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DEVELOPMENT OF WHITE OXIDE-PLASMIC COATINGS WITH IMPROVED THERMO-OPTICAL PROPERTIES FOR SPACE APPLICATIONS

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Abstract: The optical and electrical properties of aluminum oxide layers formed by Micro-Arc Oxidation (MAO) process for potential application in spacecrafts have been investigated. The operational conditions of the MAO process have been correlated to the structural features of the coatings and to the optical properties. Results show that, although environment tests (UV, particles and thermal cycling) remain to be done, by selecting appropriate electrolyte formulation, the measured thermo-optical parameters could fit the specification range of cold coatings. Furthermore, the electrical properties of such coatings have been investigated by means of surface and volume conductivity measurements as well as dielectric spectroscopy. Results highlight that materials exhibiting the best thermo-optical properties are those having the higher electrical conductivity, with values appearing favorable regarding the targeted application.

Keywords: Aluminum oxide, MAO process, dielectric and optical properties.

1. INTRODUCTION

Spacecraft and scientific instruments usually contain hardware, including sensitive detectors, which require specified temperatures ranges. The knowledge of the thermal properties (absorptance and emittance) of the used coatings is therefore essential for the thermal design of the spacecraft according to mission specifications. In addition to these basic requirements, it is also necessary to be compliant with other spacecraft requirements such as electrostatic discharges and particulate and molecular contamination. Then, before choosing the proper thermal control coating, the way of degradation of these properties has to be investigated under exposure to UV, high energy protons and electrons and thermal cycling.

Coating designed to have specific radiative properties are called thermal control coatings. In the case of very

high temperature applications, black coatings, prepared by using a micro-arc oxidation process (MAO), are already qualified to the space constraints. As heat absorbing surface, they provide high absorptivity and emissivity properties. For very specific missions, like solar orbiter, a radiator surface through a white coating with low absorptance, lower than 0.3 and high emissivity could provide significant benefits.

The MAO process, also called “plasma electrolytic oxidation”, is an electrochemical surface treatment generating oxide coatings on some metallic substrates (Al, Ti or Mg). Such coatings are generally used for their high hardness in tribology applications but the very good adherence on the substrate at high temperature is considered here for a use as an external coating on passive thermal protections. Hence, resulting thermo-optical properties have been investigated.

2. MATERIALS AND CHARACTERISATION TECHNIQUES

Rectangular specimens of aluminum 1050 of size 180x150x1 mm³ were used as substrates. The MAO process was carried out with conventional oxidation equipment consisting of a stirring, cooling system and a power supply. The electric parameters such as voltage, current, frequency can be adjusted. During the experiment, the aluminum specimen and stainless steel plates were used as anode and cathode respectively. The electrolyte was a solution of sodium silicate (concentration between 5 and 30 g/L) and potassium hydroxide (1 g/L). During the oxidation, the temperature of the electrolyte was kept below 25°C. Coatings obtained with different process conditions, were characterized. The main process parameters are summarized in Table 1.

Table 1: Process parameters for coatings preparation (J=current density, t= process duration, d = substrate thickness). J is given in relative value for confidentiality purpose

Sample	J (r.u.)	t (min)	d (μm)
#1	J ₁	150	200
#2	2.4xJ ₁	50	2000
#3	1.5xJ ₁	30	1000
#4	2.8xJ ₁	30	1000

The solar absorptance was measured with an Elan Informatique Absorptiometer IR EL520 using an integrated sphere (hemispherical measurement). The normal measurement of emissivity was performed on an Elan Informatique Reflectometer EL510. The absorptance α quantifies the amount of solar rays absorbed by the coating and the emissivity ϵ the coating capacity to convert its thermal energy into IR ray.

The microstructure of the coatings was observed by Field-Emission Gun Scanning Electron Microscopy (FEG-SEM) with a JEOL JSM6700F device.

