

Multi-Layer, Low Emissivity, Metallized Materials for Replacing Aluminum Foils in Heat Reflection and Energy Management Applications

S. Yializis, Sigma Technologies International, LLC, Tucson, AZ

ABSTRACT

Aluminum foil has long been the dominant material used for applications requiring low emissivity surfaces for heat reflection and energy management. Metallized aluminum films, though initially exhibiting emissivity values equal to their bulk foil counterparts, are far more susceptible to performance degradation as a result of oxidation and corrosion of the reflective aluminum layer in the presence of heat and moisture. This is due in part, but primarily, to the amount of sacrificial aluminum available to be consumed by the oxidation reaction. Investigated are novel, multi-layer, low emissivity materials incorporating one or more vacuum deposited layers designed to protect vacuum deposited aluminum layers from oxidation and corrosion, as well as to enhance the emissive properties of the multi-layer structure by providing a planarized surface on which to deposit the reflective aluminum layer.

INTRODUCTION

Low emissivity, or “low-e,” materials have been used for decades as a means of managing the heating effects of radiant energy. NASA, as early as the 1960s, began using low-e materials to protect spacecraft, equipment, and astronauts from thermal radiation. Building and construction applications have seen the use of such materials in the form of low-e glass, where low-e materials are sputtered onto glass for reflecting, and controlling the emission of, radiant heat energy.

Unlike the applications mentioned above, where low-e surfaces are generally not exposed to oxidizing and/or corrosive elements, most applications require that such surfaces are capable of withstanding hot and humid conditions for sustained periods of time. Rather than develop solutions that limit, or prevent, corrosion from occurring to low-e layers, the convention has been to use thick materials that generally exceed the growth capacity of such oxidation/corrosion reactions are used. Historically, bulk aluminum foil, ranging in thickness from 6 μm to 12 μm , has been the material of choice due to its bulk thickness and low cost relative to other low-e materials such as gold, silver, and copper foils.

Vacuum metallized materials, generally composed of a polymer substrate and a vapor deposited low-e layer, have suffered commercially due to the thickness of the deposited low-e layer, which can range from 0.02 μm to 0.50 μm – up to 300

times thinner than bulk aluminum foil. Extreme environments consisting of high heat and moisture can result in propagation of oxidation and corrosion sites to the degree that a vapor deposited, low-e surface, is consumed entirely.

The purpose of this work is to identify multi-layer, thin film, structures capable of withstanding extreme environments. Investigated are various combinations of metals, metal alloys, and vapor deposited polymer coatings designed to protect thin films from the effects of corrosion and oxidation. Also investigated are planarizing layers designed to enhance low-e properties of finished composites.

OXIDATION AND CORROSION OF VACUUM METALLIZED ALUMINUM SURFACES

A metallized aluminum surface, when first exposed to a relatively dry oxygen-containing environment, at room temperature, will form a clear oxide layer that is tightly bound to that surface. This oxide layer, also identified as Al_2O_3 , will increase in thickness over a period of a few hours. Growth will cease as a result of the barrier properties of the oxide layer. Nominal thickness of this Al_2O_3 layer is 2-4 nm [1]. This phenomenon, and the impact it can have on the properties of an aluminum surface, changes dramatically in the presence of moisture, which triggers the formation of a spectrum of compounds, mostly hydrated aluminum oxide, aluminum hydroxides, and various sub-oxides that are not entirely stoichiometric [2]. Unlike oxide layers grown in air, in dry conditions, aluminum hydroxides formed from a water reactions lack the ability to protect the aluminum from further corrosion - a more “porous”, friable complex oxide/hydroxide layer replaces the self-limiting pure oxide layer, permitting the ingress of gases and moisture. Further, even in instances where a protective aluminum oxide layer has been formed prior to exposure to moisture, the layer sometimes fails to protect the aluminum surface, as water molecules have the ability to penetrate both the oxide layer, and the underlying aluminum layer, via grain boundaries in the structure. This reaction is accelerated in the presence of heat.

The phenomenon described above applies to almost all aluminum surfaces, and is indeed consistent for thin vacuum deposited aluminum layers, as well as and bulk aluminum foil. The difference, however, is in the amount of sacrificial

aluminum available to be consumed by the reaction. In the case of an aluminum foil, for example, thicknesses for heat reflective applications generally range from 6 μm to 12 μm ; even in the most aggressive of environments, heavy oxidation of the foil surface will have little, if any, impact on the emissive and reflective properties of the surface. This is generally due to the fact that the oxide layer will rarely grow to a thickness that either absorbs large amounts of thermal radiation, or consumes the aluminum entirely, resulting in an optically clear film composed of aluminum oxide and aluminum hydroxides. Metallized aluminum, however, is made up of a very thin layer of aluminum deposited onto a polymer film. Compared to aluminum foil, the vacuum deposited aluminum layer can be more than 300 times thinner. This means that very little oxidation of the aluminum layer needs to occur to consume the aluminum in its entirety, rendering it useless for most application where a low emissivity surface is desired.

