ICSO 2016

International Conference on Space Optics

Biarritz, France

18–21 October 2016

Edited by Bruno Cugny, Nikos Karafolas and Zoran Sodnik

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esa icso proceedings cnes

International Conference on Space Optics — ICSO 2016, edited by Bruno Cugny, Nikos Karafolas,
Zoran Sodnik, Proc. of SPIE Vol. 10562, 1056212 · © 2016 ESA and CNES
CCC code: 0277-786X/17/$18 · doi: 10.1117/12.2296152

INNOVATIVE CNT-BASED COMPOSITE COATINGS FOR THE STRAY LIGHT REDUCTION

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The status of carbon nanotubes (CNT) as outstanding superblack coatings has been established in the recent years, and records in terms of absorbance in the UV-visible-NIR spectral range have been reported. Beside the high absorbance, superblack coatings need to fulfil other requirements for a realistic implementation in optical devices destined to space applications. These requirements include but not restricted to the oxidation resistance, sufficiently high cohesion and adhesion, compatibility with various substrates, reasonably low processing temperature, and compatibility with complex three-dimensional structures.

CNT-based composite coatings offer a high degree of freedom in terms of concept and architecture, but their reliable synthesis is challenging. An innovative one-pot chemical vapour deposition process has been established for the growth of this family of coatings with absorptance of ~99%, while satisfying the scotch tape adhesion test (3M-250). These coatings exhibit appealing resistance to environmental tests.

This study is supported by ESA funding in the framework of its Research and Technology Program (Contract number 4000112130/14/NL/SW).

I. INTRODUCTION

Observation from space with guaranteed end-of-life optical quality requires an accurate control of the optical payload parameters. Stray light rejection is a major concern wherever bright off-axis sources are present. Preserving the instrument geometric and radiometric image quality requires the reduction of the stray light. This is conventionally attained by the implementation of highly sophisticated baffles/vanes assemblies that are inherently associated with an increased cost and mass. Therefore, highly absorbing coatings (black coating) in the spectral range of interest have to be implemented to avoid the necessity of implementing expensive and complex/heavy baffles/vanes assemblies. In such a case, the coating should satisfy a number of requirements related to the baffle use, space environment and production technology.

The most important characteristics of the black coating are naturally related to the optical performance. In the context of our study, a minimized light reflection in the visible-near infrared range should be reached irrespective of the radiation incidence angle (Lambertian behavior). The quantified acceptance criteria in terms of angle-dependent total hemispherical reflection (THR) and specular reflection (SR) are listed in Table 1. Besides the optical properties, the black coatings should withstand aggressive space environments with marginal impact on their adhesion and optical performance. These environments involve vacuums, radiation, atomic oxygen and thermal environment (illumination/deep space cooling).

The implementation of additive manufacturing, 3D-printing, adds supplementary degrees of freedom for the baffling design conciliating light-weight and geometric complexity. Therefore, developing black coating processes that are compatible with current and future manufacturing technologies is a prerequisite. This would include the conformal deposition of the black coatings on complex shapes and sharp edges. Aluminum and titanium are the most frequently used materials for the baffles/vanes assemblies, and therefore the coating technology should implement appropriate temperatures and atmospheres to avoid their degradation.

Requirements	Values
Optical performances in the 0.4 – 2.5 μm range	THR < 1.5 % for normal incidence THR< 3% for incidence angles lower than 50° (with a goal < 70°) THR < 5% (with a goal < 3%) for incidence angles from 50° to 70° THR < 10% for angles of incidence from 70° to 85°
	Specular Reflectivity < 5% of THR
Adhesion	Adhesion : category 0 or 1 according to the standards
Substrate	Aluminum and Titanium
	Applicable to Baffle geometry (accessibility constraints, …)
Temperature	Temperature range from -45°C to +80°C
Outgassing	RML < 0.1%
	CVCM < 0.01%
Legislation	Coating could be submitted to export license (ITAR)
	Compliant with European directives RoHS and REACh.

Table 1 : Specifications of high performance black coating.

