



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Nyman, Leo

Coatings on Metals and Plastics for Lunar Habitats and Equipment

Published in: Proceedings of the International Astronautical Congress

Published: 01/01/2019

Document Version Publisher's PDF, also known as Version of record

Please cite the original version:

Nyman, L. (2019). Coatings on Metals and Plastics for Lunar Habitats and Equipment. In *Proceedings of the International Astronautical Congress* Article IAC-19_D3_2B_11_x49434 (Proceedings of the International Astronautical Congress). International Astronautical Federation (IAF).

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

IAC-19-D3.2B.11.x49434

Coatings on Metals and Plastics for Lunar Habitats and Equipment

Leo Nyman

Aalto University, Finland, leo.nyman@aalto.fi

The lunar surface is a harsh environment for future habitats and equipment. Lunar nighttime survival, in particular, will pose a considerable engineering challenge. Coatings applied on various substrate materials will be one of the key technologies for thermal engineers. Although many known coatings can provide desirable thermo–optical properties in a lab environment, the use of such coatings on the lunar surface will be complicated in many cases. For example, lunar dust particles can become electrically charged, and the adherence of such particles to coated surfaces must be minimised. The extreme range of surface temperatures on the Moon leads the thermal engineer to prefer coatings with a very low emissivity factor. Such coatings are highly sensitive to the accumulation of dust. Technologies such as atomic layer deposition (ALD) and indium tin oxide (ITO) coatings show promise as coating of metals and plastics, resulting in lower mass for the overall thermal system.

keywords: Lunar exploration, Space thermal, Coatings, Emittance, ALD, ITO

Abbreviations

ALD	Atomic layer deposition
AO	Atomic oxygen
BOL	Beginning of life
CTE	Coefficient of thermal expansion
CVD	Chemical vapour deposition
ISS	International Space Station
ITO	Indium tin oxide
JPL	NASA jet propulsion laboratory
LDEF	Long duration exposure facility
LPD	Liquid phase deposition
PC	Polycarbonate
PECVD	Plasma enhanced CVD
PEEK	Polyether ether ketone
PLD	Pulsed laser deposition
PVD	Physical vapour deposition
PVDF	Polyvinylidene difluoride
RMS	Root mean square
TRT	Transfer radiation thermometer
UV	Ultraviolet light

1. Introduction

A JPL study concluded that the key environmental challenges on the lunar surface are temperatures, lack of atmosphere, radiation, soil properties, meteorites and seismic activity [10].

For the upcoming lunar surface missions, the surface location will drive the design requirements for habitats, rovers and other equipment. Hot and cold temperatures are experienced at the mid and equatorial latitudes, whereas a less dynamic temperature environment is present at the poles. Passive thermal control coatings can be utilised to provide mass savings in all these temperature environments. In addition to thermal aspects, coatings can also be used to combat against dust accumulation, if voltage potentials and electrically conductive surfaces or circuits are used. Although the lunar atmosphere is not inherently corrosive, exhaust volatiles from descent and ascent stage engines may contain corrosive elements, and this should be taken into account in the selection of coating materials. Also, many polymeric materials need protective coatings against vacuum UV.

For space applications, the lack of atmosphere makes radiative heat transfer the dominant mode for thermal engineers [32]. This is also the case on the lunar surface, since the regolith has a very low thermal conductance [8, p. 38]. Coatings belong to a group of *passive thermal control* systems. Their use is limited by the degradation of thermo-optical properties [2, p. 209]. A *coating* is a system consisting of a layer or multiple layers upon a substrate. A layer can be made of any substance. Further division can be made between *pigmented, contact* and *conversion* coatings [32].

When selecting materials that provide a very low emissivity, gold is a natural choice. The physical and optical properties of gold are excellent in this respect. Gold has an inherently shiny and spotless surface, because of its resistance to corrosion. This was almost certainly the reason why it was one of the first distinct metals discovered by man.

The objective of this work is to evaluate a small group of coatings, including gold, which might prove useful for the upcoming lunar missions. The focus of the experimental part is to study the emissivity of potentially useful coatings. Next in this introduction section, we briefly look at some historical missions and generic requirements. The following section, *Materials and Methods*, explains the experimental part. The *Theory and Calculation* section provides supporting information, and the final section presents and discusses the results, drawing some conclusions.

1.1 History of Space Habitat Coatings

When the first Skylab crew arrived at the orbiting station a week and a half after the station itself had been launched, visual inspection revealed discoloration and blistering on the station's surface. It was clear that better protective coatings must be developed for future space habitats.

The Salyut 6 mission operated an experiment called the *Vaporiser*, which used the *Isparitel* apparatus installed in the scientific airlock. The cosmonauts used it to produce thin-film coatings of aluminum and silver [14, p. 84]. Later, they executed more experiments with substrate materials including glass, carbon, titanium and various other metals. The thin coatings applied included gold, silver, copper and aluminum.

Since the early space stations, the various experiments conducted on the space station Mir, LDEF and ISS have provided a wealth of long-term exposure data on various materials and coatings, exposed to low Earth orbit conditions. Similar long duration test campaigns will eventually be conducted on the lunar surface, due to its special characteristics.

$1.2 \ Requirements$

The requirements for space habitat coatings depend on several factors. Plastics need protection against UV radiation, whereas metals do not. Both of these substrates, however, should be protected from atomic oxygen (AO). The ultra-thin lunar atmosphere does not contain AO particles in significant quantities. However, cargo transported from Earth will pass through the AO zone in low Earth orbit. Also, the lunar crust contains 45 % oxygen by weight, which will be one of the first valuable lunar resources to be extracted by man [8, p. 635]. Lunar habitats will leak some amount of O₂, which will be split by solar UV into atomic oxygen particles. Therefore, right from the beginning, coatings should be implemented

that are resistant to AO.

