An Overview of Aluminum Protective Coating Properties and Treatments

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OPTI 521
November 9, 2009

Introduction

Aluminum is the most widely used non-ferrous metal. It is low cost and has a unique set of fine material properties that have made it ideal to be used in many common applications; such as in structural components and mirror reflectors. Pure aluminum has a low tensile strength but when it is chemically treated and alloying with other metals, it can exhibit significantly improved strength and other mechanical properties. Aluminum alloys are especially important in the aerospace, transportation and architectural industries where result of their high strength to weight ratio. Nonetheless, pure aluminum naturally oxidizes to provide thin layer of barrier oxide for corrosion resistance. However, in harsh environment, aluminum must be chemically treated to provide enhanced protection. Moreover, types of treatment can vary substantially depending on different application requirements.

Background

Aluminum is one of the most abundant metals found on Earth, and the recent advancement in the efficiency of extracting aluminum from ore has made it relatively cheap to procure. It has about one-third the density and stiffness of steel; it is ductile and can be easily machined. Naturally, pure aluminum reacts readily with oxygen in air creating a thin barrier oxide layer known as the aluminum oxide next to the metal surface that is about 2-3 nanometers thick. This barrier oxide layer stabilized the surface and prevents it from any further reaction with its environment and is an excellent electrical insulator. However, when it is exposed to harsh environment such as in the presence of aqueous salt, the corrosion resistance can be greatly reduced. Therefore, it must be further treated for enhanced protection.

Aluminum is also common used in mirror coatings. It is one of the few metals that retain its full silvery reflectance in finely powdered form, making it an important component for mirror coatings. Aluminum mirror finish has the highest reflectance of any metal in the 200–400 nm ultraviolet and the 3000–10000 nm infrared spectral ranges. However, its reflectance in the 400–700 nm visible range is slightly lowered compared to silver and tin and in the 700-3000 near infrared when compared to silver, gold and copper. Regardless of all the benefits above, the advantages are only temporary because of oxidation tarnishing. Aluminum naturally reacts with air creating a barrier oxide layer and so effectively reducing nominal reflectance. Therefore, to maintain optical integrity of aluminum coatings, it must be treated with a protective coating.

Aluminum Coating Properties and Treatments

Anodizing is a common electrochemical process used to grow an oxide film on the aluminum metal surface for enhanced protection. Aluminum is unique among other metals in a sense that in addition to its naturally forming thin barrier oxide, anodizing aluminum alloys in certain acidic electrolytes produces a thicker layer of oxide coating that also contains a high density of microscopic pores. This coating is mostly important for prevention of corrosion in many applications such as automobile and aerospace structures. It is also critical for electrical insulation as such barrier and porous oxide coating blocks any charged ions from reaching the metal.

In general, there are two types of oxide films that can be deposit to the aluminum surface known as the barrier and porous oxides. The bath electrolyte compositions are the main determinant factor of whether the oxide film will be barrier or porous. Barrier oxides are typically grown in near neutral solutions in which aluminum oxide is hardly soluble; therefore, not creating any pores in the cell. Since the oxide has low solubility in the solution, this process generally forms a fairly uniform oxide layer. The most common chemical compositions of the solution include ammonium borate, phosphate or tartrate. However, porous oxides are grown in acidic electrolytes where the oxides can also be dissolved creating pores in the cell. The most commonly used bath is dilute sulfuric acid but there are other commercial processes that use phosphoric acid, chromic acid, oxalic acid, and mixtures of inorganic and organic acid. The common goal to this different anodizing bath is to retain a relatively high concentration of aluminum in the solution.