A number of black coating solutions are available for space applications including the non-selective solar paints that have been the first developed in this respect. The widely implemented diffuse black paint named Aeroglaze Z serie (Z-306), which is a urethane resin with silica and carbon-black fillers, belongs to this category.[1, 2] Among the listed black paints, Table 2, only AMES 24E (loaded ethyl silicate paint with silicon carbide grit and carbon black)[3] appears to satisfy an absorptance superior to 98.5% at near normal incidence. Nevertheless, the excessive required thickness of this coating, 250 μm, is a limiting factor.

Paints, in general, present drawbacks related to the thickness uniformity on small baffles with sharp edges,[4] and to the stringent guidelines to which they are subjected within the context of the International Traffic in Arms Regulation.

Unlike paints, anodization treatment is more appropriate for 3-D structures and sharp edges. Within this category, we might state Martin Black, which is anodized aluminum surface with sealed aniline dye inclusions. With an enhanced absorptance in the visible range, such treatment results in a high reflection in NIR and IR. The sensitivity of the treatment to the presence of welding in the structure and of copper in the aluminum alloys (e.g. Al 6061) is a significant drawback.

Plasma spray technique has been developed as alternative for the performance of diffuse black coatings. The plasma sprayed beryllium can be distinguished among this category;[4] nevertheless, the potential release of particles as a result of vibration is considered a non-negligible issue.

An outstanding diffuse absorptance was reported for the chemically vapor deposited layers of Carbon NanoTubes (CNTs), which is considered an inexpensive alternative material.[5] These coatings are typically grown by thermal activation above 700°C,[6, 7] which is not compatible with structures made of aluminum or thin titanium. Alternatively, photo-thermal activation at 425°C is implemented to achieve such coatings.[8] Nevertheless, the concept hardly applies to 3D structures.

Pristine CNTs are, however, prone to reaction with atomic oxygen with an inherent shortening of the lifetime. Furthermore, the vertical alignment of the CNTs might induce angle selective light reflections and high sensitivity to slight mechanical aggressions.[9] These drawbacks are not observed for Acktar solutions, carbon containing coatings that feature a competitive optical performance. It is worth noting that exposure to atomic oxygen leads to surface smoothening and formation of micro-cracks.[10] The implemented Physical Vapor Deposition (PVD) process is inherently line-of-sight which is not ideal for complex three dimensional structures. This short and non exhaustive list of the commercially available solutions for stray light reduction indicates clearly that carbon-containing coatings hold the highest potential to satisfy the specifications summarized in Table 1, while complying with the European directives (RoHS and REACh).

Name	Absorptance (α)
Paints	
Carbon Black Paint NS-7	0.96
Catalac Black Paint	0.96
Chemglaze Black Paint Z3O6	0.96
Delrin Black Plastic	0.96
Ebanol C Black	0.97
Ebanol C Black-384 ESH* UV	0.97
GSFC Black Silicate MS-94	0.96
GSFC Black Paint 3l3-1	0.96
Hughson Black Paint H322	0.96
Hughson Black Paint L-300	0.95
Martin Black Paint N-15O-1	0.94
Martin Black Velvet Paint	0.91
3M Black Velvet Paint	0.97
Paladin Black Lacquer	0.95
Parsons Black Paint	0.98
Polyethylene Black Plastic	0.93
Pyramil Black on Beryllium Copper	0.92
Tedlar Black Plastic	0.94
Velesat Black Plastic	0.96
AMES 24E	0.99
DeSoto Black	0.97-0.98
Plasma	
Boron Black	0.89-0.97
Beryllium	0.99
Titanium	0.93
Anodized Aluminum	
Black	0,65-0.86
Metals and conversion coatings	
Black Cobalt	0.96
Black Chrome	0.96
Black Copper	0.98
Vapor deposition	
Acktar	0.97-0.99
Vantablack	0.9996

Table 2: Summary of the existing commercial solutions.