OTHER SOURCES OF OXIDATION AND CORROSION (“FADING”)

Though it may not be obvious, oxidation and corrosion of vapor deposited aluminum films can occur as a result of adsorbed, and absorbed, moisture in the base substrate. Some substrate materials, such as polyester, have high moisture content when compared to other olefin-based substrates; this adsorbed moisture can trigger, or accelerate, the oxidation process in the wound roll. Even if the aluminum/polymer structure is unwound in a dry, low moisture containing environment, aluminum hydroxides will have already formed immediately after metallization inside the film roll. This phenomenon is well known in the metallizing industry and is often referred to as “fading.”

OXIDATION AND EMISSIVITY

Emissivity (“ ϵ ” or “ e ”) is a measure of a material’s ability to radiate absorbed energy at a given temperature and wavelength. It is defined as the ratio of energy radiated from a material, to the energy radiated by a theoretical black body [3]. A true black body, where all incident radiation is absorbed and radiated, has an emissivity expressed as “ $\epsilon = 1$.” The material is said to reflect 0% of incident radiation. Conversely, a perfect reflector, where all incident radiation is reflected zero radiant emission, has an emissivity expressed as “ $\epsilon = 0$ ” (100% of incident radiation is reflected).

Aluminum, in both foil and vapor deposited form, has an emissivity of $\epsilon = 0.03$. Figure 1 illustrates the effect that moisture, and heat, can have on the emissivity of aluminum surfaces deposited as a thin film. Though thicker aluminum foil is not immune to oxidation and corrosion, as evidenced by increase in emissivity after 15 minutes exposure to steam, it is still adequate for most low-e applications. On the contrary, the thin metallized aluminum, when exposed to steam for only 5 minutes, is completely consumed by the oxidation

and corrosion reactions caused by the water vapor. In addition to having the emissivity of the material being entirely compromised, the thin metallized film is corrupted visually. Whereas the visual impact of the corrosion reaction is not visibly obvious on the thicker foil, the thin metallized film has been rendered entirely transparent.

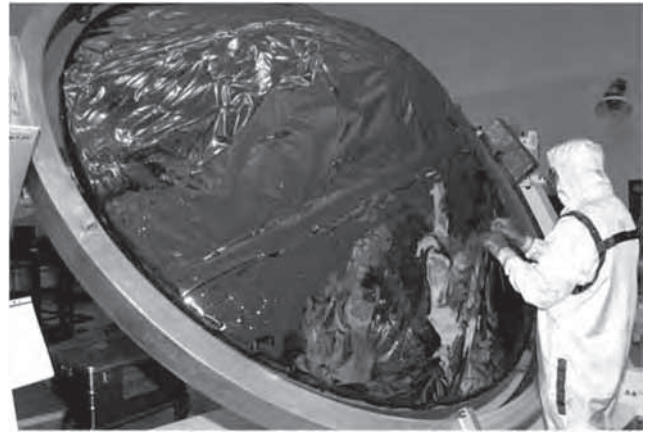


Figure 1: Space satellite component utilizing low-e materials for insulation from radiant heat energy.

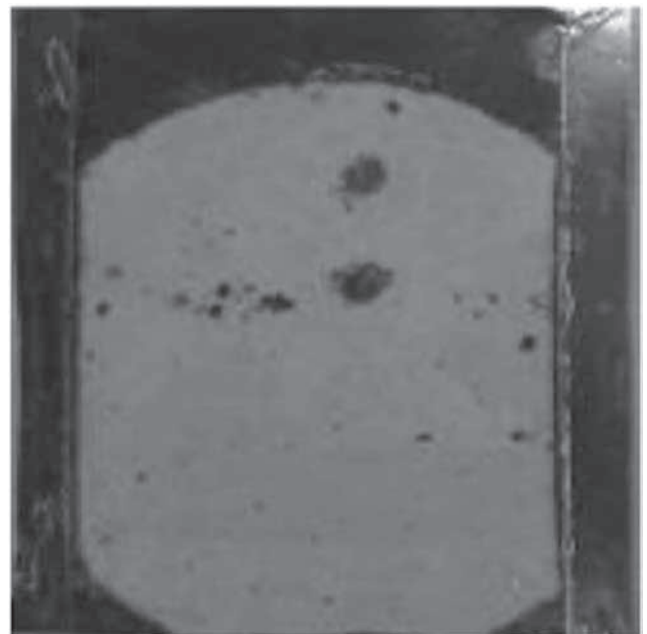


Figure 2: Metallized PET exposed to steam for five minutes.

