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Outgassing Studies on Thermal Control Coatings for Micro-satellites

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Abstract

Purpose: With the advent of micro satellites technology, passive thermal controls in the form of surface coatings have become important for on-board thermal management. The thermal coatings, however, suffer outgassing and mass loss due to their direct exposure to harsh thermal environment and high vacuum in space. This paper discusses testing and evaluation on outgassing of AA6061-T6 specimen surfaces treated with various types of anodized coatings of different thicknesses and the related mass loss before and after thermal exposure.

Design/methodology/approach: Samples of chromic acid, PTFE polymer, and black- and brown-colour anodized aluminum coupons were subjected to high vacuum (~1x10^{-6}mbar), before and after thermal baking at 120^{o}C. Spectrum analysis of the outgassed material to know their quantities and proportion was conducted subsequently using a Quadrupole mass analyzer.

Findings: The surface coatings under study complied with the spacecraft requirements for the mass loss of less than 1 percent of the total mass of the coating material used for that surface. The mass spectrum analysis of the outgassed material indicated that the majority of the coating mass loss was on account of water vapours and organic solvents like ethylene.

Practical implications: These results provided a good insight into the reliability of the coating materials studied and the bonding between the aluminum substrates and the coatings.

Originality/value: The coatings and the technology needed for their application on aluminium are readily available. The present work on outgassing and mass loss in a simulated space environment will provide useful insight on their usage for micro-satellites.

Keywords: Micro-satellite; *Anodizing; Thermal control; Outgassing; Total mass loss; Baking*

Paper type: *Research paper*

Introduction

Satellites and spacecrafts moving in Low Earth Orbit (LEO) are constantly subjected to thermal cycling and other harsh environmental conditions. In order to ensure smooth functioning of a spacecraft, the physical and thermal properties of the equipment on-board have to be maintained [1].

Many active and/or passive thermal controls are commonly used in satellites and spacecrafts to maintain the operating temperature of the equipment in the sunlit-eclipse type of thermal cycling environment in space. In micro-satellites, it is often not possible to house an active thermal control onboard due to space, cost and power constraints. One has to depend on various thermal coatings in the form of special paints, films and surface treatments to maintain the operating temperature of its equipment [1]. Many anodized coatings along with their different variants have been in use for space applications [2-3].

Space objects orbiting in LEO experience atomic oxygen (AO) attack, ultraviolet radiations, impact of meteoroids and other debris, spallation, plasma and high vacuum effects, contamination and the thermal cycling. Exposure to high vacuum environment can cause spacecraft materials including surface coatings to outgas (i.e. the escape of embedded gas and other loose particles from a solid as a result of reduced surface pressure) due to moisture desorption (i.e. removal of moisture) or material volatilization, evaporation or decomposition [4] leading to deterioration of those materials to some extent. The outgassed molecules may collide with each other and stick on to the surface of the spacecraft. This molecular contamination can degrade critically the performance of in-tact thermal control surfaces and solar cells [5]. In addition, satellites in orbit undergo thermal cycling while moving in and out of the earth's shadow. This generally induces micro-cracks in the materials used for the spacecraft, which may promote further outgassing.

This paper discusses the high vacuum tests carried out, with and without high temperature baking, on aluminum specimen with four different types of anodized coatings varying in thickness. Chromic acid anodized, clear anodize with PTFE (polytetrafluroethylene) polymer, and black and brown anodized coatings were selected for the studies on aluminum substrates. It may be noted that PTFE is one of the approved materials for space applications [6]. The samples were subjected to high vacuum tests at ~1.33×10^{-6} mbar (or ~1×10^{-6} Torr) pressure, some as received and some after thermal baking at 120^{o}C. The experimental data was analysed to determine total mass loss (TML) for the coating. In addition, mass spectrum analysis of the outgassed content conducted using Quadrupole mass analyzer is discussed.