II. EXPERIMENTAL

Deposition of the black coatings:

The deposition process was performed in hybrid Chemical Vapor Deposition-Atomic Layer deposition CVD-ALD equipment. The delivery of highly volatile precursors is performed using a bubbler system with electro-pneumatic valves, whereas precursors with insufficient volatility are introduced using the direct liquid injection system with solenoid valves. Both types of valves are controlled in using a Labview program to allow simultaneous (CVD) or sequential (ALD) surface exposure to the deposition precursors. Ethanol was implemented as the carbon source for the growth of carbon nanotubes (CNT) whereas $Co(acac)_2$ was used as precursor for the growth of CNT-catalyst. The matrix of the composite is prepared by the $Al(CH_3)_3$-H_2O for the growth of Al_2O_3; $Ti(OC_3H_7)_4$ for the growth of TiO_2; $Si(OC_2H_5)_4$ for the growth of SiO_2; $Mg(acac)_2$ for the growth of MgO and $VO(OC_3H_7)_3$ for the growth of VO_2.

Characterization:

Film thickness was measured using an Alpha step d-500 Profilometer from KLA-Tencor. Whereas, the surface and cross-section morphologies were characterized by FEI Helios Nanolab 650TM scanning electron microscope (SEM) equipped with an Energy Dispersive Spectroscopy (EDS) for the elemental analysis. The working distance was set at 4mm and an acceleration voltage of 25 kV.

The light absorption was measured using a Lambda 950 UV/Vis/NIR spectrometer (Perkin Elmer) from 250 nm up to 2500 nm with a step of $\Delta\lambda$=0.5nm. This equipment was used to measure the integrated reflection at an incidence of 8°. Two baselines are recorded for each series of measurement: the 100% reflection is collected with a diffuse standard reflectance material (99% Spectralon® LabSphere) and the 0% reflection with the uncover port.

The specular reflection (SR) and the angle-of-incident (AOI) dependent total integrated scattering (TIS) and the bidirectional reflection distribution function (BRDF) are measured at the Light-Tec and ESTEC (BRDF) facilities.

Mechanical and environmental tests:
The **adhesion test**, in-line with the ECSS-Q-ST-70-13C, was performed using pressure sensitive tape 3M 250. This tape is characterized by 8 N/cm as adhesion strength. The adhesion test with grid, 1 mm spacing, was implemented as the coatings are far thinner than 60 µm. Successful adhesion should correspond to only slight peel-off at cross points of cutting (Class 0 or 1).

Cleaning process was performed by using Kimtech tissues (or equivalent) soaked with isopropyl alcohol and then with acetone. The tissue is folded twice and soaked with the solvent before its placement and one way displacement on the surface of the coating. This operation is reiterated before allowing for the solvent to evaporate. The adhesion and optical properties inspection are used to validate the cleanability of the coating.

The **hygroscopic test** was performed via the extended exposure (7 days) of the coated samples to an atmosphere with controlled temperature (45°C) and humidity (95%). After this exposure the samples are visually inspected and subjected to optical characterization and adhesion test.

III. DEPOSITION RESULTS

In this study we address the potential of CNT-metal oxide composite coating with adjusted architecture to secure a compromise between the absorption, mechanical stability and the protection against the reaction with atomic oxygen. The challenge is twofold in this concept:

- Reconciliating the growth of CNT (reducing atmosphere) with that of metal oxide (oxidizing atmosphere)
- Lowering the growth temperature of CNT below 500°C to avoid the degradation of Al and Ti substrates

The deposition experiments were performed using thermal Chemical Vapor Deposition. Adsorbed ethanol reacts with surface cobalt acetylacetonate ($Co(acac)_2$) above 220 °C to form coatings of metal, carbide or a mixture thereof depending on the temperature used.[11-15] Based on this observation, a proprietary approach was implemented to grow decorated non-aligned CNTs (Figure 1) at 350-450 °C using either a sequential or simultaneous surface reactions. The growth temperature has a substantial impact on the growth rate of the CNT-based nanocomposites. The thickness of films obtained after a deposition time of 170 min at various temperatures was evaluated. The film obtained at 350 °C features a thickness of 1.2 µm, which corresponds to a growth rate of ~6.8 nm/min. Deposition at 400 °C yields a film with a thickness of 7.03 µm (40.2 nm/min), whereas 11.5 µm (69.7 nm/min) is obtained at 450 °C. The growth rate in this temperature window (350-450 °C) features a linear dependence.

