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Atmospheric pressure air plasma treatment of glass substrates for improved silver/glass adhesion in solar mirrors

Rodolfo Múgica-Vidal[a], Fernando Alba-Elías[a,*], Elisa Sainz-García[a], Mariola Pantoja-Ruiz[b]

[a] Department of Mechanical Engineering, University of La Rioja, c/ Luis de Ulloa 20, 26004 Logroño, La Rioja, Spain
[b] Materials Science and Engineering Department, IAAB, Materials Performance Group, University Carlos III of Madrid, Av. Universidad 30, 28911 Leganés, Madrid, Spain

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ABSTRACT

Atmospheric pressure air plasma treatment was applied to glass substrates to improve the adhesion of the reflective silver layer of mirrors used in solar power systems. This treatment attempts to prevent problems related to the detachment of this layer that affect its energy performance. Untreated and plasma treated glass substrates were subjected to a spray coating process to fabricate mirrors. Chemical characterization by X-ray Photoelectron Spectroscopy (XPS) and measurements of the water contact angle (WCA) were undertaken on the glass substrates before the plating process. The reflectivity of the mirrors was studied by spectrophotometry in the wavelength range of 280–2500 nm, and the adhesion between the glass substrates and the silver layers was measured by pull-off tests. In order to determine the relationship between the parameters of the plasma treatment and the adhesion and reflectivity of the mirrors, different combinations of treatment speeds and gap distances between the glass substrates and the plasma nozzle were used. It was observed that the plasma treatment has a cleaning effect and forms oxygen-based functional groups that promote the hydrophilicity of the glass substrates. This double effect resulted in improved adhesion of the silver layer to the plasma treated substrates, with no significant loss of solar reflectance of the mirrors. The plasma treatment with the lowest gap distance (2 mm) and the lowest speed (1 m/min) achieved the best results in this work. It brought an improvement of 85.8% in the breaking strength of the untreated glass mirror and no significant variation in the solar reflectance in as-fabricated conditions. After accelerated aging, it maintained an improvement of 27.2% in the breaking strength and showed higher solar reflectance than the untreated glass mirror.

1. Introduction

Solar reflectors are one of the main components of Concentrating Solar Power (CSP) plants. Any imperfection in these reflectors (e.g., the detachment of the reflective layer) has an impact on their optical performance, thereby affecting the efficiency of the plant [1]. This issue has motivated recent research on the manufacturing process [1], durability [2–4] and degradation of the reflective and protective layers [5]. For instance, Fernández-García et al. [2] studied the durability of solar reflector materials by simulating accelerated aging under different ambient parameters and concentrated exposures. They tested one type of an aluminum reflector and eight different types of silvered glass reflectors, and evaluated the reflectance in different aging tests as an indicator of the quality and degradation of the materials. They observed that silvered glass reflectors had greater initial reflectance than aluminum reflectors and that most of them suffered little significant reflectance loss during the tests. Silvered glass mirrors with a thickness of the glass layer of 1–4 mm are commonly used as reflectors in CSP systems. An advantage of glass mirrors with a thickness of 4 mm over thinner mirrors is that their mechanical strength enables them to withstand wind loads without requiring special backing structures to avoid breakage and maintain their shape [3]. Silver, which has a hemispherical reflectivity of 97%, is known to be one of the best solar reflectors [6]. However, it may corrode under atmospheric conditions. Therefore, it must be protected from this. The most common type of mirror for CSP applications consists of several layers in the following arrangement: a front glass, a reflective layer made of silver, a copper layer that protects the silver from corrosion and back paint that protects the mirror's back and edges [3,7].

A suitable way to apply metallic coatings on non-conducting substrates, such as glass or plastics, is by using an electroless plating process [8,9] that consists on the spontaneous reaction of different solutions without applying electrical current to them. Since adhesion is one of the most important factors in the application of coatings, a

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[*] Corresponding author.
E-mail addresses: rodolfo.mugica@alum.unirioja.es (R. Múgica-Vidal), fernando.alba@unirioja.es (F. Alba-Elías), elisa.sainzg@unirioja.es (E. Sainz-García), mpruiz@ing.uc3m.es (M. Pantoja-Ruiz).

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pretreatment of the glass substrate is needed to improve its adhesion to the film [8]. Such pretreatment comprises decontamination, coarsening, sensitization and activation of the substrate to assist the subsequent formation of the metallic layer and to accelerate the reduction of the plating metal ions [9].

Several chemical methods have been used to clean and activate the glass surfaces. However, these methods are being replaced by more recent cold plasma technologies. These technologies are also faster and more environmentally friendly than chemical methods. The application of plasma has a double effect on the preparation of the glass surface that assists the adhesion of coatings: (1) it cleans the glass surface by removing organic contaminants and (2) it generates oxygen-based polar groups that increase the hydrophilicity of the surface [10]. Surface energy, which has an important influence on adhesion, is related to wettability. The more hydrophilic a surface is, the higher its surface energy is. Generally, a higher surface energy results in greater adhesion between different materials [10,11]. Therefore, a cold plasma treatment seems to be appropriate to fulfill some of the tasks of the pretreatment in order to achieve good adhesion of the silver layer to the glass substrate in mirror manufacturing.