1.2.1 Thermo-Optical Properties

Considering the case of lunar nighttime survival, the (thermal) emissivity of the coated surface should be as low as possible, to reduce the amount of power required for heating. In the ideal case, the spectral response should be flat in the range of about 2.5..300 μ m and have a 100 % reflectance. To simplify engineering work, we can argue that the range of 3..50 μ m is relevant in practice. For the lunar daytime, the surface absorptivity is also important, due to the solar irradiance. Related to this, we know that about 98 % of the solar spectrum is within the wavelength range of 0.28–3.9 μ m. More details will follow in Chapter 3.

2. Materials and Methods

A total of 22 test articles were prepared for the experimental part of this study (Table 1). 14 of these test articles were machined and polished using basic machine shop methods, with the copper and stainless steel used during the tests being of normal *hardware store* grade. The nickel used was 201 grade. The remaining 8 test articles (silicon, transparent polycarbonate and one copper plate) had an industrially-prepared smooth surface when received, and for these test articles the machine-shop-polishing was omitted. The silicon wafer test articles were cut from standard 100 mm discs used by the semiconductor industry.

The surfaces of the test-articles-to-be-polished were first smoothed using grade 400, 800, 1200 and 2000 grinding papers. The final smooth surface was obtained with a polishing compound, as shown in Figure 1. During the grinding and polishing, the surface was inspected with an optical microscope, to determine the proper time of switching to a finer grade paper and to the final polishing stage.

With all the test articles having a smooth surface, the coating of the test articles began. Before coating, all the test articles were cleaned for 5 minutes in an ultrasonic cleaner, filled with de-ionised water. Next, they were wiped with standard IPA (isopropyl alcohol) wipes. Most of the test articles were coated, while five test articles were left uncoated, to act as a reference for the emittance measurements. The coatings were deposited by the following companies: ALD coatings by *Picosun Oy LTD*, ITO coatings by *Beneq Oy LTD*, electroplated-gold coatings by *Eforit Oy LTD* and gold-palladium coatings by *VTT Technical Research Centre*. All of these companies are based in Finland. Both the ALD Al_2O_3

Table 1: Test articles were 30x30 mm plates. Only the polished side was coated and measured for thermal emissivity at room temperature. The label is a unique identifier of a test article. The substrate is the material from which the test article was cut. The test article surface was either polished in the Aalto University's Design Factory machine shop or as received. The last columns show the coating type and estimated or measured thickness. Reference test articles received no coating at all. The LL91 was otherwise identical to LL2, except that LL91 had a few visible scratches on its surface.

Label	Substrate	Surface	Coating, thickness \ast
LL1	Copper	MP	SP ITO, 94 nm
LL2	Copper	MP	ALD Al_2O_3 , 9.5 nm
LL3	Copper	MP	ALD Al_2O_3 , 19 nm
LL4	Copper	MP	ALD Al_2O_3 , 28.5 nm
LL5	Copper	MP	EP Au, 500 nm
LL6	Nickel	MP	EP Au, 500 nm
LL7	Steel	MP	EP Au, 500 nm
LL9	\mathbf{PC}	AR	SP AuPd, 30 nm
LL11	Copper	MP	No coating
LL12	Steel	MP	No coating
LL13	Nickel	MP	No coating
LL14	Si wafer	AR	No coating
LL21	Copper	MP	SP AuPd, 30 nm
LL22	Copper	AR	ALD Al_2O_3 , 95 nm
LL31	Si wafer	AR	ALD Al_2O_3 , 9.5 nm
LL32	Si wafer	AR	ALD Al_2O_3 , 19 nm
LL33	Si wafer	AR	ALD Al_2O_3 , 28.5 nm
LL34	Si wafer	AR	SP ITO, 94 nm
LL41	Steel	MP	SP AuPd, 30 nm
LL51	Nickel	MP	SP AuPd, 30 nm
LL91	Copper	MP	ALD Al_2O_3 , 9.5 nm
LL92	PC	AR	No coating

* AR – As received (industrially prepared)

MP – Mechanically polished

SP - Sputtered

Fig. 1: Some of the test articles were polished in a machine shop. Farecla G3 regular grade polishing compound was used together with a cotton covered rotating foam polishing head.

gold content was 99.8 %. The gold-palladium coatings were produced with a Leica EM ACE200 with an Au/Pd 80/20 (Leica) sputtering target. The process was magnetron sputtering with argon plasma in directional mode, pressure $4 \cdot 10^{-2}$ mbar and 35 mA sputtering current. Some of the finished test articles are shown in Figure 2.



Fig. 2: A few examples of the finished test articles.

Emittance was measured using a Heitronics TRT device. The measured spectral range was 8–12 $\mu \rm{m},$

ing produced a *hard-gold* coating, following typical methods used by the supplier, except for the copper test article which did not receive the nickel interlayer that is normally applied. The exact alloying constituents of this particular hard-gold are unknown to the author, except that it contains cobalt and that the

and sputtered ITO coatings were produced by using

industry standard methods and 150 °C process tem-

perature. The processes selected for the electroplat-

EP – Electroplated

which does not fully cover the applicable black-body curve (Figure 3), but is well positioned around the peak of the curve to give meaningful results. The measurement was done in a temperature and humidity stabilized environment. The temperature of the test articles was room temperature. A reference black-body target with a known emittance of around 0.98 was used as a reference target during measurements.