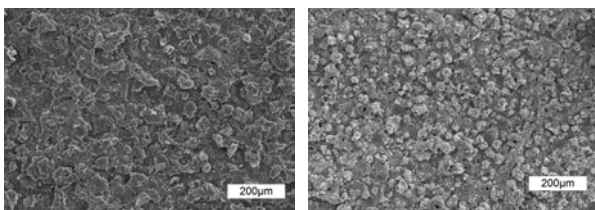
Structural characterization of the coatings was achieved by a set of techniques ranging from XRay diffraction (Bruker D4 Endeavor using a Cu K α radiation), thermogravimetric analysis –TGA-, differential thermal analysis –DTA- and Electron Probe MicroAnalyser (EPMA).

For DC current measurements, an aluminum top electrode, 12mm in diameter, was deposited on the sample surface by CVD (chemical vapor deposition) while the ground electrode was the aluminum substrate. Current measurements were carried out under vacuum (3.10^{-7} mbar) at room temperature by means of a Keithley 617 ammeter. The surface resistivity was measured using the concentric ring probe configuration. The inner electrode and the guarded ring were deposited by CVD.

3. RESULTS AND DISCUSSION

3.1. Characterisation of the coating

The surface microstructures of the coatings are presented in Figure 2. The surface roughness which can be observed is characteristic of the MAO process. The pores corresponding to the spark channels can also be seen.



#2 #3
Figure 2: SEM images of the coatings

Figure 3 shows that the coatings are made up of crystalline phases as described by the literature but also by a part of amorphous phases. The crystalline phases of external layer of the coatings are a blend of α and γ alumina and also aluminum silicate. The internal layer is more crystallized even though an amorphous part is still present. The internal layer is constituted by the same crystalline phases than those of the external layer. The crystallinity of the external surface is dependent of the process.

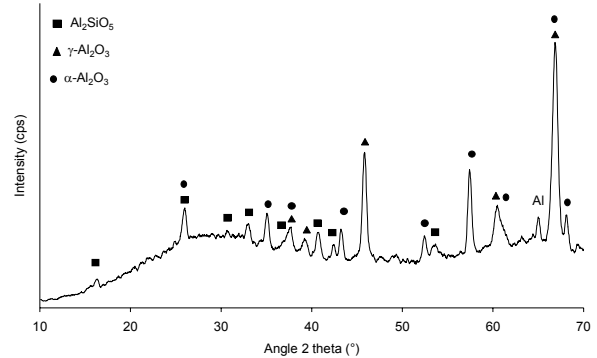


Figure 3: XRD pattern of the external layer

3.2. Optical measurements

Table 2 gives the optical parameters of the coatings. Samples #2 and #4 have optical properties complying with the specification of a cold coating. The comparison between table 1 and 2 indicates that high current density and high silicate concentration are required to obtain good optical properties.

Table 2: Thickness, solar absorbance α and thermal emissivity ϵ of the coatings.

Sample	Coating Thickness (μm)	α (± 0.04)	ϵ (± 0.04)	Cold coating specification s
#1	95	0.55	0.77	$\alpha < 0,3$ $\epsilon > 0,8$
#2	100	0.26	0.83	
#3	50	0.38	0.76	
#4	100	0.30	0.77	

3.3. Electrical measurements

Electrostatic discharges (ESD) can occur in space between various parts of a spacecraft due to differential charging of the spacecraft caused by energetic charged particles. A design rule consists in avoiding resistive materials. Specifications are:

- Surface resistivity $< 10^9 \Omega/\text{square}$
- Volume resistivity $< 10^{13} \Omega.m$

Nevertheless, these values are given as indications only. Indeed they are not sufficient to evaluate the risk of ESD as it also depends on the thickness and on the

location on the satellite (internal, external under MLI,...).

Figure 4 shows typical current transients obtained when applying voltage steps in the range 0 to 100 V followed by short-circuit steps. The polarization time was fixed to 10 minutes and can be considered as leading to a representative conduction current. The volume resistivity values, estimated from the value of the current at the end of the polarization step, and obtained from a linearization of the I(V) data are given in Table 3, along with surface resistivity results.

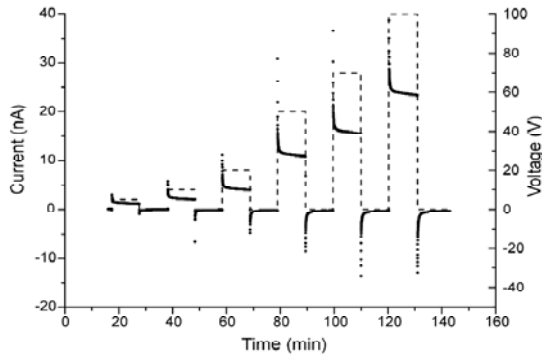


Figure 4: Transient currents for sample #4 under vacuum at room temperature.