Anodizing Surface Treatment

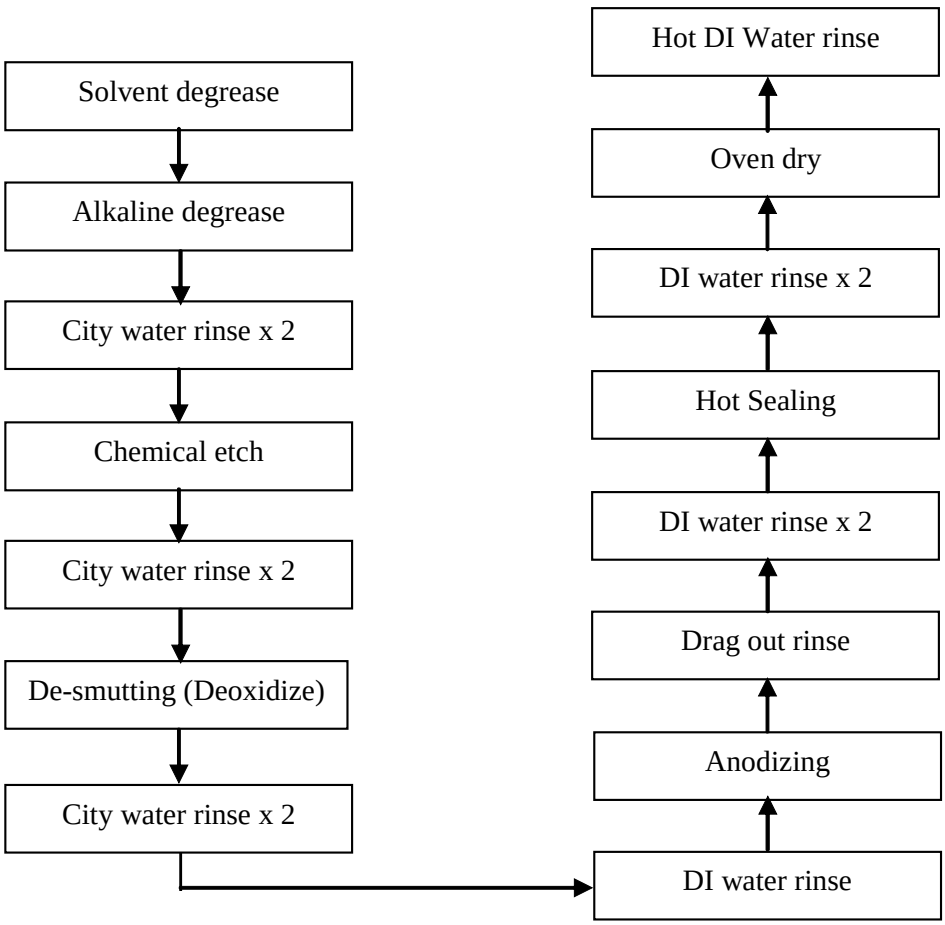
Anodizing, an electrochemical conversion process [7], is recommended for all exposed aluminum hardware on spacecrafts except for some radiators that have extremely low absorptance-to-emittance ratio (α/ε) requirements. It provides corrosion resistance on Earth, resistance to AO attack in space and reduction in spectral reflection [2, 3]. The

anodize coating is integral with their substrate so that debonding from the substrate does not occur easily. Three most common methods of aluminum anodizing are chromic (type I), sulfuric (type II) and hard (type III) anodizing. Chromic anodizing uses a chromic acid electrolyte and produces coatings that are 0.5 to 2.5microns (0.02 to 0.1mil) thick. Approximately 50 percent penetration into the substrate and 50 percent growth over original dimensions occurs. Sulfuric anodizing utilizes sulfuric acid and can yield up to 25 microns (or 1mil) thick coatings. In this case, 67 percent penetration into the substrate and 33 percent growth over original dimensions occurs. Sulfuric anodizing is good for colour dyeing due to its permeable nature. Hard anodizing uses higher concentration of sulfuric acid electrolyte at a lower temperature. The process result in a tough and hard layer as surface coating for a substrate with excellent abrasion resistance, corrosion resistance, colour fade resistance, dielectric strength and surface hardness [8]. About 50 percent penetration into the substrate and 50 percent growth over original dimensions occurred for a total coating thickness of 13 to 100 microns (i.e. 0.5 to 4mil). Thus, hard anodized metals have a heightened surface roughness.

Sample Preparation

A 1mm thick plate of an aluminum alloy (AA6061-T6) was cut into a number of 40 x 40 mm pieces that were then send for anodizing treatment. A brief outline (prepared in accordance with MIL-A-8625 standard [9]) of the anodizing procedure is presented as flow chart in Figure 1.

Figure 1 Flow Chart of Anodized Coating Process Procedures.

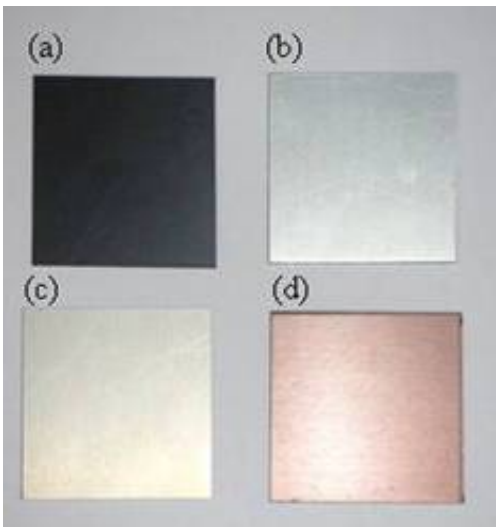


The various specimen as shown in Figure 2a were prepared with the specifications as in Table 1.