The traditional ways to generate cold plasma involve low pressure plasma technologies. However, these technologies involve the use of high vacuum equipment, which makes them expensive and difficult to integrate for in-line manufacturing processes. Another way to produce cold plasma is by atmospheric pressure plasma technologies. This alternative lowers the cost of the process and is more suitable for in-line processing in large-scale industrial applications [12,13].

Atmospheric pressure plasma pretreatment of glass surfaces has been used in several studies to improve the deposition of different coatings on glass substrates [11,12,14–16], as well as silver nanoparticles [17]. For instance, in our previous work [14,15] we treated glass substrates with atmospheric plasma to clean and activate their surfaces before the plasma-polymerization of coatings that promoted their hydrophobic and tribological properties. Hluschi et al. [11] used an atmospheric plasma treatment with a dielectric barrier discharge (DBD) on glass surfaces to increase their surface energy and promote the adhesion of multiple dielectric and metal layers, including a silver layer. They observed that plasma treatment had a cleaning effect and led to an increase in surface tension. This resulted in improved adhesion of silver layers, as revealed by their qualitative adhesion tests. Thus, it might be interesting to study the possibility of improving the adhesion of reflective silver layers on glass surfaces for CSP applications.

In this work, an in-line mirror manufacturing process was simulated by coating glass samples in a spraying process that used electroless plating solutions as described below. Atmospheric pressure air plasma pretreatment is used to decontaminate and activate the glass surface, whereas sensitization is carried out in the usual way by spraying a stannous chloride solution onto the glass surface. The purpose of this work is to determine whether the atmospheric plasma pretreatment improves the adhesion of the reflective silver layer and how solar reflectance is affected by such pretreatment. Furthermore, different combinations of the nozzle speed and distance to the glass surface are used in the atmospheric plasma pretreatment to determine the relationship between pretreatment conditions, adhesion and reflectance.

2. Materials and methods

2.1. Atmospheric pressure air plasma pretreatment

Glass samples of 50 mm × 50 mm × 3.9 mm were pretreated with atmospheric plasma on the face that was to be silver-plated. The equipment used to apply this pretreatment was a Plasma Treat GmbH (Steinhagen, Germany) atmospheric pressure plasma torch (APPT) device. This device is equipped with a rotating torch ending (1900 rpm) in a nozzle from which the plasma is ejected through a round orifice. The voltage was set at 20 kV and the frequency at 17 kHz. Air was used as the supply gas to generate the plasma with a working pressure of 2 bar in the rotating nozzle. The samples were placed onto a mobile platform with adjustable speed. The values of two parameters of the pretreatment process were varied for the different samples: (1) the gap distance between the glass surface and the plasma nozzle, and (2) the speed at which the glass samples moved under the nozzle during the pretreatment. Three gap distances (2, 4 and 6 mm) were combined with three movement speeds (1, 3 and 6 m/min) to prepare each type of pretreated sample. Therefore, ten types of glass samples (Table 1) were studied in this work: nine types of pretreated glass samples, as well as untreated glass samples for comparison with conventional mirrors.

Table 1
Designation of samples according to the parameters of the plasma pretreatment.

Sample	Parameters	
	Gap (mm)	Speed (m/min)
Untreated glass	–	–
S_{21}	2	1
S_{23}	2	3
S_{26}	2	6
S_{41}	4	1
S_{43}	4	3
S_{46}	4	6
S_{61}	6	1
S_{63}	6	3
S_{66}	6	6

2.2. Fabrication of mirrors

Silvered glass mirrors were fabricated in this work with the following layers: a reflective silver layer, a protective copper layer and a protective layer of back paint. Firstly, this section describes the solutions used in the fabrication of mirrors. Special attention is paid to the silver solution preparation process due to its particular complexity (Fig. 1). Secondly, the process by which the mirrors were fabricated is described and the amount of each solution used for each mirror is specified (Fig. 2).

The solutions used in this work were prepared with distilled water as solvent and the following chemicals: tin(II) chloride ($SnCl_2{\cdot}2H_2O$), ammonia (NH_3) (25%), silver nitrate ($AgNO_3$), sodium hydroxide (NaOH), glucose ($C_6H_{12}O_6$), copper(II) sulfate ($CuSO_4{\cdot}5H_2O$) and sulfuric acid (H_2SO_4) (96%).

A 1.1×10^{-3} M tin(II) chloride solution (Fig. 2, Sol. A) was used to sensitize the glass substrates.

Silver and copper layers were applied by a spraying process that involved the use of a silver solution, a reducing solution and a copper solution. The silver solution (Fig. 2, Sol. B) was prepared under vigorous stirring, according to the following steps (Fig. 1):

a) 0.125 mL of NH_3 (25%) were added to 25 mL of 0.235 M silver nitrate solution. Then, the solution turned from transparent to brown and formed a precipitate.
b) A more diluted 2.657 M NH_3 solution was added drop by drop until the solution recovered its transparency and the precipitate dissolved completely.
c) 12.5 mL of 0.25 M NaOH solution were added and the silver solution became dark brown again, with the formation of a precipitate.
d) 2.657 M NH_3 solution was added drop by drop until the solution recovered its transparency and only a few particles of precipitate remained.
e) The silver solution was left to stand for 10 min without stirring before being applied to the glass surface.

A 0.371 M glucose solution (Fig. 2, Sol. C) was used as the reducing