3. Theory and Calculation

This section is useful for a thermal engineer, as it covers the critical aspects that govern the thermooptical properties of a solid surface. It is common to express the performance of a thermal control coating using the factor α/ε , where α is the ratio of the normal solar absorptance to the hemispherical total emittance (ε). All the required details of these two properties are explained by Touloukian *et al.* [32].

3.1 *Thermal Radiative Properties*

The main thermal radiative properties are emittance, reflectance, absorptance and transmittance. These properties change as a function of material, wavelength, polarization, temperature and the angle of incidence with the solid. For convenience, the wavelengths are grouped as shown in Table 2.

Table 2: Thermal radiant energy range [32]. Wavelength is denoted by λ .

Range	Labelling	λ (nm)
Ultraviolet	UVC	100-280
	UVB	280-315
	UVA	315-400
Visible	VIS	380-780
	IRA	780-1,400
Infrared	IRB	1,400-3,000
	IRC	3,000-1,000,000

3.2 Physics of Emissivity

When a body is irradiated, part of the incident flux is reflected, part is absorbed and the rest is transmitted. Based on this, we can write an equation $1 = \rho + \alpha + \tau$, where ρ is the reflectance, α the absorptance and τ the transmittance. For opaque materials, we can set $\tau = 0$, and we get $1 = \rho + \alpha$. Now, we use Kirchhoff's law of thermal radiation, which states that if the wave properties are constant and the body is in thermodynamic equilibrium, then $\varepsilon(\theta) = \alpha(\theta)$, where ε is the emittance and the angle θ specifies the observer angle. Based on these equations, Touloukian et al. [32, p. 7a] used a simplified formula for opaque objects, $\rho + \varepsilon = 1$. This simplification has certain restrictions, which are explained in their book. However, we can interpret this equation as follows. If we maximize the surface reflectance, we also minimize the emittance. For example, a coarsely polished aluminum surface at room temperature might have an emittance of $\varepsilon = 0.15$ at a specific narrow spectral range. Assuming that this block of aluminum is thick enough to be opaque, we know that its surface reflectance is $\rho = 0.85$ in the same spectral range. A perfect *black-body*, a useful theoretical concept, has an emittance of $\varepsilon = 1.0$ and zero reflectance at all wavelengths.

Polished metals typically have low emissivity and high reflectivity in both the visible and infrared spectrums. However, there are important variations and some materials may exhibit different characteristics in the visible versus infrared bands. For nonmetals, the geometric distribution of the radiant energy emitted or reflected from the surface is nearly constant over the hemisphere. For metals, the geometric distribution is markedly different. For smooth metal surfaces, the radiance increases with the angle from the surface normal, with the maximum being somewhere less than 90° [32, p. 17].



Fig. 3: Spectral radiance curve for a black-body at two temperatures. At 300 K, the peak of the curve is around 10 $\mu \rm{m}.$

3.2.1 Surface Temperature

The radiant exitance of a black-body is given by the Stefan–Boltzmann law $M_t = \sigma T^4$, where M_t is the total emitted power in watts per square meter over the total wavelength range, σ is the Stefan–Boltzmann constant and T is temperature in Kelvin.

3.2.2 Surface Roughness

The fact that radiant energy does not travel more than some tens of nanometers in metallic solids before being completely absorbed, is also important when considering emissivity [17, p. 636]. Because of this small length scale, the surface roughness, oxidation and defects are as important as the material itself, for determining the optical and thermal radiative properties for metals. According to Touloukian et al., a mechanically-polished surface will have a lower reflectivity compared to PVD films [32, p. 24]. Some surface defects can be caused by mechanical Dielectric coatings are less sensitive to stresses. the surface condition, because the emittance and absorptance is affected by a much thicker skin depth (i.e. bulk or volume phenomena) [32, p. 3a]. These factors should be taken into account, especially when designing coatings for inflatable structures and pressurised vessels.

A surface is considered as being optically smooth, if $d < \lambda/(8\cos\theta)$, where d is the RMS surface roughness height, λ is the wavelength of the EM wave and θ is the the angle of incidence. Therefore, a surface which is smooth in the visible range is also smooth in the infrared range, but not necessarily vice versa. By selecting an arbitrary wavelength limit of 1.4 μ m, we can derive the required RMS surface roughness of 0.175 μ m. Many commercial polishing compounds have particles sizes in the range of 1..6 μ m, with some finishing compounds consisting of smaller particles as small as 0.25 μ m. Therefore, it should be possible to polish a large metallic surface to optical smoothness in the infrared band with inexpensive materials and tools.

The final surface roughness is a combination of the substrate and the coating. In some cases, the coating may increase the final surface roughness significantly. Bessonov *et al.* deposited gold CVD films using different precursors. The resulting gold coatings had large differences in their surface roughness [3]. In this case, even if the substrate was sufficiently smooth, the applied coating was not.

3.3 Low Absorptance, Low Emittance Coatings

Several metals feature high reflectance and corresponding low emissivity of thermal radiation. According to Macleod, gold is probably the best material for infrared reflecting coatings [24]. However, recent projects in the field of infrared telescopes have used protected silver for the construction of lowemissivity mirrors [4]. The Gemini telescopes use multilayer coatings, where one of the first layers is metallic (silver), and the top layers protect this metal from oxidation and other degrading reactions. According to Touloukian et al., metallic films with a thickness of 200-300 nm will be opaque, and the characteristics are nearly identical to bulk metal [32, p. 24]. This can be used as a guideline for determining the thickness of the metallic layer. The protective layers should be as thin as possible, in order to affect the thermo-optical properties as little as possible, but thick enough to provide a robust protection. This drives the protective layer thickness down to a few nanometers or to some tens of nanometers. This sounds very thin. However, ceramic coatings thicker than this are often more prone to cracking, so limiting the thickness of this layer has a number of benefits. Because low emittance in most cases will be achieved using conductive metals, the following lists some of these metals with relevant information.