Table 1 Specifications of various specimens

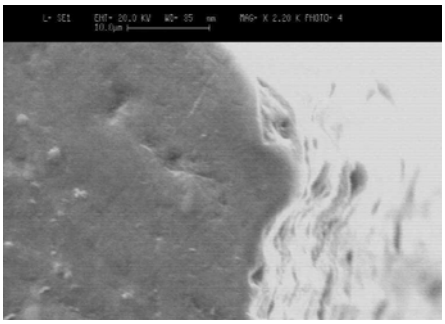
No.	Description	Coating thickness (microns)	
1.	Clear Chromic acid anodizing (MIL-A-8625, type I)	(a) 2 to 5.	
2.	Sulfuric acid clear anodizing with PTFE (MIL-A-8625, type II* and type III)	(a) 5 to 10 (II*); (b) 10 to 15;	(c) 15 to 20; (d) 20 to 25.
3.	Brown colour hard anodizing (MIL-A-8625, type III)	(a) 10 to 15; (b) 15 to 20;	(c) 20 to 25.
4.	Black colour hard anodizing (MIL-A-8625, type III)	(a) 10 to 15; (b) 15 to 20;	(c) 20 to 25.

Figure 2a Samples of anodized aluminium alloy AA6061-T6.

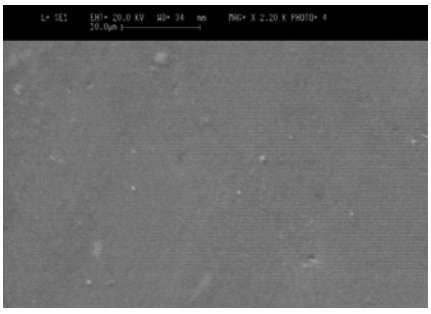


(a) Black colour anodized;
(b) Clear anodized with PTFE;
(c) Chromic acid anodized;
(d) Brown colour anodized.

Figure 2b SEM images of a typical chromic acid anodized AA6061-T6.



(a) across the thickness at a corner



(b) planer surface

A few peculiar scanning electron micrographs (SEM) of the anodized aluminium are shown in Figure 2b. There were two batches of the specimen and each batch underwent a different type of test. The first batch of samples

was subjected to vacuum testing only for investigating their outgassing characteristics. Samples from the second batch were heated up in a thermal chamber before placing in a vacuum chamber for outgassing studies.

Equipment

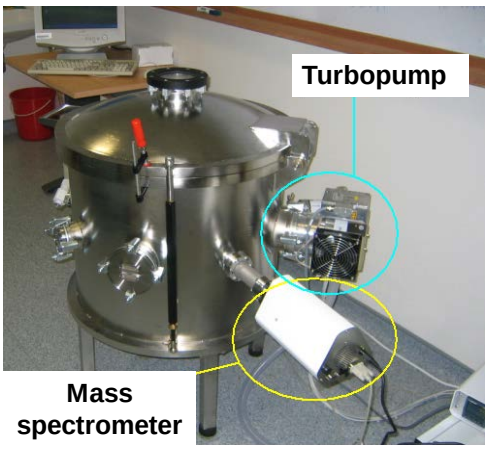
The testing equipment included a vacuum chamber and an environmental chamber. The vacuum chamber was a part of an integrated vacuum system from PFEIFFER VACUUM, North America, that included a Quadrupole mass spectrometer Prisma™ 80 [10] and a turbomolecular drag pumping station TSH 521. The pumping station consisted of a vacuum pump DUO 10/10C [11] and a Turbopump TMH/TMU 261 [12]. Prisma™ 80 spectrometer had a dual iridium filament design with selectable partial pressures for a mass range of 1 to 80 amu. The pumping station could generate the final pressure lower than $1x10^{-8}$ mbar. A Thermotron SE-Series environmental chamber, supplied by Thermotron Industries, Holland, was used to bake the anodized samples. The chamber offered a temperature range from -40ºC to 180ºC with controllable humidity.

Vacuum Test Procedure

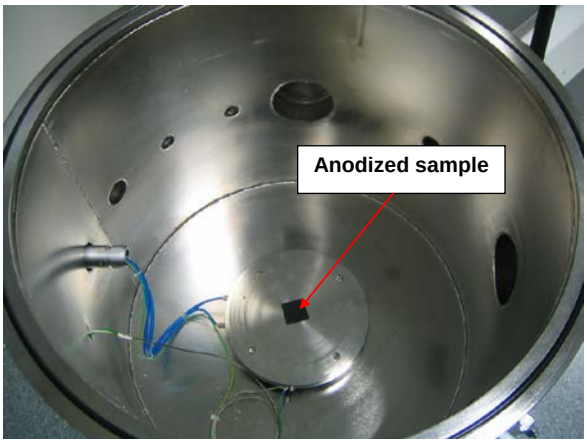
High vacuum

The vacuum test was conducted on each sample separately. The samples were weighed before placing them into the vacuum chamber; refer Figure 3. The process of evacuation was started after closing the lid of the vacuum chamber tightly. When the pressure reached about $1.33x10^{-4}$mbar (or $1x10^{-4}$Torr), the mass spectrometer was turned on. When the pressure reached about $4.67x10^{-6}$mbar (i.e. $3.5x10^{-6}$Torr), the final ion distribution charts were obtained using the mass spectrometer. In the end the samples were removed from the chamber, visually inspected and weighed again to calculate the TML.