To deposit an oxide film on the aluminum surface, the work piece is bathed in the electrolytic solution where it is made anode by connecting it to the positive terminal of a DC power supply. An unreactive electronic conductor is made cathode by connecting it to the negative terminal of the power supply. When the circuit is closed, the applied electric potential causes the oxide anions (negatively charged ions) to move inward to react with aluminum at the metal-oxide interface. At the same time, aluminum cations (positively charged ions) move outward from the valence band of the metal to react with water at the oxide-electrolyte interface. As a result, oxides are formed and continue to thicken at the two interfaces creating a dense layer of aluminum oxide as shown in **Fig. 1**. The thickness of the oxide layer depends on the applied electric potential. Typically, oxides support a very high electric field on the order of 1 volt per nanometer thickness. At the breakdown voltage of about 1000 volts, the barrier oxide is about 1 micrometer thick, which is a substantially improvement compared to the naturally oxidized layer thickness of 2-3 nanometers.

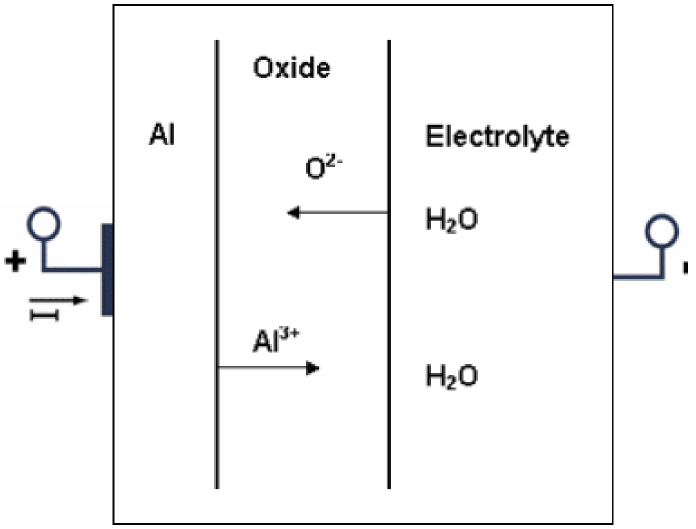
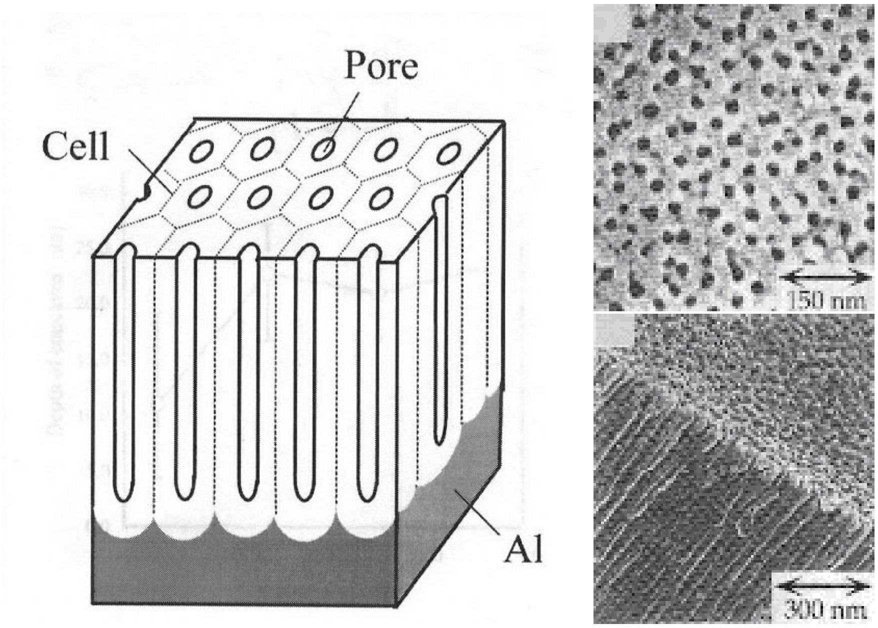


Fig.1*: Sketch illustrating ion transport through the oxide layer under applied electric potential

Barrier anodic oxides are nice but they are often not sufficient enough for many industrial applications that require better corrosion resistance or electrical insulation. Porous anodic oxides give an option to significantly increase the thickness of the oxide film.