$3.3.1 \ Gold$

Almost any solid substrate can be coated with a thin gold film using, for example, electroplating, electroless deposition or PVD [7, p. 21]. It has been shown that sputtering produces less porous gold coating than electroplating, thus providing a better protection for the underlying substrate. Also, sputtering can be used to deposit very thin gold coatings. For example, a 4..50 nm coating thickness is common for scanning electron microscope targets.

It has been shown that low thermal emissivity is related to low electrical resistivity of the material near the surface [9]. This phenomenon, known as the *Hagens–Rubens relation*, was discovered in 1903. For gold, its excellent electrical conductivity and resistance to oxidation results from its special electronic configuration. The first ionization potential of gold is 9.2 eV, which explains its high corrosion resistance [7, p. 13–15]. Gold has a high reflectance, but there is a dip for wavelengths shorter than about 600 nm. Silver does not have a similar dip, and therefore has a colour closer to white. Figure 4 shows the IR reflectance curve for a high quality gold coating.

Practical gold coatings on optical components have reflectance of > 98 % for wavelengths longer than 1 μ m [22]. Commercially available polymer films with gold coating have BOL emittance of $\varepsilon = 0.02$ and absorptance of $\alpha = 0.28$. These values are listed in the well-known *Sheldahl Red Book*.

A robust coating system must be compatible with the underlying substrate. Gold coatings on copper are typically done with a nickel layer between Cu and Au to prevent the diffusion of these two metals. Magnesium is a good engineering material for space applications, due to its high strength to weight ratio and other properties. However, it must be treated with a complex multilayer coating system for protection against corrosion. Gold is one good choice for the top surface layer. This will result in a robust coating, suitable for space applications [13]. Gold coating on nickel is very common. When deposited with *immersion plating*, the gold film has a thickness of 50–100 nm [7, p. 235].

Pure gold is relatively soft, and as such, unsuitable for several applications. Hard-gold coatings are used in many industries. For electronics, these coatings have a thickness in the range of $0.5-5 \ \mu$ m. The alloying metal used for gold hardening is commonly cobalt, nickel or iron, with the final alloy still containing over 99 wt% gold [7, p. 269].



Fig. 4: Normal spectral reflectivity of evaporated gold on a fused quartz substrate in the spectral range of 2–32 μ m at temperature of 298 K. Deposition was done in an ultra-high vacuum (5 · 10⁻⁹ mm Hg). Data reproduced from [32, p. 670].

3.3.2 Silver

Silver has very high reflectance in visible and IR bands. This metal is chemically unstable and soft, and these properties necessitate the use of an additional protective coating. The Gemini telescopes are using the following coating system: 1. Substrate, 2. NiCrN_x adhesor layer (5 nm), 3. Silver reflector layer (200 nm), 4. NiCrN_x adhesor layer (0.8 nm) and 5. SiN_x overcoat (15 nm). See Figure 5.



Fig. 5: Reflectivity of the 4-layer protective coating of the Gemini telescopes' silver coated mirrors. The protective multi-layer coating had a negligible effect on the surface reflectivity. Data reproduced from [4].

3.3.3 Aluminum

An oxide surface of Al₂O₃ quickly forms on aluminum, even in a high vacuum. Therefore, surfaces of pure Al cannot exist for long periods of time even in the lunar environment [29, pp. 369–406]. This alumina layer has a much lower reflectivity. MgF₂ or LiF are often used to coat pure aluminum, in order to prevent oxidation. However, this lowers the reflectivity slightly [5]. Leafing aluminum paints may have an emittance of $\varepsilon = 0.2$, but these are not often used in spacecraft [11, p. 142]. If the surface oxidation can be prevented, aluminum offers an excellent reflectivity over a wide spectral range (Figure 6).

3.3.4 Copper

Copper is a relatively noble metal, thus having a good corrosion resistance. Copper alloys with excellent resistance to stress corrosion cracking include the following, listed here by their UNS number: C10200, C12200, C10400–C10700, C70600 and C71500 [1, p. 252]. If the surface oxidation can be prevented, copper offers an excellent reflectivity in the infrared range (Figure 7).

3.3.5 Other Metals

Nickel-based coatings are very common. In terrestrial applications, nickel coatings are typically 5– 250 μ m thick, depending on the requirements [1, p. 284]. Chromates are highly toxic and, therefore, alternatives are currently being researched [1, p. 293]. Rhodium is sometimes used as a protective coating for silver [1, p. 284]. It reflects light well, and



Fig. 6: Normal spectral reflectivity of 65..110-nm thick aluminum coating in the spectral range of 2–32 μ m at temperature of 298 K. Aluminum rod of 99.998 purity was evaporated on a fused quartz substrate in vacuum (1 · 10⁻⁵ mm Hg). Measured immediately after deposition. Data reproduced from [32, p. 596].



Fig. 7: Angular (45 °) spectral reflectivity of a copper coating in the spectral range of 2.24–14.38 μ m at 298 K temperature. Data reproduced from [32, p. 643].

is used in optical coatings. Metal alloys containing rhodium have good resistance to oxidation. Cobalt has a rather poor corrosion resistance [1, p. 292]. For many coating systems, stainless steel is the underlying substrate. However, stainless steel can also be used as the coating material. It does not have as high reflectance as the best metals in this respect, but it is highly resistant to mechanical wear and chemically inert [26, p. 10]. It can therefore provide a robust coating system for many substrates.