Figure 3 Vacuum equipment used in outgassing studies.



(a) Vacuum Chamber.



(b) Placement of the sample.

Baking and high vacuum

Similar to the earlier experiments, this test was conducted separately on each specimen. Upon weighing each anodized sample was placed in the thermal chamber where its temperature was raised to 120°C. The specimen was maintained at that temperature for one hour at atmospheric pressure. The sample was then quickly transferred from the thermal chamber to the vacuum chamber where the same procedure, as discussed in section 5, was followed to examine outgassing and to calculate the TML.

Results and Analysis

Total mass loss

For the thermal control coatings, the TML observed during the vacuum test was calculated as in equation (1):

$$TML = \frac{Wt(\ anodized\ sample\ before\ vacuum) - Wt(\ anodized\ sample\ after\ vacuum)}{Wt(\ anodized\ sample\ before\ vacuum) - Wt(\ aluminum\ substrate\ before\ coating)} \quad (1)$$

where (*Wt*) denotes weight of sample at various stages.

The mass loss results for the vacuum test (i.e. of the outgassing without thermal baking) are graphically presented as the percentage TML in Figure 4. It may be seen that as the thickness of the clear (PTFE) anodized layer increased, the percentage TML decreased. An upward going trend was observed for the brown and black anodized samples where percentage TML increased with the coating thickness. However, the increase in the TML for the black anodized samples was not as high as compared to the other three types of anodized samples.

Figure 4 Percentage TML for non-baked samples during the high vacuum test.

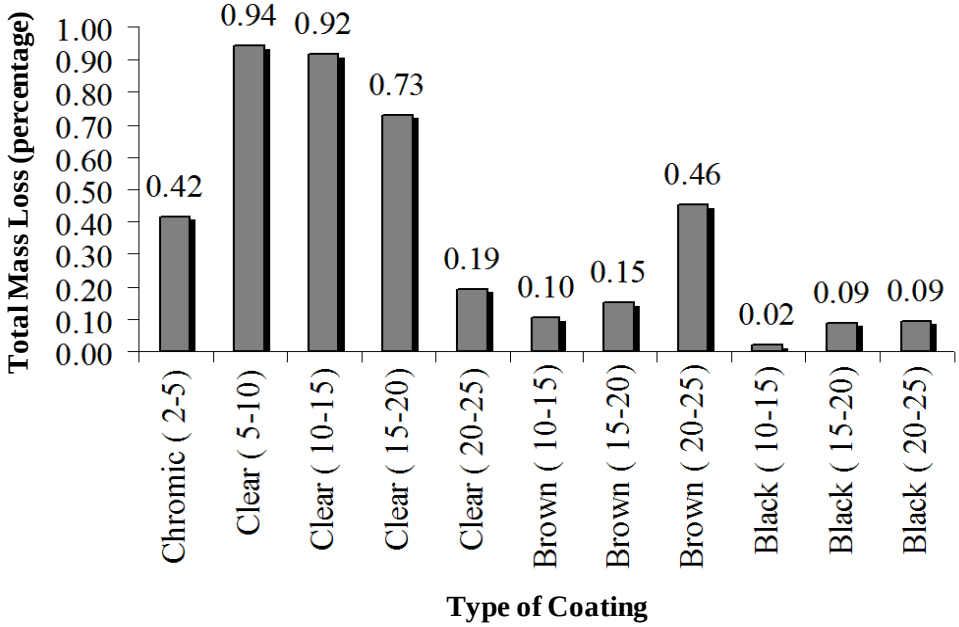


Figure 5 is the graphical representation of the percentage TML observed during the outgassing test conducted after thermal baking. It may be seen in Figure 5 that when the thickness of the clear PTFE anodized layer for the baked samples increased to 20 microns, the percentage TML in the high vacuum environment decreased. However,

there was a slight increase in the percentage TML when the coating thickness was 25 micron. This may be considered as the result of the response of the PTFE coating to the baking. An increasing trend was noted for the brown and black anodized samples after they were baked, where the percentage TML increased with the coating thickness.

Figure 5 Percentage TML for anodized samples in high vacuum after baking.