The process to deposit porous anodic oxides, as was mentioned earlier, is similar to the case with barrier oxide, except that the aluminum work piece is immersed in soluble acidic electrolyte where some of the oxides are dissolved to create porous structures as shown in **Fig. 2**. In this process, large fraction of the oxidized aluminum is not retained in the film but passed into the solution. In a case where the anodizing solution is sulfuric acid, roughly 60% of the oxidized aluminum is retained in the while the remainder are suspended in the solution. With this process, porous film with 100 micrometer thickness can be made easily and it does not require high voltage as it is the case with barrier anodic oxides. This provides another leap in improvement compared to about just a 1 micron thick barrier oxide film.

Ideally, oxide creates hexagonal cellular structures with pores in the center as shown in **Fig. 2 A)**. However, in reality, most anodization conditions produce film with seemingly randomly distribution of cell and pores shapes and sizes as shown in **Fig. 2 B)**. Although the cell and pore sizes can vary with solution composition, temperature and voltage, the common end result is always a film with high density of fine pores. This is one of the fundamental reasons why metal anodizing tends to be inconsistent among different vendors. Nonetheless, the cell density can range from 10 to more than 100 cells per square micron. The typical cell diameter ranges from 50-300 nanometer and the pore diameter is in the range of 1/3 to ½ of the cell diameter.



(A) **(B)**

Fig. 2*: A) Sketch illustrates ideal structure of anodic porous aluminum oxide. B) Scanning electron microscope showing surface and cross section near the outer surface of porous oxide.

At the completion of the oxide growth, the pores in the cells must be sealed otherwise the film’s mechanical integrity can be jeopardized, limiting its usefulness. Clear anodizing is commonly done to close the pores. It is a secondary process where anodized coating is reacting with hot water to make less dense hydrous oxides to fill the pores in the cells. Due to its lower material density, the hydrous oxides occupies a greater volume than anodic oxide from which it formed and so fills the pores and makes a transparent and stable impermeable anodized layer. Moreover, color dye can be added to the aqueous solution before sealing to create colored surfaces. In optics, black anodize is often specified as a mean to suppress stray light.

For more demanding structural applications, hard anodize can be utilized to provide optimum corrosion resistance. In this process, aluminum is oxidized in sulfuric acid at low temperature. As a result, it produces a coating with large cell and small diameter pores that is extremely hard and durable. For even more severe environments, phosphoric acid and chromic acid anodizes are used for optimum corrosion resistance. They are often found in aerospace and military applications.

As mentioned earlier, aluminum has a fairly broad spectral band of high reflectivity and therefore, it is not surprising to see that one of its prevailing uses is in metallic mirror coatings where a thin film, typically in the order of microns, of pure aluminum is deposited on a substrate by evaporation in vacuum. Also as discussed earlier, the said advantages of inherit high reflectance are only temporary because of oxidation tarnishing. Aluminum naturally oxides and creates a thin barrier oxide layer which reduces nominal reflectance and it is especially horrific in the ultraviolet region. Therefore, almost all optical grade aluminum mirrors are coated to provide corrosion resistance. This gives rise to the three common types of aluminum mirror coatings; pure aluminum, protected aluminum, and enhanced aluminum.

Pure aluminum mirror is not protected with an overcoat. It is prone to oxidation tarnishing, and a barrier oxide layer is formed when aluminum is reacting with oxygen in air. The resulting oxide layer is tough and corrosion resistant in normal environments. However, it can become susceptible to changing environmental conditions and cannot be easily cleaned without damaging the aluminum coating. In addition, even though oxidation reduces aluminum reflectance by creating unnecessary scattering, the effect is quite limited in the visible spectrum. Therefore, for low end consumer and non-critical applications, the cost benefits of using just bare aluminum can significantly outweigh the marginal reflectance improvement in visible spectrum. The avaerage reflectivity for bare aluminum is above 90% from 400 to 1200 nanometers. Because it is also not coated, it is not sensitive to polarization and angle of incidence and so provides consistent high reflectance throughout the near-ultraviolet, visible and near-infrared regions as shown in **Fig. 3**.