3.4 High Absorptance, Low Emittance Coatings

Solar absorber surfaces are useful, for example in solar thermal power systems. A black nickel coating can be applied on copper, steel and many other substrates. Tabor investigated a system [31], where a smooth copper substrate provided low emissivity, and a thin black nickel coating provided a high absorptance of the solar spectrum (Figure 8). Ni-pigmented aluminum oxide has been measured to have an absorptance of $\alpha = 0.93$ and emittance of $\varepsilon = 0.16$ [30]. Other similar coating systems include black cobalt and black chromium. For low temperature applications, special paints could be used. The lowest emissivity values for opaque paints seems to be around 0.15 [18].



Fig. 8: Reflectance of black nickel coating on copper substrate in the spectral range of 0.4–20 μ m. The graph suggests a high α/ε ratio. Data reproduced from [31].

3.5 Low Absorptance, High Emittance Coatings

Among all the metals, aluminum and silver have the highest reflectance over the solar wavelength range. One study reported, that high quality aluminum films can have 92 % solar reflectance, whereas silver films reach 96 % [26, p. 32–33]. Austenitic steel has a reported solar reflectance of 67 % [27]. In order to obtain high emittance, dielectric coatings can be used, transparent in the solar spectrum. One option for this could be PVDF coatings.

A study by Hass *et al.* showed that a two-layer coating of Al_2O_3 and SiO_x with a suitable thickness, can have high emissivity in the thermal IR band. The same coating can also have a low solar absorptance, making it suitable for applications where low α/ε is required [15]. However, for this coating the emittance reduces rapidly at around 8- μ m wavelength, so

if high emittance is required, the temperature of the body should be kept at less than about 100 $^{\circ}\mathrm{C}.$

White thermal control paints have been used extensively during the history of spaceflight. However, they are not an ideal solution. The α value is known to increase due to prolonged exposure to UV, and many paints are a source of outgassing. A white anodized aluminum is able to provide an α/ε ratio of 0.2, with a 10.5- μ m thick coating layer [21] and minimal outgassing.

3.6 High Absorptance, High Emittance Coatings

Black anodization of aluminum is a common method for spacecraft. Care must be taken that the oxide layer becomes thick enough, or otherwise the coating will lose its colour under UV exposure or mechanical wear. On the the other hand, an anodized surface that is too thick will be prone to chipping under thermal loads – a process that produces unwanted loose microscopic metal chips to the surroundings. There are several anodization techniques, a good choice for space applications being anodizing with an inorganic black colouring process [28].

3.7 Inorganic Coatings

Inorganic coatings protect the substrate by their barrier effect and by their ability to attenuate short wavelength radiation. Matching of the CTE is important between the coating and the substrate. Some examples are coatings of oxides, nitrides and borides.

3.7.1 Indium Tin Oxide (ITO)

ITO has several interesting properties. It is an electrically conductive oxide, transparent in the visible and near-IR bands and highly reflective in longer IR wavelengths [20]. For the Aalto-1 CubeSat, the external black anodized aluminum surfaces were coated with 100-nm layer of ITO. As a result, the solar absorptance of the surface was reduced only by 1.5 %, while the coating created an electrically conductive surface. The ITO process temperature for the Aalto-1 black anodized aluminum panels was 150 °C. Earlier trials using 300 °C caused surface cracking for some of the panels. Because various colours can be created for aluminum surfaces with the use of anodization techniques, it should be possible to manufacture a hybrid coating of pigmented alumina and ITO, which possesses a desired α/ε ratio. If the lowest possible thermal emissivity is sought, the ITO layer should be made as smooth as possible. Kim et al. [20] used a pulsed laser deposition (PLD) to create smooth ITO layers. Another important aspect

of their research was that they were able to deposit ITO films at room temperature. This makes PLDdeposited ITO compatible with many polymeric materials that would not survive high process temperatures.

3.7.2 Tin Oxide

Tin Oxide, or SnO_2 , deposited using LPD, is less prone to cracking compared to ITO. The electrical conductivity of tin oxide is low, but it can be used as a dissipative material to avoid static buildup. It shows promise as a protective coating for plastic parts in space applications [12].

3.7.3 Silicon Oxides

Silicon Oxides, or SiO_x , are commonly used coatings for protecting polymers in space. For the large ISS solar panels, SiO_x coatings have been used to protect the underlying polymers. PECVD is commonly used to deposit the SiO_x coatings. However, this method produces uneven deposition, so relatively thick coatings have been used (around 130 nm). Thick coatings are nevertheless prone to cracking under thermal cycling [25].

3.7.4 Alumina

Alumina (Al_2O_3) is a widely used coating, with an excellent strength-to-density ratio. It can be deposited with an ALD process. ALD can be used to coat complex shaped parts, resulting in a highly uniform conformal coating. The part to be coated can have almost any type of geometry. Alumina has a good adhesion to a wide range of materials, including silver [24]. As a dielectric material, an alumina coating on silver is expected to increase emittance. A crucial parameter is the coating thickness. In one study, an Ag-Al₂O₃ system had a measured emittance of approximately 0.035 at 4- μ m wavelength [4].

ALD Al_2O_3 is a promising coating, which could substitute PECVD SiO_x coatings for protecting polymers in space. Several benefits can be recognized:

- ALD produces a highly conformal and uniform coating layer.
- Coating thickness can be controlled in steps of a single monolayer, which is about 0.1 nm for Al_2O_3 .
- Parts with any geometry can be coated.

