High Corrosion Resistant Reflective Coatings

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ABSTRACT

We consider the method of the deposition of high corrosion resistant and high reflective coating. It is shown that the coating, consisting of alternated layers of titanium and aluminum, is an optimum layer design. Formation of a continuous intermetallic layer of aluminum-titanium is a necessary component of the design. Data on reflectivity in visible spectrum and corrosion resistance of the coating are presented.

INTRODUCTION

Reflective coatings deposition is one of the most widespread applications of the vacuum deposition technologies. Conditions of such coatings usage vary to a great extent. The most stringent requirements are made for the coatings, which high reflectivity and long-term corrosion resistance are to be combined in. It is known that the reflectivity of newly-deposited films of some metals, except aluminum and silver, are low in the visible spectrum and rather high in the IR spectrum [1]. Various protective layers are used for corrosion protection and improvement of abrasive wear properties. Usage of vacuum deposited transparent protective layers is limited both by their high costs and difficult deposition onto large-area substrates and parts of complicated configuration. Apart from that, some transparent protective layers have a certain spectral selectivity.

EXPERIMENTAL DETAILS

Corrosion resistant metals and compounds does not provide reflectivity above 0.65, as it may be seen below in Table 1. At the same time, a protective layer on high reflective metals whether decreases reflectivity or their deposition is difficult and expensive.

Table 1. Reflectivity of some metals, alloys and compounds.

Materialof reflecting layer	Material of protective layer	Refl. factor	Spectra 1 range
Al	-	0.86	Visible
Al	Lacquer	0.7	Visible
Al	Titanium oxide	0.7	Visible
Al	Teflon	0.75	IR
Ag	-	0.92	Visible
Ag	Silicon nitride	0.87	Visible
Ag	ITO	0.6	Visible
Ag	ITO	0.8	IR
Cu	-	0.65	Visible
Cu	Lacquer	0.6	Visible
Cu	ITO	0.79	IR
St. steel	-	0.6	Visible
Ti	-	0.52	Visible
Ti oxide	-	0.35 - 0.42	Visible

We considered a version of the deposition of a coating of enough corrosion resistance, a high reflectivity and free of a protective layer. The present work is based on the data of publications [5,6], where corrosive protection of aluminum with thin layers of titanium, chromium and nickel was discussed. Relative number of the samples, tested on moisture resistance at temperature 40°C, is shown on Fig. 1 [6]. Aluminum coated samples with and without a titanium protective layer are presented. The coatings were deposited onto glass. Reflectivity was measured on the glass side. It is shown that reflectivity does not change after climatic testing in case of the deposition of the titanium layer 0.02 - 0.08 µm thick.

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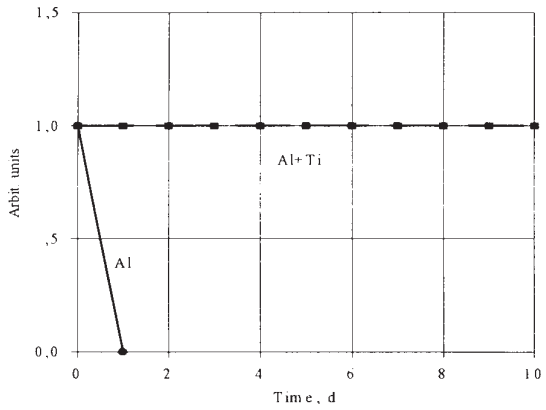

Figure 1. Number of climatic tested samples.

Conditions of the deposition of the aluminum-titanium coating of high reflectivity (no less than 80 %) and long-term resistance to atmospheric and moisture exposure are discussed in the present paper. The experiments were carried out on the laboratory and industrial equipment. Both rigid and flexible polymeric substrates were used in the experiments. The following deposition methods were used:
- thermal aluminum evaporation and magnetron titanium sputtering atop of the aluminum layer;
- thermal aluminum evaporation and electric arc titanium vaporization atop of the aluminum layer;
- alternated deposition of aluminum and titanium layers by magnetron sputtering;
- simultaneous magnetron sputtering of aluminum and titanium layers.

As far as the thickness of the titanium layers was not high, correlation between the deposition speed of titanium, optical density and layer thickness was found (preliminary). The coating corrosion resistance was determined by measurement of the reflectivity in visible spectrum after exposure in a climatic chamber and in NaCl solution. The samples were exposed in the climatic chamber at temperature 40°C and humidity 100%. During the NaCl testing the samples were immersed in 5 % solution periodically (once an hour for 10 minutes) and extracted on the air. The reflectivity was determined with a globe photometer. Its dependence on the titanium layer thickness (the latter calculated on the basis of the titanium deposition rate and time) is given in Fig. 2. Aluminum and titanium were deposited onto rigid polystyrene substrate by magnetron sputtering.