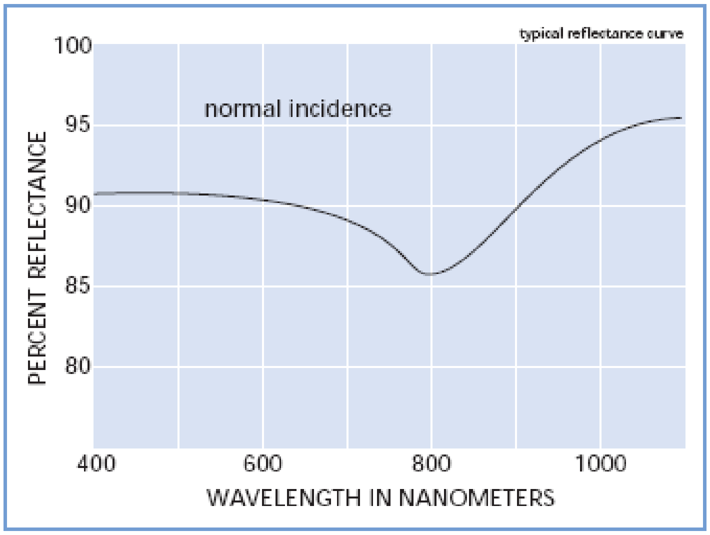


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Fig. 3: Bare aluminum spectral reflectivity**

Protected aluminum provides an alternate solution to the bare aluminum with enhanced corrosion resistant and can also be made fairly low cost. It is typically coated with a dielectric film of disilicon trioxide or magnesium fluoride of half-wavelength optical thickness centered at the peaking of photopic response curve, at about 550 nanometers. The protective overcoat extends the life of an aluminum mirror by preventing it from oxidization. This combination produces a first-surface mirror which is rugged enough to withstand ordinary handling and cleaning, and some minor scratches. The compromise, however, is lowered average reflectivity across the visible spectrum and increasing sensitivity to angle of incidence and polarization. Aluminum coated with disilicon trioxide is shown in **Fig. 4**.

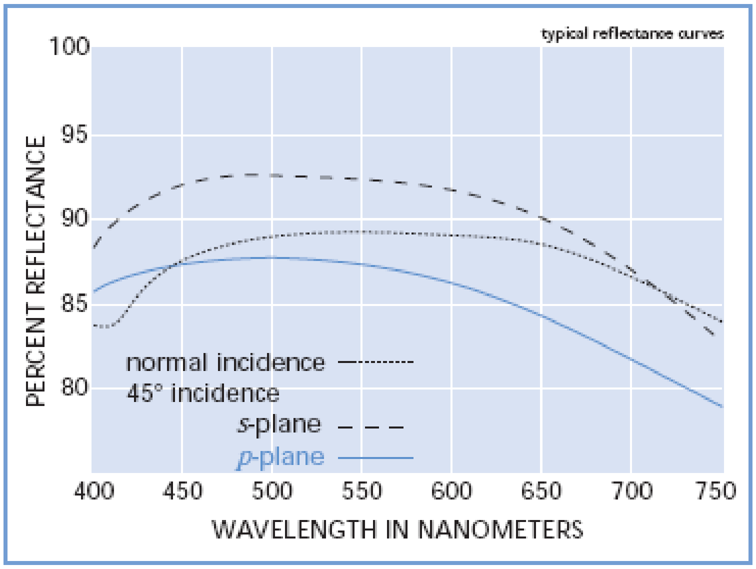

Fig. 4: Protected aluminum spectral reflectivity**

Enhanced aluminum is similar to protected aluminum except that it consists of multiple layers of dielectric coatings to improve mirror reflectivity at certain spectral regions. The percent reflectance can increase with increasing number of dielectric coating layers. The typical reflectance curve for enhanced aluminum is shown at **Fig. 5**. The coating is suitable for application requiring the durability and reliability similar to protected aluminum but with much higher reflectance at any desired spectral regions. However, the compromise is cost and significantly increased sensitivity to angle of incidence and polarization. In general, at higher angle of incidence, there will be a leftward shift of spectral reflectance (about 0.6nm per degree increase) and the peak reflectance is also reduced as shown in **Fig. 6**.