PROTECTION AND ENHANCEMENT OF METALLIZED FILMS FOR LOW-E APPLICATIONS

Metallized aluminum films, for reasons stated above, require additional processing, both before, and after metallization, to prevent corrosion and oxidation. Though various methods might be considered, it is generally preferred that any treatment and coating steps occur in a controlled, vacuum, environment (otherwise referred to as an “all-vacuum” process). This is

critical for a number of reasons. First, all-vacuum processing allows for a single-pass, which presents cost advantages compared to offline, atmospheric, coating and treatment processes. Second, all-vacuum processing allows for the controlled formation of a more stable, protective, oxide layer absent of aluminum hydroxides that can be formed in the presence of moisture. Third, the ability to “seal” the metal layer in vacuum, with a protective polymer coating, further ensures maximum protection of the metal and eliminates the risk of having moisture attack the aluminum surface that is otherwise exposed in a two-step processes.

The following sections describe a multi-step, single-pass, all vacuum process that includes the steps of plasma pre-treatment of the target substrate, inline plasma passivation of the vapor deposited aluminum layer, and vacuum flash evaporation and radiation curing of a nano-thick polymer layer.

PLASMA PRE-TREATMENT

Metallized films produced in high volume for applications such as decorative, food, agricultural, biomedical and electronic packaging are usually evaluated for their appearance, conductivity, adhesion to the polymer substrate, and for their gas and vapor barrier properties. It is well known that all of these properties, as well as resistance to corrosion, are enhanced by plasma treating the substrate prior to metal deposition to produce better aluminum metal nucleation and adhesion to the base substrate.

IN-LINE PLASMA PASSIVATION

The term “passivation” and related terminology are used to refer to the process of treating a metallic material to alter its susceptibility to deterioration from exposure to environmental factors. It is understood that, in order to produce a corrosion-stable, vapor deposited, aluminum coating, it is necessary to create an Al_2O_3 protective layer directly on the aluminum surface. The terms “passivating agent” or “passivating component” are intended to describe any molecule that, in a plasma field, is capable of producing Al_2O_3 onto the aluminum layer when it is exposed to it. Similarly, the term “oxidizing,” in relation to metallic aluminum, is intended to refer to the formation of Al_2O_3 .

Plasma passivation of the aluminum surface is performed immediately after deposition of the aluminum layer. Oxygen, or preferably a plasma gas containing an oxygen-bearing component (such as molecular oxygen or a molecule containing oxygen, e.g., CO_2 , N_2O , dry air, etc.) in addition to conventional plasma gases (such as nitrogen, argon and helium), is introduced into the vacuum chamber under conditions designed to promote the formation of activated oxygen, which favors rapid oxidation. The result is the formation of an aluminum oxide layer that is guaranteed not to contain damaging hydroxides.

FLASH EVAPORATION AND RADIATION CURING FOR DEPOSITION OF PROTECTIVE POLYMERS

All chemicals used for coating the aluminum layer are contained inside a de-gas vessel, which continuously mixes the formulation to eliminate any unwanted residual gasses. Formulations consist of radiation curable, acrylate-based, liquid monomers composed of 100% solids. The liquid monomer formulation is pumped from the degas vessel and is injected into a temperature controlled monomer evaporation chamber. The walls of the chamber are heated so that when the monomer makes contact with the chamber walls, it instantly evaporates and undergoes a phase change from liquid to vapor. This creates a higher-pressure zone, which causes the monomer vapor to be driven from the evaporation chamber to a monomer deposition nozzle, which is located in the main vacuum chamber and is situated in close proximity to the substrate surface. Monomer vapor passes through the nozzle to create a vapor curtain across the entire width of the substrate. When the vapor makes contact with the substrate, it condenses back to liquid form, forming a uniform, pinhole-free, conformal, layer on the substrate surface. The deposited monomer layer remains in liquid form for a very short time before it is radiation cured using an electron beam gun, which converts the condensed monomer liquid to a fully cross-linked, solid, polymer layer ranging in thickness from 0.02 μm to up to 0.50 μm . The result is a protective layer capable of preventing ingress of moisture in quantities sufficient to facilitate formation of aluminum hydroxides.