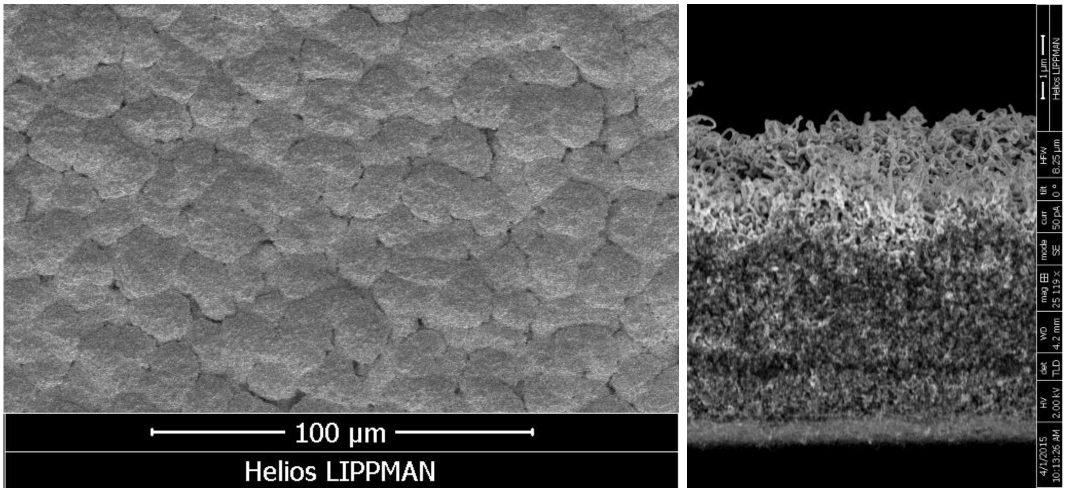

Figure 1: SEM inspection of the surface (left) and cross-section (right) of the CNT-based nanocomposite as infiltrated by 20 nm Al_2O_3.

The optical properties of the grown nanocomposites were evaluated using the total hemispherical reflection method (THR) at an incidence angle of 8°. All obtained films feature a very low reflection in the UV-Vis-NIR spectral range. The integration of the THR in the 300-2300 nm spectral range reveals a reflectance of 2.47 % for the film obtained at 350 °C which is 1.2µm thick, whereas 0.6 % and 0.55 % are calculated for films obtained at 400 °C and 450 °C successively. Above 3µm the film thickness has a marginal impact on the integrated THR as depicted in Figure 2.

The resulting nanocomposite coatings are porous and feature poor mechanical resistance: the coatings scratched easily upon contact with tweezers. Therefore, a subsequent pores filling is necessary to enhance the mechanical integrity of the coating. The example displayed in Figure 1 corresponds to nanocomposites that have been reinforced with the infiltration of a 20 nm of a conformal Al_2O_3 layer. Filling the present pores in the nanocomposite coating comes with an inherent modification of the optical performance. In the example illustrated in Figure 1, the deposition of an alumina layer (20 nm) yields an increase of the reflectance in the UV-Vis-NIR from 0.55 % to 1.1 %. This reflectance is still exceptionally low despite the implementation of an oxide with relatively high refractive index.