Table 3 highlights that the surface and volume resistivities of sample #1 are more than two orders of magnitude higher when compared to the three others. This result will be commented in the Discussion.

Table 3: DC electrical characteristics of coatings.

Sample	Volume resistivity ($\Omega \cdot m$)	Surface resistivity (Ω/square)
#1	$4.1 \cdot 10^{12}$	$1 \cdot 10^{16}$
#2	$6.4 \cdot 10^9$	$5 \cdot 10^{11}$
#3	$8.6 \cdot 10^9$	$2 \cdot 10^{12}$
#4	$2.0 \cdot 10^9$	$3 \cdot 10^{11}$

3.4. Thermal treatment and air storage effects on optical and dielectric properties

Thermal effects in space can affect the efficiency of the thermal control coatings through changes in emittance, solar absorptance, loss of adhesion or changes in electrical conductivity.

Sample #4 is the most appropriate sample for a space application as cold coating, because of its good optical properties and low conductivity compared to the other tested samples. In the following, the effect of a thermal treatment will be investigated on structural, optical and electrical properties.

For structural properties, the thermal treatment consisted in annealing samples under air atmosphere at 200°C during 5 hours. Figure 5 shows the effect of this treatment on the crystalline structure of the coating. It

can be seen that an increase of the temperature increases the crystallinity of the external coatings even though a part of amorphous phases is still present. At 200°C, the amount of γ alumina increases, it can be explained by the crystallization of the hydrated amorphous phases of alumina such as $Al(OH)_3$ or $AlOOH$.

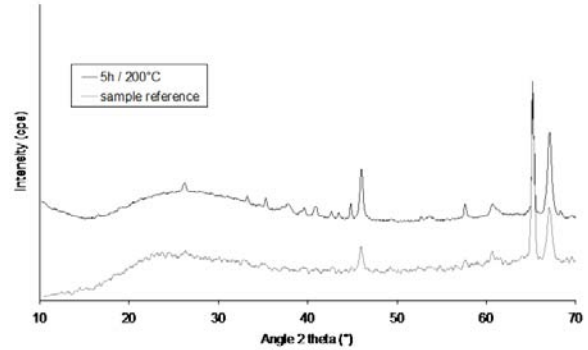


Figure 5: Effect of temperature on Xray Diffraction patterns

The thermo-optical properties were measured at room temperature just after the treatment to avoid water absorption along with after storage in air at room temperature. The results do not reveal any significant variation of the optical properties after heating or after storage in air, pointing towards stable optical properties of the coatings.

For dielectric measurements, the thermal treatment consists of an in situ annealing at 200°C for 1 hour. Figure 6 shows the corresponding results. The peak observed at around 100°C on $|Z|$ for the untreated sample is most probably due to the release of water from the coating. After the thermal treatment, this peak disappears, and the value of the impedance increases, clearly indicating an increase in the resistivity of the material.

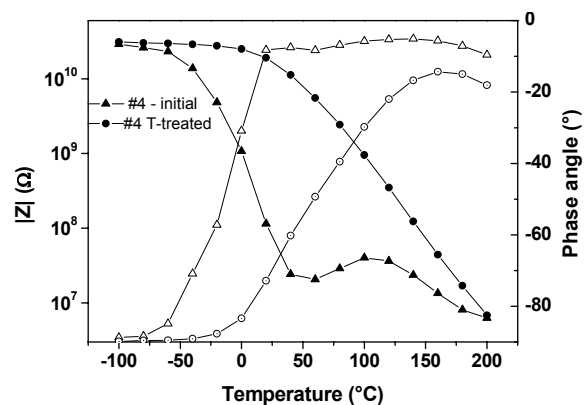


Figure 6: Impedance (solid symbols) and phase angle (open symbols) measured at 0.1Hz as a function of temperature prior to (triangles) and after (circles) thermal treatment on sample #4

4. DISCUSSION

X-ray diffraction patterns indicate that the layers are constituted of several crystalline phases. To sum-up, an increase in silicate content of the electrolyte favors the formation of silicate phases in the coatings: the ratio of alumina (Al_2O_3) to silicate (Al_2SiO_5 -called mullite-) is around 90:10 in sample #1 and 50:50 in the others. An important point is that large silicate content induces an increase in the amorphous phase fraction of the coatings (cf. broad band in the region $15\text{-}30^\circ$ in Fig.7).