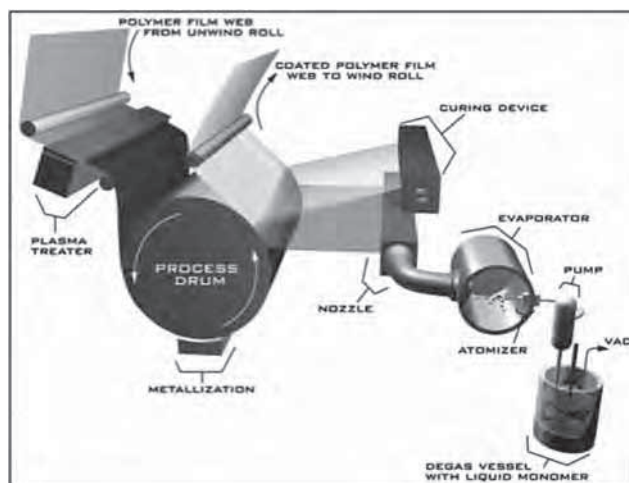


Figure 3: Schematic of flash evaporation coating process with vacuum plasma treatment and radiation curing.

PLANARIZATION OF MICRO-ROUGH SURFACES FOR ENHANCED EMISSIVITY

In addition to providing corrosion and oxidation protection of metallized aluminum layers, flash evaporated and radiation-cured polymer layers were used to enhance the emissivity properties of substrates with micro-rough surfaces. Certain

materials, such as polyethylene, possess surface roughness that, when metalized directly, result in a hazy appearance caused by diffraction and scattering. Using flash evaporation, coatings are deposited, prior to metallization, to smooth or “planarize,” the substrate surface to reduce scattering and improve surface emissivity.

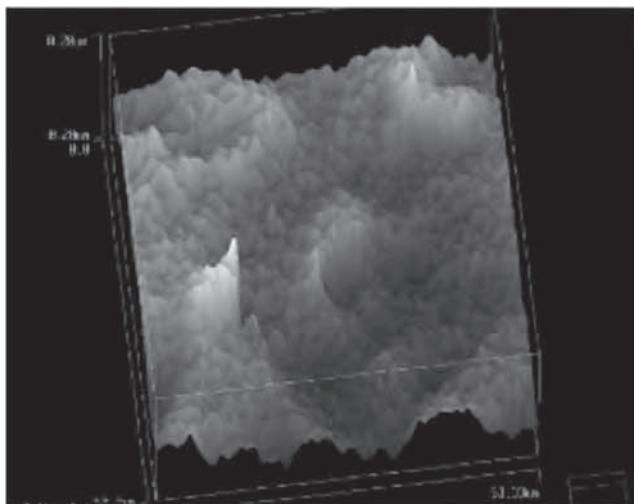


Figure 4: Micro-rough polycarbonate surface.

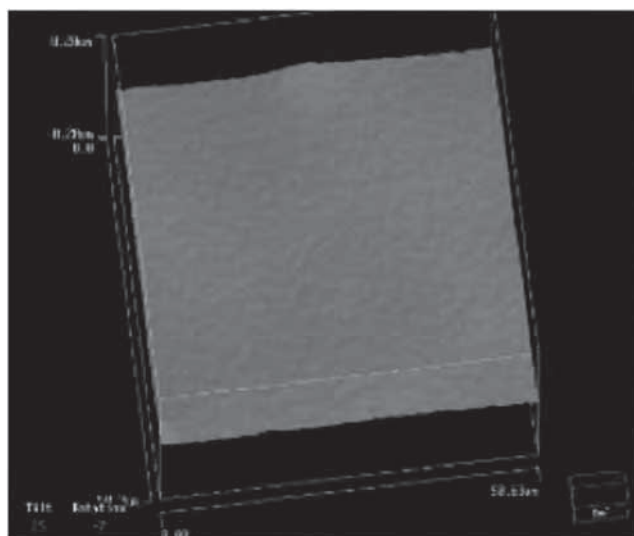


Figure 5: Polycarbonate surface with flash evaporated, planarized, layer.

EXPERIMENTAL CONDITIONS AND TEST PROCEDURES

Multi-layer, low-e, composites were produced using an industrial vacuum metallizer outfitted with pre-plasma treatment, resistive evaporation source for depositing aluminum layers, plasma passivation module for controlled growth of Al_2O_3 ,

flash evaporation system for depositing monomer layers, and a linear electron beam source for crosslinking deposited monomer layers. Planarizing layers were deposited using a second flash evaporation and electron beam source prior to metallization.

Substrates used for experimentation included a 12 μm , packaging-grade, polyester (PET) film and a 76.2 μm high-density polyethylene (HDPE), the latter was used to test the effects of a planarizing layer on surface emissivity.