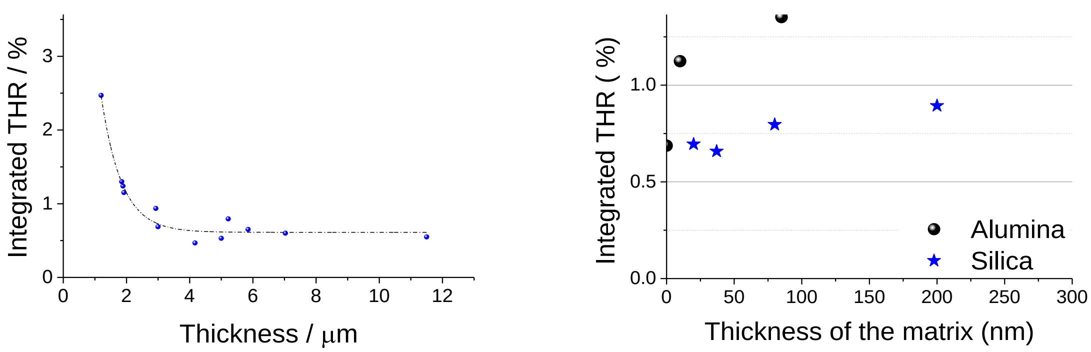

Figure 2: Evolution of the integrated THR in the UV-Vis-NIR (300-2300 nm) as a function of the thickness of the black coating (left) and the nominal thickness of the infiltrated oxide layer (right) into a ~5µm thick CNT-based composite. (AOI: 8°)

Increasing the nominal thickness of the infiltrated alumina film results in a substantial increase of the reflected light as displayed in Figure 2. Fulfilling the THR<1.5 % requirement prohibits the implementation of Al_2O_3 reinforcement with nominal thicknesses exceeding 100 nm. Materials with lower refractive index should be involved instead of Al_2O_3 if thicker reinforcements are needed. The illustration Figure 2 provides evidences that reinforcements with thicknesses far exceeding 200 nm can be implemented when SiO_2 is used to infiltrate the CNT-based composite.

The one-pot deposition process was implemented to coat Al (6061) and Ti (Ta6V) substrates as they are currently the materials of choice for the manufacturing the baffles systems.

IV. TEST RESULTS

Adhesion

The obtained films using this process feature a low level of reflectance with an integrated THR of 0.31% (300-2300nm spectral range) collected at an incidence angle of 8°. The BRDF measurements performed at ESTEC show no impact of the nature of the substrate (Si, Al or Ti) and of the angle of incidence (4° or 45°). In these cases, the reflection behavior is Lambertian

These films withstand gentle handling, vibration, flushing with ethanol jet and drying with nitrogen. Nevertheless, they scratch easily with the tips of tweezers and leave considerable residue on the adhesion test’s tapes (3M-250). Strengthening step with the infiltration of Al_2O_3 was integrated into the black coat deposition reactor (One-Pot multi-step process). It is worth mentioning that the infiltration process was successfully performed implementing SiO_2, TiO_2, MgO and VO_2. Nevertheless, the highest impact on the cohesion of the film was observed with Al_2O_3. Owing to their low refractive index SiO_2, MgO reinforcements have the lowest impact on the optical properties. A nominal thickness, as low as 10 nm of Al_2O_3, was shown to enable an appropriate strengthening to the film yielding a successful adhesion test with the 3M-250 tape.

Coating on sharp edges

Commercial stainless steel scalpels, which present an angle (~30°) and low curvature radius, have been used as substrate to demonstrate the possibility to coat sharp edges. The deposition of a black coating layer, ~8 μm, does not form defects at the edge. The curvature radius is estimated in this case at 24 μm.

Cleanability

The cleaning process was applied to an aluminum sample coated with a 10 nm-alumina reinforced black coating. A soaked tissue with isopropanol and then with acetone was used to clean the surface. After two cleanings and dryings no difference could be perceived by visual inspection. The process was repeated to, in total, 8 times. The wavelength-dependent reflection of the cleaned sample was measured using an incidence angle of 8°. The reflection spectrum shows a relatively flat profile with an increase of reflection on the visible and UV range as observed for the as-deposited films. The total hemispherical reflection, integrated in the 300-2300 nm, reveals a value of 1.03%, which is clearly within the specifications. The difference with the non-cleaned sample (THR=0.72%) is relatively negligible and might be attributed to the non-complete drying. The performed adhesion test with and without cross-cuts, see Figure 3, reveals that even after repeated cleaning, the black coatings retain a good adhesion/cohesion behavior.

