held in place without making contact to their holder or cover. Erosion of the polyimide by atomic oxygen was mitigated by applying a silicon dioxide coating on the outermost sheet. The openings in the cover were specifically designed to be slightly smaller than the specimens, ensuring that the specimens were fully captured for safety. In addition, the edges of each opening were chamfered to enable illumination of the surface as much as practical. A diagram showing the features of the hardware is shown in Figure 2.

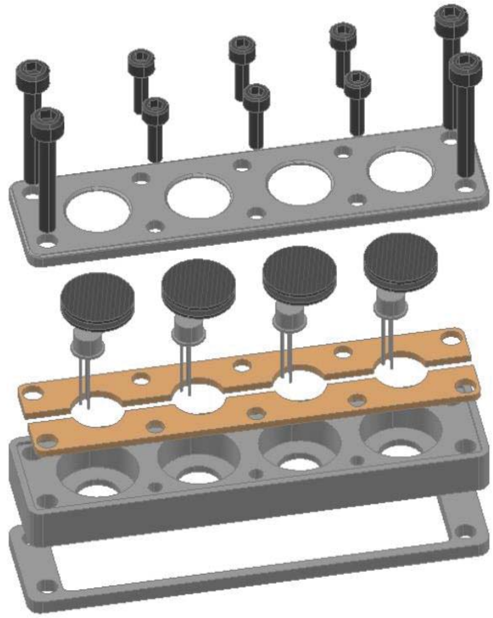

Figure 2.—Exploded view of the Thermal Control Paints Experiment with the four thin polyimide sheets shown in yellow.

The electronics monitoring the specimens were derived from MISSE 5 heritage, sampling data every 10 min (Ref. 13). Temperature data were downloaded in hexadecimal format and converted to numeric format utilizing an Excel Visual Basic program. To-date, the first 80 days of temperature data have been converted and archived.

Previous work utilizing ideal calorimeter disks illuminated with a quartz halogen lamp and suspended by thin thermocouple wires in a liquid nitrogen cooled thermal vacuum chamber demonstrated a technique for calculating solar absorptance and infrared emittance from GRCs Low Temperature Calorimetric Vacuum Emissometer (LCVE) facility (Ref. 14). In this method, the change in sample temperature with time is plotted as a function of the product of the Stefan-Boltzmann constant and mean sample temperature to the fourth power. The slope of this plot is a function of infrared emittance and the intercept is a function of solar absorptance. The LCVE method relies on a thermal energy balance based on the absence of conductive heat leaks into or out of the calorimeter disk. The temperature data from the Thermal Control Paints Experiment, however, suggests that the nickel disks were not sufficiently thermally isolated to merit this type of analysis.

Ground-based optical property measurements continue to be the essential means of identifying optical property durability. Ground-based measurements were obtained utilizing several different instruments. Solar absorptance was obtained initially utilizing a Perkin-Elmer Lambd-19 uv-vis-nir spectrophotometer. Special care was taken to align the sample so that the small spot size from the spectrophotometer was impinging solely on the surface of the sample. Post-flight solar absorptance was obtained on a Cary 5000 uv-vis-nir spectrophotometer, and again, special care was taken to align the small spot size to the sample. Once total reflectance data were collected in the wavelength range of 250 to 2500 nm, they were subtracted from unity and convoluted with respect to the air mass zero solar spectrum to yield a single solar absorptance value. Infrared emittance was obtained pre- and post-flight utilizing a Surface Optics Corporation SOC-400t portable infrared reflectometer. Data collected in the wavelength range of 2 to 25 μm were subtracted from unity and convoluted with respect to the blackbody spectrum at 300 K to yield a single infrared emittance value.

Results and Discussion

The temperature data in the vicinity of zero beta angle confirm the expectation that the cermet coating absorbs more solar energy than its plasma sprayed counterpart. The maximum temperature observed for the ram-facing cermet coating was 57 °C while that for the PS–16 coating was 26 °C. The minimum temperatures observed in the vicinity of zero beta angle were 11 and 2 °C for the cermet and PS–16 coatings, respectively. No further evaluation utilizing the temperature data was performed.