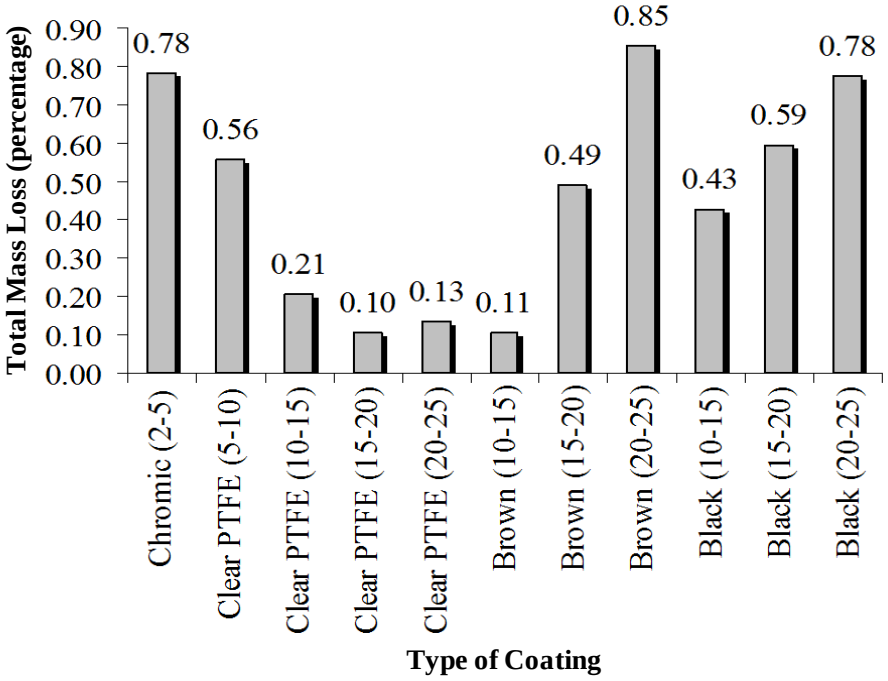
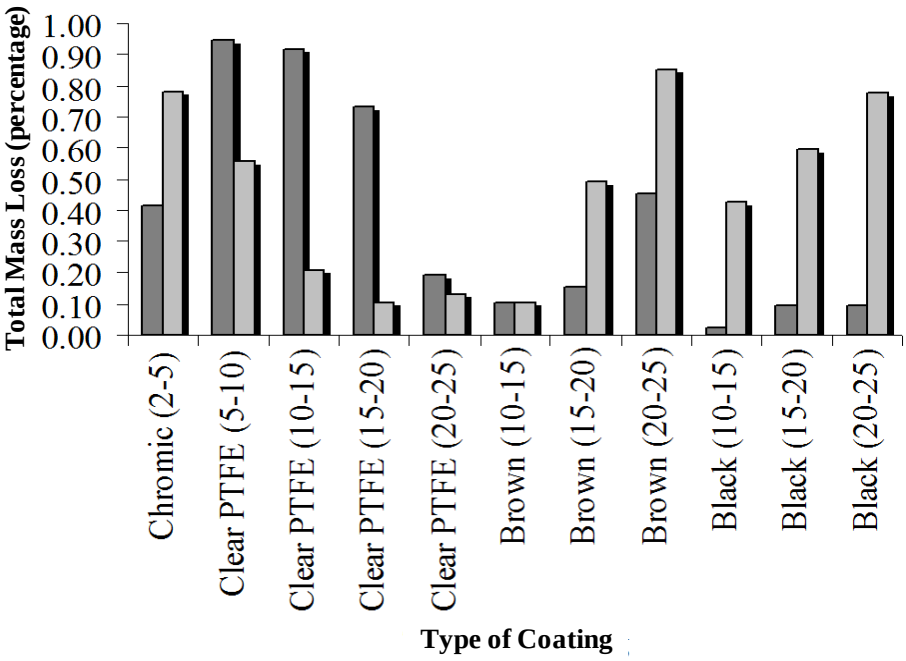


Figure 6 shows the comparison of the TML for the baked as well as non-baked samples after the vacuum test. The percentage TML for the baked chromic acid anodized samples was 0.78 percent while it was 0.42 percent for the non-heated samples. Similar observation was made for the brown and black anodized samples where the percentage TML for the baked samples was considerably higher than (up to 0.69 percent increase) for the non-baked samples. The brown anodized coating of 10 to 15 micron had the lowest percentage TML amongst the all baked and non-baked samples.

Figure 6 TML comparisons between baked (light colour bars) and non-baked (dark colour bars) samples.