Metalized aluminum layers were deposited to an optical density of 3.0. Various coating thicknesses were investigated to determine optimum thickness of protective coatings so as to minimize absorption of radiant heat energy. Finally, planarizing layers were deposited to thickness of approximately 0.20 μm .

EMISSION MEASUREMENTS – ASTM C 1371

Emissivity data are taken per ASTM test method C 1371. The device used for gathering emissivity data is a D&S Emissometer, model AE1, with digital voltmeter. Devices and Services Company is the manufacturer of the device, which is certified accurate to within ± 0.01 .

ACCELERATED STEAM TESTING

Because oxidation and corrosion testing per ASTM 1313 requires longer cycle times (up to seven days), an alternative, accelerated, test was devised. Specimens were exposed to a controlled, steam-filled, environment to induce oxidation reactions and growth of aluminum hydroxides on the film surface. The test setup consisted of a one-liter glass beaker filled to capacity with de-ionized water. The water-filled glass beaker was electrically heated to a temperature of 90°C to create a consistent flow of hot water vapor (steam) from the water surface. Test specimens were adhesively attached to a 4 in x 4 in glass slide with the test surface exposed. Once mounted to the glass slide, specimens were mounted adjacent to the beaker opening with a 1 in headspace between the water surface and the surface of the test specimen. Samples were exposed to steam for a total of 90 minutes, with emissivity readings taken before steam exposure, as well as at 5 min intervals during steam exposure.

OTHER TEST PROCEDURES AND APPARATUSES

Optical density measurements were taken using a Cosar 70 CompuPlus transmission densitometer. Resistivity measurements were taken using a Veeco instruments four-point probe model FPP-100. Thickness measurements of protective polymer coatings were taken using a Filmetrics F20 thin film measurement system.

RESULTS AND DISCUSSION

Protection of vapor deposited aluminum layers

Test results showed that, by varying coating thickness, emissivity of the finished composite could be manipulated. Thicker coatings, as expected, resulted in finished multi-layer films with higher emissivity; thinner coatings, on the contrary, resulted in coated materials with lower emissivity values, which are more desirable for low-e applications.

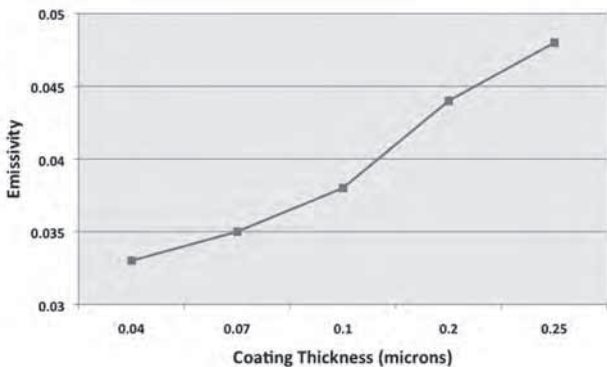


Figure 6: Emissivity as a function of protective coating thickness.

Though all coated samples were able to pass steam testing with up to 90 minutes exposure with little, to no, effect on surface emissivity, it should be noted that other factors, such as coating formulation, can have a significant impact on the ability of a coated layer to be an effective barrier to liquid moisture. Such analysis is beyond the scope of this work.

Many low-e applications do not require emissivity values equal to aluminum foil (0.03); however, for those that do have such requirements, results show that, when combined with plasma passivation of the reflective aluminum surface, coatings should be on the order of 0.07 μm .

Planarization of Micro-Rough Surfaces

A planarizing layer with a nominal thickness of 0.20 μm was deposited onto a HDPE substrate. Results showed that smoothing, or planarizing, of the film surface resulted in a 50% reduction in emissivity. Additionally, the visual appearance of the metallized, planarized, substrate was much improved and exhibited a mirror-like finish similar to metallized polyester. Non-planarized materials appeared to be more hazy, exhibiting a grey-like appearance.

Table 1: Emissivity of planarized and non-planarized metallized HDPE.

	Non-Leveled	Leveled
Emissivity	0.08	0.04

CONCLUSIONS

It has been demonstrated that, by combining plasma pre-treatment, resistive evaporation, plasma passivation, and flash evaporation and radiation curing, in an all-vacuum process, it is possible to produce metalized films that match the emissivity performance of bulk aluminum foil; further, it can be concluded that deposition of planarizing layers onto surfaces that might be considered less than ideal for low-e applications, can result in significant improvement of reflective layers deposited on such substrates.

REFERENCES

1. K. Wefers; C. Misra, "Oxides and Hydroxides of Aluminum," Alcoa Technical Paper No. 19 Revised, 64 (1987).
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