Ram-Facing Specimen Optical Properties

The pre-flight solar absorptance and infrared emittance values for the ram-facing tray are shown in Table 1, along with the post-flight values. The solar absorptance value for the cermet coating increased slightly, beyond the typical uncertainty of the solar absorptance measurements, ±0.005. Figure 3 summarizes the spectral data. This small increase in absorptance is brought about by a slightly deeper trough at 0.3 μm in the reflectance spectrum, perhaps due to a change in the labyrinth of optical pathways available to the impinging light. Although not considered in previous ground-based testing, one possible explanation could be annealing of the coating over the many thousands of thermal cycles while on orbit. The infrared emittance value for the cermet coating on the ram side decreased slightly, beyond the typical uncertainty of the infrared emittance measurements, ±0.01. This small decrease in emittance is brought about by a slightly higher reflectance in the infrared, though it is noted that the spectral features appear similar.

TABLE 1.—MISSE 7B NOMENCLATURE, COATING COMPOSITION, AND OPTICAL PROPERTIES BEFORE AND AFTER FLIGHT, RAM-FACING DIRECTION

Specimen ID	Coating composition	Solar absorptance		Infrared emittance	
		Before	After	Before	After
N3RA	Titanium-aluminum oxide cermet	0.831	0.838	0.25	0.20
	Bare nickel surface				
N3RD	Plasma sprayed PS–16 (7 mil)	0.280	0.245	0.91	0.92
N3RE	Plasma sprayed PS–16 and PS–27	0.184	0.258	0.92	0.92

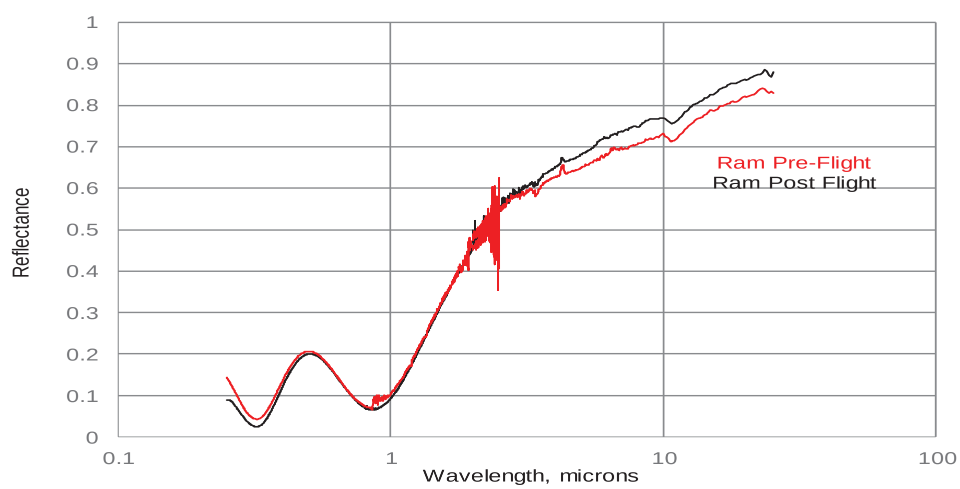

Figure 3.—Spectral data for the ram-facing cermet coating, pre- and post-flight.

For the plasma sprayed coating specimens located in the ram-facing tray, the absorptance of one plasma sprayed coating decreased by a few percentage points while that for the other plasma sprayed coating increased by a few percentage points. Well outside the uncertainty cited above, these changes are considered real.

Wake-Facing Specimen Optical Properties

The pre-flight solar absorptance and infrared emittance values for the wake-facing tray are shown in Table 2 along with the post-flight values. The solar absorptance value for the cermet coating also increased on the wake side. Figure 4 summarizes the spectral data and the increase in absorptance is brought about by both a slightly deeper trough at 0.3 μm and a subtle shift in the reflectance spectrum. The annealing mechanism posed above may apply to the wake side as well. It is interesting to note that the infrared emittance value for the cermet coating on the wake side decreased very slightly, and given the similarity in spectral features is likely consistent with the annealing mechanism posed for the ram side.