On the contrary, the percentage TML for the clear PTFE anodized samples decreased (up to 0.71 percent reduction) after baking. A downward trend in the TML values was seen for both, the baked and non-baked, clear PTFE anodized samples as the coating thickness (which also means the total percentage of PTFE) increased. When the thicknesses of the brown and black anodized coatings increased, there was a rising trend in the percentage TML regardless of the baking. Generally either the upward or the downward trends in the TML observed with the increase in the coating thickness were not affected by the baking process. However, the baking had an impact on the rate at which and the amount of the TML occurred.

It may be seen from the results presented in Figure 6 that the percentage TML for none of the anodized coatings exceeded 1 percent. This is in accordance with the “1.0 percent criterion” for TML that has to be complied before adopting the coating for space use as set by European Space Agency (ESA) or American Society of Testing of Materials (ASTM) standards [13]

The outgassed matter

When analyzed, as seen from the mass spectrum [14] in Figure 7a, only water vapours and ethylene (C_2H_3+) ions were dominantly present in the chromic acid anodized samples.

Figure 7a Ion mass distribution for chromic acid anodized samples.

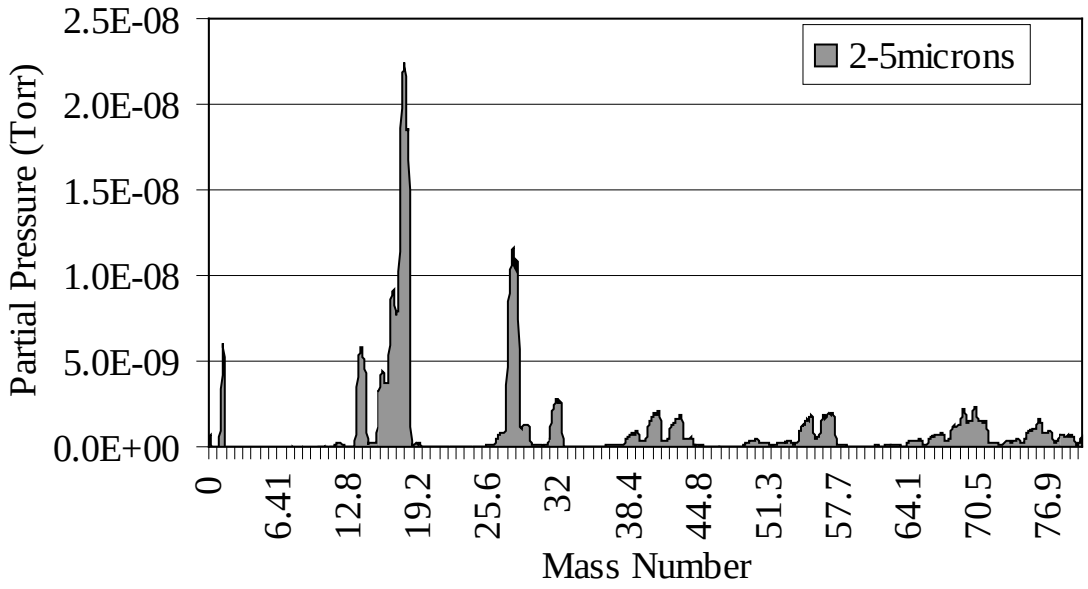
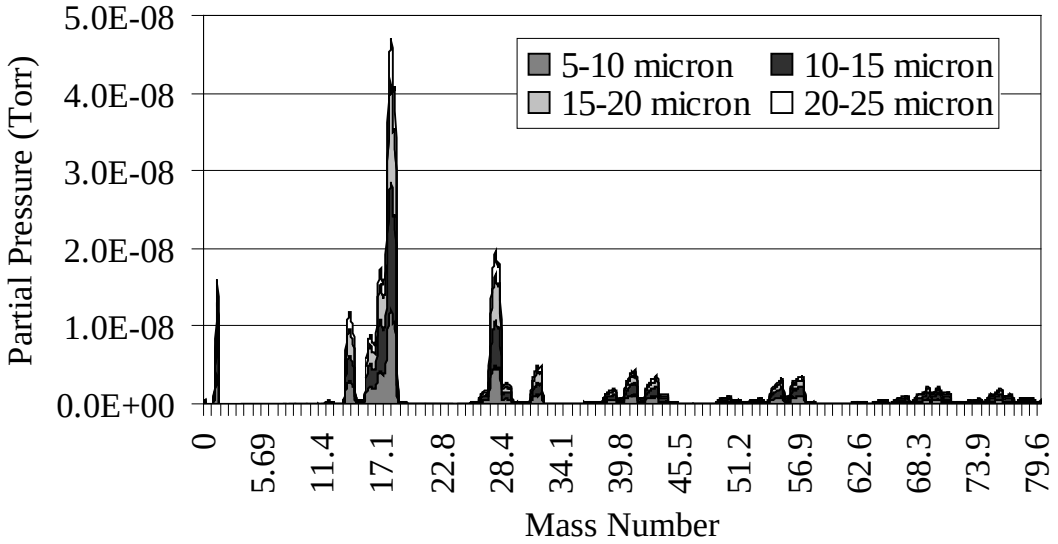


Figure 7b Ion mass distribution of clear PTFE anodized samples.