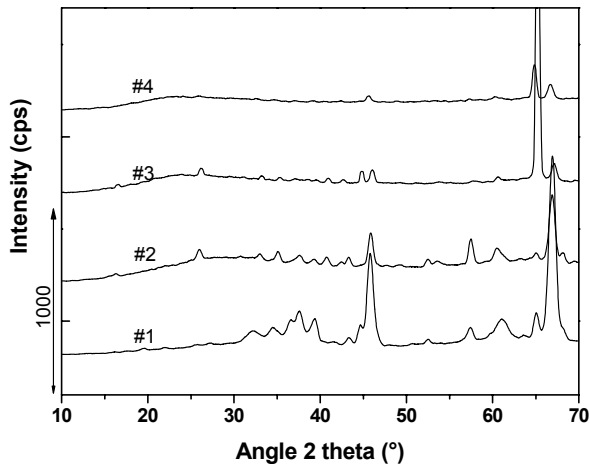
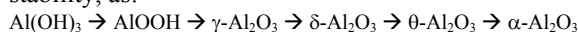


Figure 7: X-Ray diffraction patterns of the samples

Voigt and co-authors [3] studied the correlation between chemical composition and electrical properties of rf sputtered alumina films. They found that the leakage current increases with the concentration of OH groups, which act as defect sites. As OH groups are presumably located preferentially in the amorphous phase, the way of investigating it consisted in combining TGA and DTA. Table 4 shows the weight losses in the sample interpreted as arising from free water release, and from the known thermodynamic stability of aluminas given, in increasing order of stability, as:



The lower losses of water associated with OH groups in sample #1 appear to reflect the higher crystalline phase content for this material. It can be seen that electrical resistivity decreases as the concentration of Al(OH)_3 and AlOOH groups increases, being the higher for sample #4. Therefore, the presence of OH groups could explain the lower electrical resistivity of coatings.

Finally, the good thermal stability of the coatings deserves to be mentioned: the weight losses for temperature increase up to 1400°C are in the range 0.6 to 2.3%, about 20% of it corresponding to loss of adsorbed water.

Table 4: Weight losses (in weight %) attributed to water of the various samples as obtained by TGA. Temperature intervals were defined according to the range of thermal stability of the corresponding groups.

Sample	Adsorbed water ($\leq 100^\circ\text{C}$)	Al(OH)_3 ($100\text{-}400^\circ\text{C}$)	AlOOH ($400\text{-}700^\circ\text{C}$)
#1	0.12	0.22	0.13
#2	0.35	0.83	0.54
#3	0.22	0.50	0.25
#4	0.57	1.12	0.60

5. CONCLUSION

We have correlated the operational conditions of the Micro-Arc Oxidation (MAO) process to the structural, dielectric and thermo-optical properties of coatings grown onto Al substrates. The main outputs of the study are as follows:

i/ The coatings formed by the MAO process fulfill the target properties such as low solar absorptance ($\alpha < 0.3$) and high IR emissivity ($\epsilon > 0.8$) before exposure to UV, high energy protons and electrons and thermal cycling.

ii/ Strong variation in electrical conductivity of the coatings were obtained depending on process conditions. Relatively low electrical resistivity materials can be processed, which appears promising for space application.

iii/ Low resistivity appears to go with appropriate thermo-optical properties; the low resistivity could be associated to the presence of OH groups in the coatings.

A first set of tests has been performed on the developed white thermal coatings. Studies are in progress to test adhesion, thermo-optical and electrical stability in Earth storage and for space environment, especially thermal cycling, UV and irradiation by charged particles. Results will lead to select the suitable thermal control coating.

6. REFERENCES

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7. ACKNOWLEDGEMENTS

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