- Because ALD is a vacuum process, water vapour is effectively removed from the part before the application of the coating layer. The coating inhibits water absorption into the coated parts.
- Al₂O₃ can be applied at low temperatures, even 35 °C. However, better results are obtained when using a process temperature of at least 100 °C.
- Thin Al₂O₃ coatings (5..40 nm thick) maintain good adherence to flexible surfaces.

Minton *et al.* used TiO₂ combined with Al₂O₃, to evaluate the level of protection against AO and UV for a few vulnerable polymer substrates. The results indicated that a 2-nm layer of Al₂O₃, with the addition of 6 nm of TiO₂, effectively protected the underlying polymer against vacuum UV. The number of ALD Al₂O₃ cycles required to create a gas barrier film was dependent on the substrate material. A layer of Al₂O₃, with a thickness of 10 nm or more, seems to provide a good level of protection against AO [25].

3.8 Coatings for Dust Mitigation

Recent in-situ measurement of naturally occurring dust accumulation on equipment placed on the lunar surface, was conducted by Li *et al.* [23]. They measured an average dust accumulation of 21.4 μ g/cm² per annum on a horizontally-mounted sticky quartz crystal microbalance located at 1.9 m above the surface. This equals approximately a 0.7- μ m layer of accumulated dust over the exposed horizontal surfaces after a decade. Active dust removal by dielectrophoresis systems are currently in development to combat dust accumulation [6].

4. Results

This section includes the results of the experimental part, explained in Section 2. The measured emittance of the test articles at room temperature is shown in Figure 9. Due to the setup used, it is suspected that the results contain inaccuracies, stemming from small fluctuations in the room and test article temperatures. Some inaccuracies can be caused by alignment errors of the test articles and the measuring device. Because of these factors, these results should be treated as *advisory only*, and it is better to mostly compare the test articles against each other, rather than to treat these values as an accurate data source. The view angle of the TRT was fixed and parallel to the test article's surface normal. Therefore, the results represent normal emittance $\varepsilon_{\rm N}$.



Fig. 9: The measured normal emittance ($\varepsilon_{\rm N}$) of the test articles' surface. The values represent the ratio of the integrated radiant exitance at room temperature to that of a black body, in the measured spectral range of 8–12 μ m. The LL2 is a copper part coated with a very thin layer of ALD Al₂O₃. See Table 1 for the descriptions of all test article labels.

The LL2, which was a copper test article coated with a very thin layer of ALD Al_2O_3 , had the lowest emittance in this study. An almost identical test article except for the few scratches on its surface, the LL91 also had a very low emittance. The third test article with a very low emittance was the LL11 (uncoated copper). The highest emittance was measured for the copper test article with a 28.5-nm thick ALD Al_2O_3 coating (LL4). All the other test articles had emittance between these extremes.

5. Discussion

The results suggest that inexpensive polished copper plates could be manufactured and coated with a thin protective ALD Al₂O₃ coating to produce lowemittance surfaces that are suitable for lunar missions. These surfaces would have a high α/ε ratio, so they would warm up significantly in sunlight. During a lunar daytime, this heat could be channelled to a thermal energy battery or to a radiator. In the lunar nighttime, the low-emittance surface would help to reduce the power required for heating. Copper is an excellent conductor of heat. The CTEs of copper and alumina are both fairly low, and this should alleviate concerns over thermal-cycling induced cracking of the coating.

The Hagen–Rubens relation [16, p. 225] suggests that a dielectric coating on copper should increase the surface thermal emittance. The results of this study support this, although the emittance of the LL22 test article was lower than the LL4 test article, despite the latter having a thinner Al_2O_3 coating. The difference in emittance of these two test articles might be caused by the fact that they had a different surface roughness. It should be recalled that the surface roughness affects the emittance. By having an *optically smooth* copper surface, and a thin enough protective coating (e.g. 5..10 nm of ALD Al_2O_3), the surface emittance should remain very low in the thermal IR band.

The test articles cut from silicon wafers had extremely smooth surfaces compared to the other test articles. However, the electrical conductivity of the surface of these silicon substrate test articles was only moderate. The results are consistent with the previous observations. Surface smoothness must be coupled with a good electrical conductivity for obtaining low surface emittance.

Gold coatings thinner than about 100 nm are more and more transparent to visible light. This fact has been utilized in visor coatings for astronaut helmets. The *Canadarm* used in the ISS is protected using gold coatings, in addition to Beta cloth blankets. Gold coatings are the preferred choice for fulfilling many of the needs for lunar missions, inside and outside of the habitats and equipment used. The material consumption of this precious metal can be reduced, by selecting a thickness for the coating layer that fulfils the requirements. For low-emittance surfaces, about 300 nm should be enough. For example, let's consider a geodesic dome structure with a diameter of 18 m on the lunar surface. If we apply a 300-nm hardgold coating to two-thirds of the surface area, the coated area will be about 680 m^2 and the amount of gold required about 4 kg. This is roughly 190,000 USD with today's market value. Considering the requirements, this is not an expensive solution. If the gold is only used to provide a barrier coating, then a thinner layer would be sufficient. Gold is highly ductile, and a surface area of at least 25 m^2 can be coated with just 30 g of Au. For the dome example just introduced, just 0.8 kg of gold would be sufficient for a barrier coating. Other metallic elements are less ductile, and more material would be required to cover an equivalent area [7, p. 17]. As it was earlier stated, almost any material can be gold coated. However, gold-coated aluminum should be avoided, as there will be a growth of intermetallic non-conductive layer above temperatures of 125 $^{\circ}C$ [19]. It is common to use a nickel interlayer when gold coating stainless steel. However, the supplier of electroplated gold coatings for this study has an alternative method which does not require a nickel interlayer for stainless steel. Gold coatings have extensive spaceflight heritage, and should prove useful also for the upcoming lunar missions. If the surface is intended to be cleaned with mechanical brushing, for dust removal, then hard-gold alloys must be used for wear resistance.