The solar absorptance values for the three plasma sprayed coatings on the wake side remained essentially unchanged within measurement uncertainty. This lack of change for these three specimens bodes well for their wake-facing durability. The infrared emittance values for the cermet coating and plasma sprayed coatings were all considered comparable to their pre-flight values, though curiously all post-flight values were above the pre-flight values.

TABLE 2.—MISSE 7B NOMENCLATURE, COATING COMPOSITION, AND OPTICAL PROPERTIES BEFORE AND AFTER FLIGHT, WAKE-FACING DIRECTION

Specimen ID	Coating composition	Solar absorptance		Infrared emittance	
		Before	After	Before	After
N3WA	Titanium-aluminum oxide cermet	0.832	0.844	0.22	0.21
N3WC	Plasma sprayed PS–20	0.308	0.311	0.93	0.94
N3WD	Plasma sprayed PS–16 (4 to 5 mil)	0.284	0.285	0.93	0.94
N3WE	Plasma sprayed PS–16 and PS–27	0.308	0.308	0.92	0.94

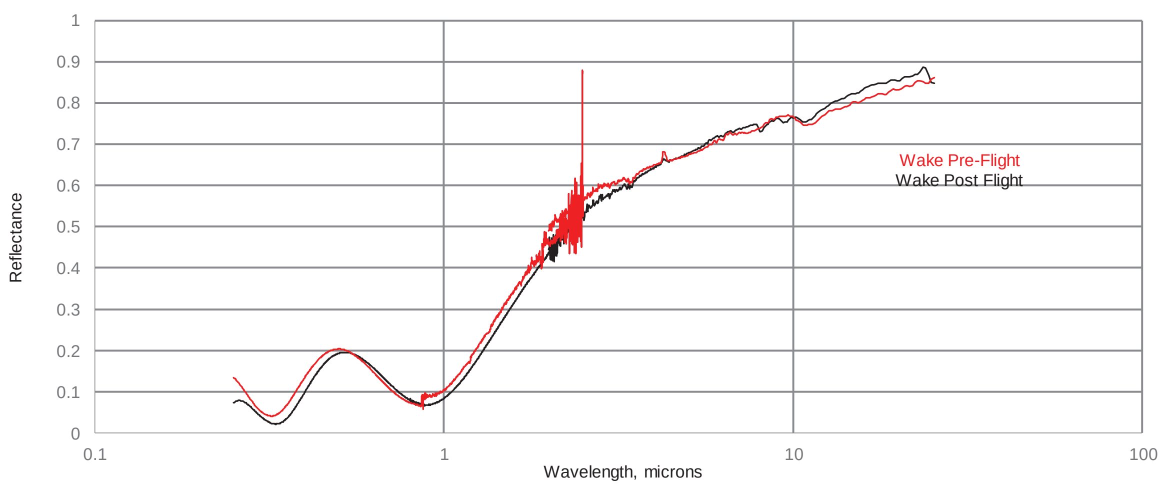

Figure 4.—Spectral data for the ram-facing cermet coating, pre- and post-flight.

Future Work

Cermet coatings offer an interesting combination of high solar absorptance and low infrared emittance via an ion beam sputtered coating of several hundred nanometers. A study of the molecular mobility of the constituents of the cermet coating at extreme temperatures would be interesting, to estimate the durability of cermet coatings at such temperatures. In addition, there may be opportunity to better understand the interaction of light with the underlying labyrinth with additional optical modeling. The plasma sprayed coating process is mature, available commercially, and is ideally suited for carbon-carbon composite radiators, as demonstrated on the GRAIL mission.

Conclusions

Selected specimens of a recently developed plasma sprayed coating and cermet coating were subjected to 1.49 yr of low Earth orbit exposure on MISSE 7, in both the ram-facing and wake-facing directions. Optical properties measurements before and after flight suggest the plasma sprayed coatings were durable to the space environment in the wake orientation. However, in the ram orientation the plasma sprayed coating results were indeterminate. Small changes in the solar absorptance and infrared emittance of the cermet coating, in both the ram and wake orientations, suggest a change to the coating over the duration of the MISSE 7 space exposure, potentially due to annealing of the ceramic due to repeated thermal cycling or some other mechanism that altered the light path into and out of the underlying metal labyrinth. Additional optical modeling is recommended.

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