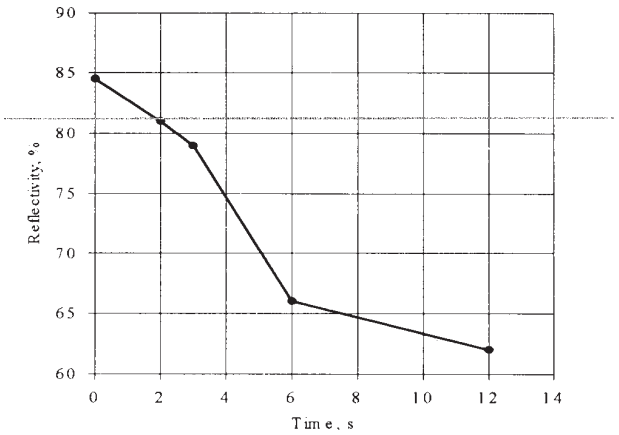

Figure 2. Reflectivity vs titanium deposition time. (Magnetron sputtering, titanium deposition rate is 0.5 nm/s).

Reflectivity of the aluminized PET film, protected by the titanium arc vaporization, versus the titanium deposition time is shown in Fig. 3.

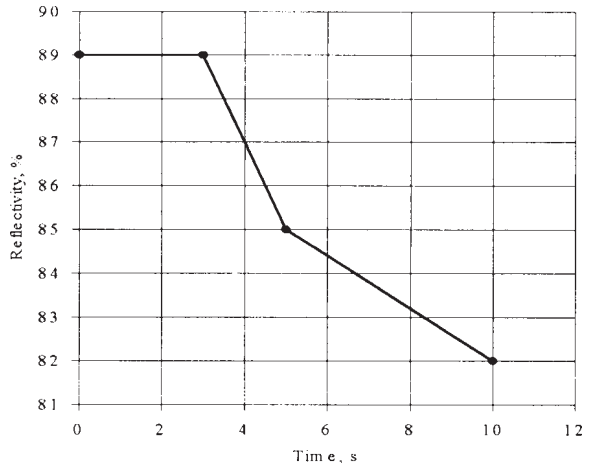

Figure 3. Reflectivity vs titanium deposition time. (Arc vaporization, titanium deposition time is 0.25 nm/s).

The aluminum was deposited by thermal evaporation. Comparison of Fig. 2 and 3 shows that the character of the reflectivity variability at magnetron and electric arc methods is identical and has three zones of various inclination. Very thin titanium layers decrease reflectivity insignificantly. Further increase of the titanium thickness leads to sharper decrease of the reflectivity. Then, still further growth of the titanium layer leads to gradual decrease of the reflectivity, finally resulting in the reflectivity value of pure titanium (0.52).

Reflectivity of the two-layer aluminum-titanium coating versus the time of the exposure in the climatic chamber and NaCl solution at various titanium thicknesses is shown in Fig. 4 and 5.

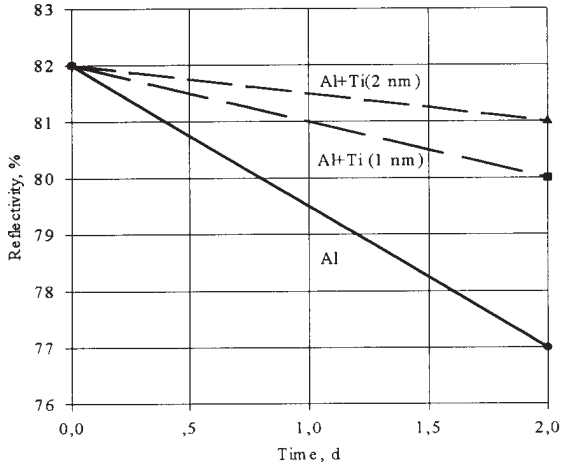

Fig. 4. Reflectivity after exposure in the climatic chamber.

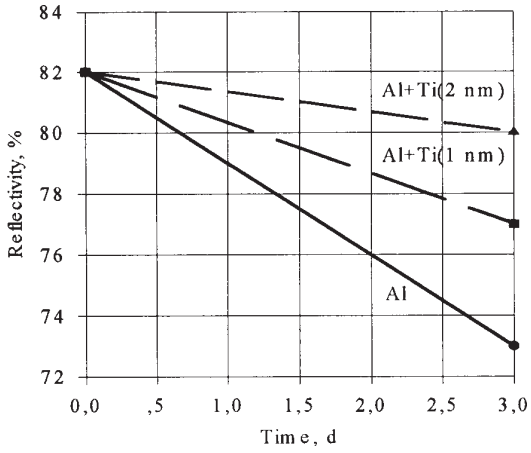

Figure 5. Reflectivity after exposure in NaCl solution.

As it is clear from Fig. 4 and 5, corrosion resistance of the two-layer coating is as higher as more titanium thickness, but it sharply increases even at minimum thickness of the titanium layer.

It can not be accounted by protective properties of the titanium film, because it is too small to form a continuous protective layer.