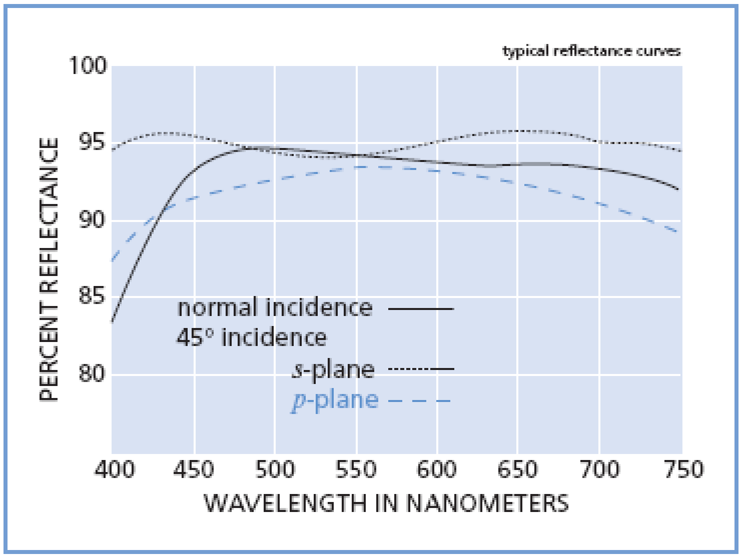

Fig. 5: Enhanced aluminum spectral reflectivity**

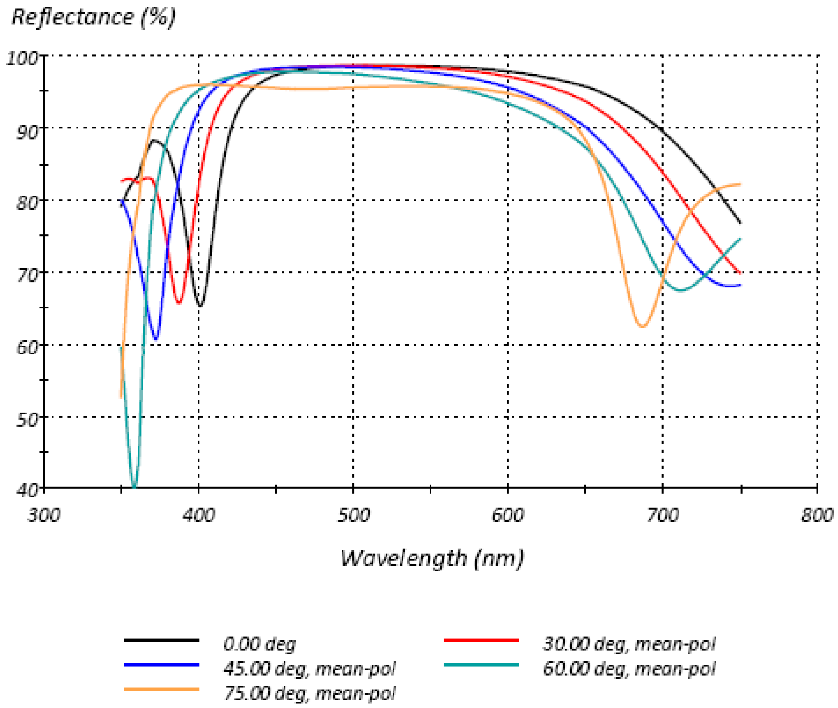

Fig. 6: Enhanced aluminum spectral reflectance as function of angle of incidence

Conclusion

Protecting coating requirements for aluminum vary substantially depending on application. For structural applications, a number of anodizing techniques is utilized to improve structural integrity of aluminum alloy. For metallic mirror coating applications, dielectric coatings by vacuum deposition technique are used to improve durability and corrosion resistance of aluminum.

Reference:

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