For lunar habitats and equipment placed on the surface, the temperature of the coating will very much depend on the insulation used in the main structure. In order to minimize the power used by heaters in keeping a habitat interior warm during a lunar nighttime, the habitat surface (coating) temperature should be kept as low as possible. The following examples will illustrate this. For a black-body surface with a temperature of 100 K, the emitted power (thermal radiation) is approximately 6 W/m². The corresponding values for temperatures of 200 K and 300 K are 91 W/m² and 459 W/m², respectively. Figure 3 illustrates this for 200 K and 300 K.

5.1 Recommendations for Further Studies

Although copper, gold and other excellent conductors of electricity provide a low emittance surface, their use in large construction elements incurs weight and cost penalties. In order to get the best of both worlds, we could create large elements from thermoplastics and then coat them to obtain the desired thermo-optical properties. This sounds easy, but some complications exist. The substrate and the coating should not have a large gap between their CTE values. Metals typically have a much lower CTE compared to thermoplastics, and this must be taken into consideration. Also, the adhesion of different material bonds must be ensured. The list of requirements is long, and is driven by the generic requirements of man-rated space habitat design and the lunar surface environment. In short, the coating system should be robust, and compatible with the selected substrate(s). We could start by selecting some suitable engineering plastics, such as PC or PEEK, for the structural base (substrate). For the multilayer coating, the initial layer could be made using copper electroplating. This process requires that an initial conductive layer is first applied. This could be made from a conductive nanosilver ink, which has a cured film thickness of $1..2 \ \mu$ m. The cured ink might be a good interlayer between the polymer and the copper, which have dissimilar CTE values. In order to provide a low emittance, the copper layer should have a minimum thickness of about 300 nm. The top layer could be made with Al₂O₃ ALD, which provides a good adhesion, and does not increase the surface roughness. This layer should be as thin as possible, while still acting as an effective gas barrier. Based on the results of this study, an ALD Al_2O_3 coating with a thickness of 5..10 nm should be tested as part of this concept. The emissivity measurements should be done using multiple incidence angles, in order to derive the total hemispherical emittance ($\varepsilon_{\rm H}$).

6. Conclusions

The goal of this study was to derive recommendations for further work, based on: 1) The feasibility of the methods used to produce the 22 test articles, 2) the measured thermal IR emittance of the test articles, 3) relevant theory and 4) reported work of other authors.

Although we cannot guarantee the accuracy of the results in Section 4 to a great degree, they do provide a useful comparison of different types of coatings and substrates. For example, the polished copper plates with a very thin ALD Al_2O_3 coating show great promise as a technology for upcoming lunar missions. This Cu-Al₂O₃ system might provide an alternative to gold coatings in some applications. Our results suggest that the polishing of the copper plates could be done in a typical machine shop using inexpensive tools and materials.

ITO coatings are a robust system that have been used in spacecraft over several decades. This, and the unique properties of such a coating will ensure its part in various missions to the lunar surface. Active dust removal by dielectrophoresis systems could be built using area-selective ITO and ALD coatings.

Book values for absorptance and emittance should

be used with caution. The aim should always be to measure the actual values of sample parts, in order to improve the performance of a passive thermal system in question. When designing coating systems for lunar nighttime survival, accurate measurements should be performed over a temperature range of at least 100..400 K and covering as much as possible of the 3..50 μ m spectral range.

Acknowledgements

For assistance related to coatings, the author would like to thank the following persons: Paavo Porri (VTT), Marko Pudas (*Picosun Oy LTD*), Lauri Virta (*Eforit Oy LTD*), Pertti Malvaranta and Markus Vala (*Beneq Oy LTD*). Also, the author thanks the following persons, who made this study possible: Prof. Esa Kallio and Vesa Saarijärvi (*Aalto University*), Dr. Antti Kestilä (*Finnish Meteorological Institute*), Maiju Ojanen-Saloranta and Timo Dönsberg (VTT). Aalto University has provided part of the funding for this study as part of the CAM3DEC (*complex additive manufactured 3D electric circuits using atomic layer deposition*) research and the author expresses his gratitude for this support.

References

- [1] BARDAL, E. Corrosion and protection. Springer, London, 2007.
- BENAROYA, H. Building Habitats on the Moon: Engineering Approaches to Lunar Settlements. Springer, 2018.
- [3] BESSONOV, A., MOROZOVA, N., GELFOND, N., SEMYANNIKOV, P., TRUBIN, S., SHEVTSOV, Y., SHUBIN, Y., AND IGUMENOV, I. Dimethylgold(iii) carboxylates as new precursors for gold CVD. Surface & Coatings Technology 201 (2007), 9099–9103.
- [4] BOCCAS, M., VUCINA, T., ARAYA, C., VERA, E., AND AHHEE, C. Coating the 8-m Gemini telescopes with protected silver. In Optical Fabrication, Metrology, and Material Advancements for Telescopes 5494 (2004), 239–253.
- [5] BUNNER, A. Optical coating in space. NASA-CR-175441., 1983.
- [6] CALLE, C., BUHLER, C., JOHANSEN, M., HOGUE, M., AND SNYDER, S. Active dust control and mitigation technology for lunar and Martian exploration. *Acta Astronautica 69*, 11– 12 (2011), 1082–1088.