There are several explanations of the mechanism of the corrosion resistance increase of the aluminum-titanium coating. First, probability of intermetallic compounds formation on the aluminum-titanium interface is increased sharply both in the magnetron and arc discharges because of high energy and chemical activity of the titanium.

Formed compounds of the type AlTi have high corrosion resistance, especially at high temperatures. A transition zone, obtained with secondary ion mass - spectroscopy, is shown on Fig. 6 [5].

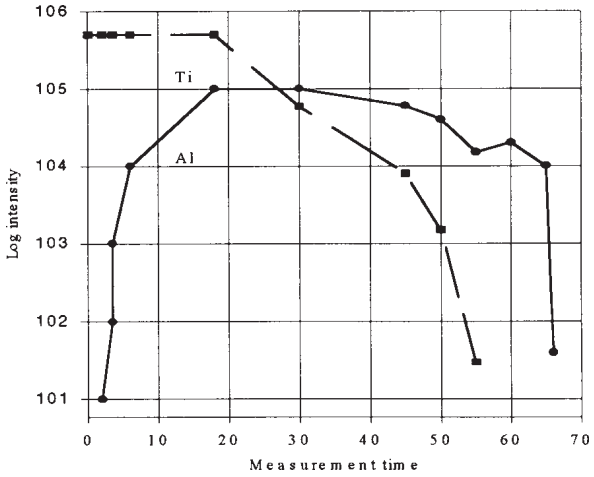

Figure 6. Profile of magnetron sputtered layers.

The transition zone width influences on the corrosion resistance. It is characteristic that at thermal evaporation the transition zone width of titanium is essentially lower (Fig. 7) [5]) and there is no corrosion protection. Secondly, the molar volume is increased and the subsurface layer is compacted during formation of the intermetallic layer.

Two technological processes of the deposition of high reflective and high corrosion resistant coatings have been developed on the basis of obtained results:
1. Coatings of high reflectivity on the transparent substrate side of the layer design;
2. Coatings of high front reflectivity of various materials.

In the first case the aluminum layer is deposited initially by thermal evaporation or magnetron sputtering and then the titanium layer 0.02-0.05 μm thick is deposited by the magnetron or electric arc method. In the second case the technology peculiarities are connected with the substrate material.

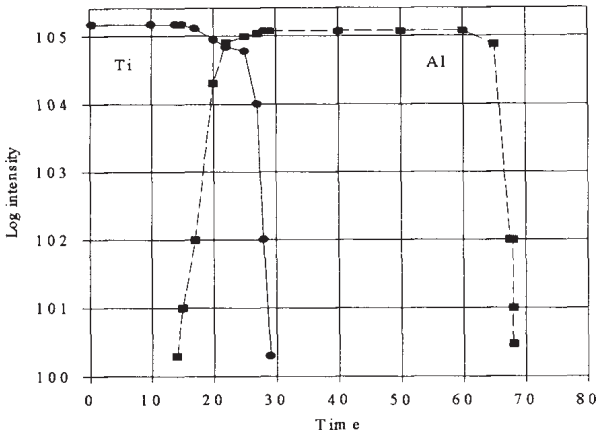

Figure 7. Profile of thermal evaporated layers.

In case of polymeric substrates, characterized by high outgassing, it is expedient to start with a titanium underlayer deposition. It will have two functions: improvement of the aluminum adhesion to the substrate and creation of a barrier layer, preventing gas penetration to the aluminum layer. The further layers are alternation of aluminum and titanium or simultaneous sputtering of aluminum and titanium with gradual reduction of the titanium fraction approaching to the top layer. An example of a seven-layer coating is given in Table II.

Table II.
Composition of the seven-layer coating.

Layer No	Ti thickness, nm	Al thickness, nm
1	30	12
2	3	12
3	3	12
4	3	12
5	3	12
6	3	12
7	1.5	0

The testing has shown that complete oxidation of the front reflective coatings was not observed even at their long-term exposure in the salt fog conditions.

Even in case of partial corrosion of aluminum, reflectivity is decreased insignificantly, because the reflectivity is reduced down to 78-80 % in the corrosion points (the intermetallic layer reflectivity) without significant decrease of the integral reflectivity of all the surface, not altering the coating appearance.

Some details of coating very thin polymeric film should be noted. First, internal stresses of the coating should be taken into account, when depositing titanium. Growth of stresses leads to cracking of the coating as a whole and sharp decrease of the corrosion resistance. Secondly, the substrate heat resistance should be taken into account, when magnetron sputtering of the layers simultaneously. Increased thermal flows could entail the substrate shrinkage and also the coating cracking.

The offered coatings can be used in the most various industries.

CONCLUSION

Feasibility of the deposition of high reflective and high corrosion resistant coatings has been shown, depositing multi-layer titanium and aluminum films onto various substrates, including flexible bases. Mirror coatings can be used both on front and back side of the substrate.

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