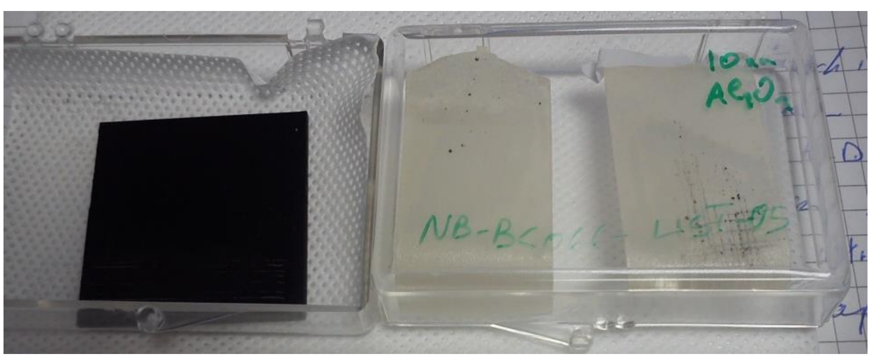

Figure 3: Adhesion/cohesion properties of coated Al sample cleaned 8 times using isopropanol and acetone soaked tissue. The black coating is reinforced in this illustration with 10nm of Al_2O_3

Environmental tests on coated Al

The **hydrothermal test** was performed using an environmental chamber at 95% humidity at +45°C during 7 days. The deposition of the alumina reinforcement was modified by extending the hydrolysis step, while keeping the nominal thickness of 10 nm.

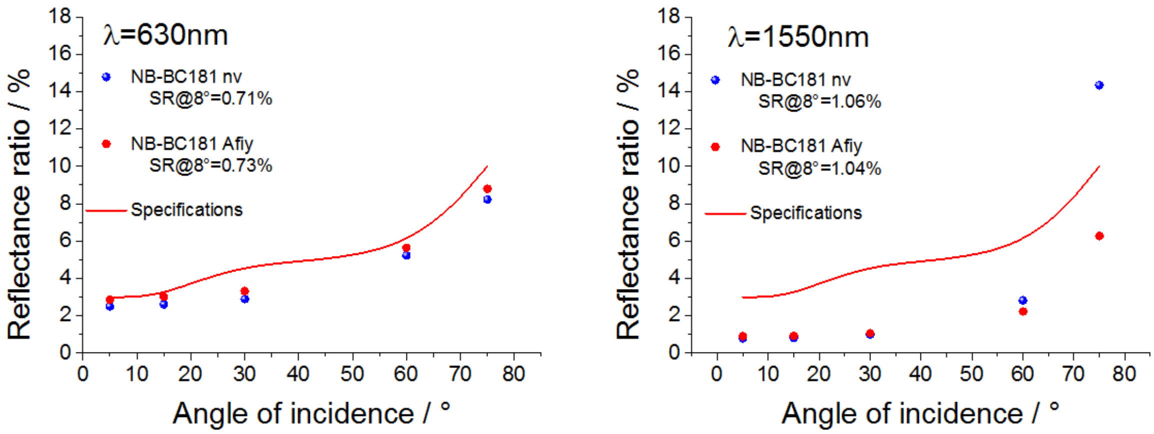

Figure 4: TIS and specular reflection measurements of the as-grown (blue) and aged (red) black coating on Al substrate. The coating process was modified by extending the hydrolysis step in the ALD process for the growth of the Al_2O_3 reinforcement layer.

The advanced optical characterization (TIS, SR and the BRDF) was performed for as grown samples and those exposed to the aging under hygroscopic environment. The recorded **TIS** results at various angles of incidence (AOI) are depicted in Figure 4. The impact of the hygroscopic test is marginal and the measurements satisfy fully the specified requirements as a function of the AOI. Irrespective of the hygroscopic test, the contribution of the **specular reflection** at 8° is measured at 0.7% in the visible and ~1% in the infrared range. The values measured are well within the specification, which is 5% of the total reflection.