- [7] CORTI, C., AND HOLLIDAY, R. *Gold: science* and applications. CRC Press., 2009.
- [8] FRENCH, B., HEIKEN, G., VANIMAN, D., AND SCHMITT, J. Lunar sourcebook: A user's guide to the Moon. CUP Archive, 1991.
- [9] FROLEC, J., KRALIK, T., AND SRNKA, A. Low temperature thermal radiative properties of gold coated metals. *International Journal of Refrig*eration 82 (2017), 51–55.
- [10] GANAPATHI, G., FERRALL, J., AND SESHAN, P. Lunar base habitat designs: Characterizing the environment, and selecting habitat designs for future trade-offs. NASA CR-195687., 1993.
- [11] GILMORE, D. Spacecraft Thermal Control Handbook: Fundamental Technologies. The Aerospace Corporation, 2002.
- [12] GOTLIB-VAINSTEIN, K., GOUZMAN, I., GIR-SHEVITZ, O., BOLKER, A., ATAR, N., GROSS-MAN, E., AND SUKENIK, C. Liquid phase deposition of a space-durable, antistatic SnO₂ coating on kapton. ACS Applied Materials and Interfaces 7 (2015), 3539–3546.
- [13] GRAY, J., AND LUAN, B. Protective coatings on magnesium and its alloys – a critical review. Journal of alloys and compounds 336, 1–2 (2002), 88–113.
- [14] HARLAND, D. The story of space station MIR. Springer Science & Business Media, 2007.
- [15] HASS, G., RAMSEY, J., HEANEY, J., AND TRI-OLO, J. Thermal emissivity and solar absorptivity of aluminum coated with double layers of aluminum oxide and silicon oxide. *Applied optics* 10, 6 (1971), 1296–1298.
- [16] HUMMEL, R. Electronic properties of materials. Springer, 2011.
- [17] IDA, N. Engineering Electromagnetics. Springer, Switzerland, 2015.
- [18] JELLE, B. P., KALNAES, S. E., AND GAO, T. Low-emissivity materials for building applications: A state-of-the-art review and future research perspectives. *Energy and Buildings 96* (2015), 329–356.
- [19] JONES, J. Gold aluminium intermetallics current and future considerations. *Electronic Component Conference – EECC 97 395* (1997), 411.

- [20] KIM, H., GILMORE, A., PIQUE, A., HORWITZ, J., MATTOUSSI, H., MURATA, H., KAFAFI, Z., AND CHRISEY, D. Electrical, optical, and structural properties of indium-tin-oxide thin films for organic light-emitting devices. *Journal of Applied Physics 86*, 11 (1999), 6451–6461.
- [21] KUMAR, C., MAYANNA, S., MAHENDRA, K., SHARMA, A., AND RANI, R. Studies on white anodizing on aluminum alloy for space applications. *Applied Surface Science* 151 (1999), 280– 286.
- [22] LAYERTEC. Optics and coatings, 2018.
- [23] LI, D., WANG, Y., ZHANG, H., ZHUANG, J., WANG, X., WANG, Y., YANG, S., SUN, Z., WANG, X., CHEN, L., YAO, R., ZOU, X., MA, J., CUI, Y., LI, C., ZHANG, H., LI, X., GAO, X., CUI, X., ZHANG, B., LI, W., AND LIN., H. In-situ measurements of lunar dust at the Chang'E-3 landing site in the northern Mare Imbrium. Journal of Geophysical Research: Planets. (2019).
- [24] MACLEOD, H. Thin-film optical filters. CRC Press, 2010.
- [25] MINTON, T., ET AL. T. MINTON, WU, B., ZHANG, J., LINDHOLM, N., ABDULAGA-TOV, A., O'PATCHEN, J., GEORGE, S., AND GRONER, M. Protecting polymers in space with atomic layer deposition coatings. ACS applied materials & interfaces 2, 9 (2010), 2515–2020.
- [26] NOSTELL, P. Preparation and Optical Characterisation of Antireflection Coatings and Reflector Materials for Solar Energy Systems. PhD thesis, Uppsala University, 2000.
- [27] NOSTELL, P., ROOS, A., AND KARLSSON, B. Ageing of solar booster reflector materials. *Solar Energy Materials and Solar Cells* 54, 1–4 (1998), 235–246.
- [28] SHARMA, A., BHOJRAJ, H., KAILA, V., AND NARAYANAMURTHY, H. Anodizing and inorganic black coloring of aluminum alloys for space applications. *Metal Finishing 95*, 12 (1997), 14– 20.
- [29] SMITH, D., SHILES, E., AND INOKUTI, M. The optical properties of metallic aluminum. In Handbook of optical constants of solids. Academic Press., 1997.

- [30] SUZER, S., KADIRGAN, F., SOHMEN, H., WETHERILT, A., AND TURE, I. Spectroscopic characterization of Al2O3–Ni selective absorbers for solar collectors. *Solar Energy Materials and Solar Cells* 52, 1–2 (1998), 55–60.
- [31] TABOR, H. Solar collectors, selective surfaces, and heat engines. Proceedings of the National Academy of Sciences of the United States of America 47, 8 (1961), 1271.
- [32] TOULOUKIAN, Y., DEWITT, D., AND HER-NICZ, R. Thermophysical Properties of Matter – The TPRC Data Series. Volume 9. Thermal Radiative Properties – Coatings. Plenum Publishing, New York, 1972.