The mass spectrum for clear PTFE anodized samples is shown in Figure 7b; the areas marked by three different shades represent the coating of different thicknesses. The spectrum represents the various forms of the gaseous matter recorded within the vacuum system, the magnitude of which is represented by their respective partial pressures. Since the spectrums are produced by electron impact ionization, some fragmentation of ions was evident. The peaks on the distribution chart show the dominant ion species that possibly existed within the samples. Those likely species were as detailed in Table 2.

Table 2 Likely species outgassed of clear PTFE anodized samples

Mass numbers	Ions presented	Names of species/ ions
17-18	OH+, H_2O	Water Vapour
27-28	CO, C_2H_3+	Carbon monoxide, Ethylene

It may be noted that there were no traces of fluorine (mass number 19) ions.

Figure 8a Ion mass distribution for brown anodized samples.

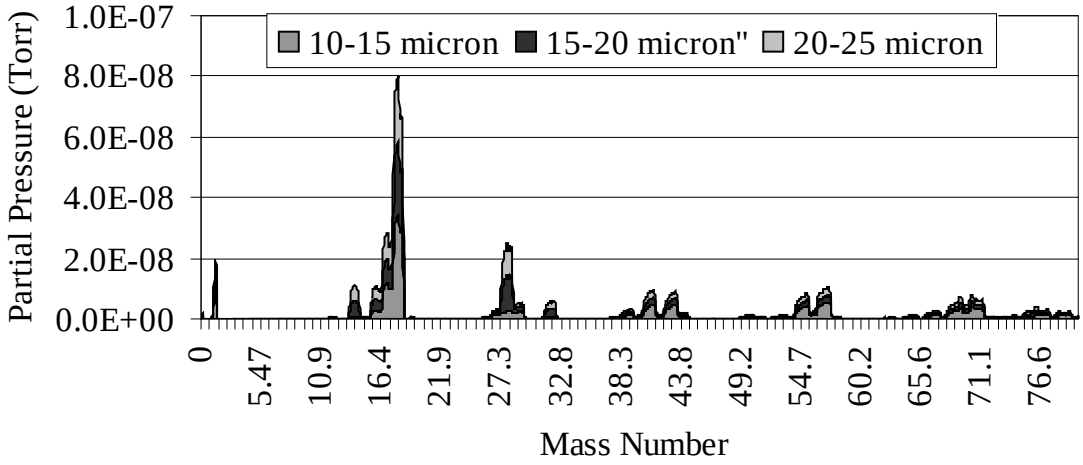
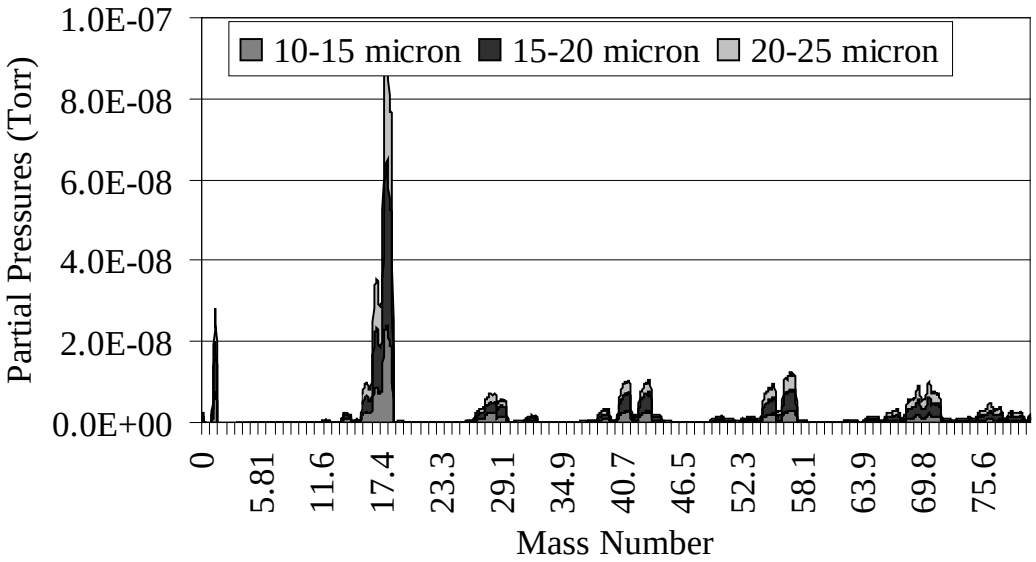


Figure 8b Ion mass distribution for black anodized samples



As for the brown anodized samples, seen from the mass spectrum in Figure 8a, in addition to the above-mentioned species, the dominant ions present were as listed in Table 3.