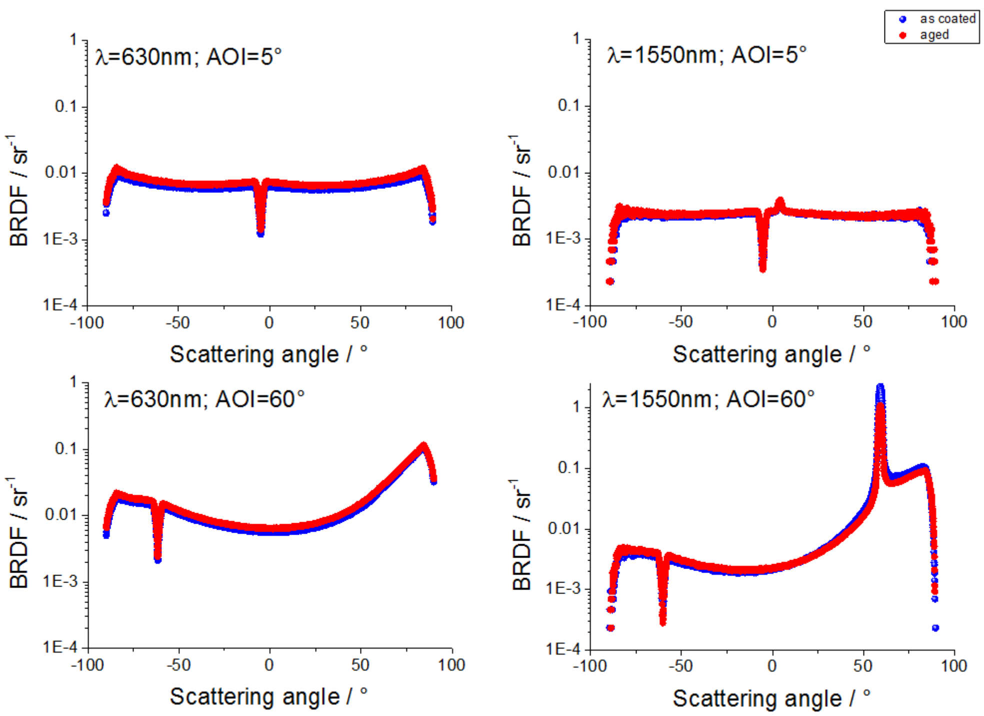

Figure 5: BRDF measurements of coated aluminum samples with the modified process. The samples correspond to the as-coated Al)blue) and the one exposed to a hydroscopic test (red).

Based on the **BRDF** measurements, it can be concluded that the impact of the hygroscopic test irrespective of the wavelength and the implemented angle of incidence is marginal. Unlike with visible light, infrared wavelength shows a measurable specular contribution that is enhanced at AOI=60° (see Figure 5). The contribution of the specular reflection for AOI of 5° is calculated at 1.224% that rises to 1.327% for exposed sample to the hygroscopic test. The contribution of the specular reflection is within the specification and its change with aging remains marginal at near normal incidence. For AOI=60° the specular reflection contributes to 18% of the total reflection for the as coated Al substrate. A thorough inspection will be necessary to understand and find a way to suppress this behavior. Surface roughening might be advantageous in this context.

V. CONCLUSION

The proposed CVD process yields porous CNT-based composite coatings at 350-450 °C, with an integrated THR of 0.35% (λ: vis-NIR) irrespective of the type of substrate used (Si, Al, Ti) and featuring a Lambertian BRDF behavior. Reinforcing the porous black coating in a second step within the same deposition reactor allows withstanding the adhesion tape test. Among the various reinforcement materials, e.g. Al_2O_3, SiO_2, TiO_2, Al_2O_3 allowed an appealing trade-off between adhesion (class 1 adhesion/3M-250) and optical properties (integrated THR of 0.72 % /λ:300-2300nm). No significant impact was observed on these films after aging (7 days, 55°C, 95% Hyg.) in terms of AOI-dependent TIS, SR and BRDF. Further fine tuning of the film structure is needed to suppress the specular reflection observed in the IR at high angle of incidence. The specifications in terms of TIS, SR and BRDF are otherwise satisfied.

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