Table 3 Likely species outgassed of brown anodized samples

Mass numbers	Ions presented	Names of species/ ions
42-43	C_3H_6+, C_3H_7+, C_2H_3O+ and C_2H_5OH	Propene, Propane, Acetaldehyde and Ethanol
54-55	C_4H_7+ and C_4H_9+	Butane

Figure 8b shows the ion distribution for the black anodized samples under high vacuum. Apart from water vapours and ethylene, other possible dominant ions present were as detailed in Table 4.

Table 4 Likely species outgassed of black anodized samples

Mass numbers	Ions presented	Names of species/ ions
40-42	C_3H_5+, C_3H_5+, C_3H_6+	Propene, Propane
54-55	C_4H_7+	Butene

Thus, the outgassed species from the all four types of thermal coating materials included generally water, solvents, additives and solids used during anodizing.

Discussions

Total mass loss

As expected, outgassing was observed in all types of coatings indicating that the TML measurements are vital and essential. Black anodizing, being the hardest amongst all, suffered less mass loss under high vacuum, followed by the another hard coating, the brown anodizing. The percentage TML, however, significantly increased after the baking. Since these coating are porous and are deep down into the metal surface, various contaminants (i.e. species that outgassed later on) might have diffused deep down into the coating. Therefore, less TML was noticed even though the

vacuum to which these coating were subjected was high. However, with the energy gained during the subsequent baking process might have helped in bringing these species to the surface. Thus, the percentage TML increased noticeably upon baking. This is consistent with the outgassing theory [13] whereby higher temperatures increase molecular activity within the object, especially near its exposed surfaces, held at that temperature. This results in loosening of the weakly adhered surface particles as well as rise in the rate of evolution of the trapped gas molecules to the surface. These particles subsequently leave the surface under high vacuum conditions thereby leading to increased outgassing and the TML.

The percentage TML for the clear PTFE anodized samples decreased with the thickness as well as upon baking. Especially the PTFE coating of 15 to 20 micron suffered reasonably small TML after baking. PTFE, by nature, is hydrophobic and non-reactive with many species. Thus, the diffusion of various contaminating species into the coatings was unlikely. The species that could have adsorbed on to the coating surface released under high vacuum showing TML. Since the adsorption depended only on the exposed surface area of the coating, the amount appeared to be the same for the coating irrespective of their thicknesses, resulting in lesser and lesser percentage of TML when calculated based on the mass of the coating applied. The little amount of gaseous species that might have dispersed within the few microns of the coating came out to the surface after baking. However, the amount was not as high, leading to lower percentage TML. This also means, the PTFE coating offers good resistance to the possible contaminants making it a good choice for space applications.

The outgassed matter

As seen from various mass spectrums, water vapours constituted the highest percentage (approximately 50 percent) of the outgassed matter in all coatings. However the presence of water was expected given the high humidity in the atmosphere where the samples were made and tested. It was, however, of little concern as the sorption of moisture can be minimized to a very large extent with the working and storing of satellite components with thermal coatings in a clean room environment.

The rest of the gaseous matter that outgassed was a lot less in quantity. Among them, the notable mass observed, in the range of 27-28 amu, with the PTFE and chromic acid coatings was possibly of ethylene and carbon monoxide. The outgassing of carbon monoxide from PTFE Teflon was reported earlier by some researchers [15]. Taking this into account the possible loss of ethylene from PTFE coating was low. For the chromic acid anodizing, although the source of ethylene was not known, most likely it would have come from a water-based cleaning compositions used for removing stains from the aluminium substrates. It is reported [16] that such cleaning compositions consist of 9-10 percent of ethylene based compounds.

Notwithstanding, the actual percentage of volatiles, which could result in some concern, outgassed before and after the baking of the samples, was insignificant and much less than 1 percent.

Conclusions

It was clearly seen from the high vacuum tests before and after the bake-out that the percentage total mass loss (TML) for the different anodized coatings was less than 1 percent. This was in accordance with the criterion set by European Space Agency or American Society of Testing of Materials standards. The percentage TML for the clear polytetrafluroethylene (PTFE) anodized samples decreased with baking. The PTFE coating of 15 to 20 micron suffered reasonably small TML upon baking. In order to minimize the effect of outgassing and contamination within satellite housing this coating may be considered for the sun-facing surfaces. Brown anodized coating of 10 to 15 micron may also be a good option for exposed and non-exposed areas as the percentage TML for the baked and non-baked samples were among the lowest. Generally, regardless of baking, the thin (2-5 micron) chromic acid anodized, the 10-15 micron thick black and brown anodized and thicker (20-25 micron) of clear PTFE anodized coating may be recommended for space applications due to their low TML.

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