

Vacuum Arc Deposition of Decorative Coatings on Architectural Glass

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2 = Coated glass

3 = Titanium nitride

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Abstract

In the vacuum arc discharge highly ionized species are formed. It allows one to control effectively the deposition process, and particularly, to deposit Ti, TiN and TiO₂ coatings on non-conducting materials like glass or plastics. The deposition rate in the case of the vacuum arc process decreases rather slow with increasing distance between the vacuum arc source and the substrate. This advantage allows a rather compact design of the deposition apparatus. It allows also to position a mask between the substrate and the sheets to be coated. Another advantage of the vacuum arc technology is the low substrate temperature during the deposition. Examples of architectural glass mask-coated with titanium nitride and oxide are presented together with the data on the roughness, composition and corrosion resistance of the coatings.

Introduction

Vacuum arc deposition is an effective and environmental friendly technique for the production of decoration coatings on architectural glass. Especially important are the possibilities to produce the patterned coatings and coatings with any interference colour (like red, purple, green, yellow etc.) on large-area glass substrates. This allows in particular to have on the glass the scratch and wear resistant drawings for the decorative and advertisement purposes or apply the unusual colours for glazing instead of "old-fashioned" brown windows.

The main frame

The industrial scale set-up "Nikolay" used for the deposition of coatings on the large-area architectural glasses has the following characteristics: size 6000x3000x3000 mm, mass 15500 kg, maximum power consumed 75 kW, ultimate vacuum 5×10^{-4} Pa, maximum size of treated glass 2100x1300x8 mm, output capacity for glass 30 glass sheets 2100x1300x5 mm in a 8 h cycle, up to 1000 m²/month. A standard procedure for glass decorative coating includes three steps. The glass sheet before being loaded into the machine is precleaned using hot distilled water. After precleaning, the glass sheets are mounted on metallic frames and placed in the machine vacuum chamber. Each frame contains two glass sheets, mounted back to back. The frame is inserted into a slot (15 slots are available) and allowed to move independently inside the machine, in order to receive different treatment operations. The displacement velocity of the frame is monitored and can be controlled. Each frame receives in turn a cleaning treatment followed immediately by a coating in order to prevent recontamination. The complete treatment involves one return of the frame for cleaning and another return for coating. Cleaning is performed using a large aperture Hall current accelerator, providing high energetic ions which impact and sputter the substrate surface. The description of the Hall current accelerator and its performances is given elsewhere [1, 2]. A Hall current accelerator is placed on each side of the machine in order to clean the two sheets of the frame in one shot.

The high power provides a sufficient cleaning of both surfaces in any circumstances. The coating in the industrial set-up is performed using four circular targets of 200 mm diameter. Three sources are placed on each side of the installation. Only two sources are normally used during the deposition. A reactive gas (oxygen) is introduced at 0,05 Pa if oxide coating is to be formed. TiN coating is obtained by introducing nitrogen at a pressure of about 0.05 Pa. The arc generation is continuous and random. As microdroplets are ejected at small angles [3] with respect to the target surface, this configuration provides shielding and enables to increase the charged particles component of the beam. As for cleaning, the thickness of the deposited layer is controlled by varying the translation speed of the frame. Glass, metal and plastic sheets have been successfully coated with Ti, TiN, TiO₂ and multilayers of TiN/TiO₂. When decorative patterns have to be produced, light nylon patterned sheets are used to provide masking. Various colours can be produced depending on the gas and deposition parameters used. In this study Ti, TiN, TiO₂ and TiN/TiO₂ coated silicate glass samples were cut from large glass sheets and analysed regarding surface morphology, composition and corrosion resistance.

The samples surface was observed using an atomic force microscope (AFM) *Autoprobe CP AFM* from Park Scientific Instruments. The AFM was operated in the contact mode using sharpened gold-coated microlevers with nominal radius of curvature of the tip less than 20 nm. The composition depth profile of TiN/ TiO₂ coated silicate glass was made by Auger electron spectroscopy (AES). The specimens were mounted in the loaders of the spectrometer carousel holder and sequentially rotated into the analysis position. The analysis was carried out with the excitation beam normal to the specimens. The spectra were taken during argon ion sputtering which produced a relatively clean surface of the sample under study without baking the system. The etching rate was considerably faster than the adsorption rate of the active residual gases. The Auger spectra were measured on a PHI-551 spectrometer with a double-pass cylindrical mirror analyzer. The base pressure was less than 2×10^{-8} Pa. The spectra were excited by an electron beam with an energy of 3 keV and a current of 8 μ A through the sample. The peak-to-peak modulation was 3V. The sputtering was accomplished using a 5 keV Ar⁺ ion beam. An ion gun was mounted to give a beam incidence angle of 70°, and in order to minimize possible crater effects, it was rastered. The pressure of argon during sputtering was 3×10^{-3} Pa. The sputter rates were determined to be 25 nm/min relative to SiO₂.

The corrosion behaviour of both TiN and TiO₂ coatings on silicate glass was characterized. The standard accelerated tests on atmospheric corrosion were carried out according to the Russian standards RST 9.012, 9.017 and 9.020 (temperature 22–25°C, humidity 96–98%, no water condensation, under influence of gaseous chlorides, ammoniac and SO₂). The accelerated test in 3.5% NaCl solution at 22–25 °C under both full and partial immersion was also carried out. Both uniform and mask-deposited TiN coatings were studied because on the boarder between coated and uncoated glass the TiN/glass interface is exposed to the corrosion medium. The polarization behaviour was measured potentiodynamically with the aid of a potentiostatic apparatus PI-50-1/PR8. All potential values are given versus the Ag/AgCl electrode ($E_{Ag/AgCl} = 0$ corresponds to – 200 mV in the hydrogen electrode scale). The scanning rate was 1 mVs⁻¹. The polarization was changed from – 0.8 V to + 1.5 V. Before potentiodynamic measurements, the corrosion potential E_c was monitored for 0.5 h. The measurements were carried out in the electrolytes of 3.0% NaCl solution and 3.0% NaCl + 3.0% NH₄Cl solution with pH = 6. The correction of the pH of the solutions was carried out by addition of 0.05 mole of NH₄OH (to the solutions containing NH₄Cl) and by addition of 0.05 mole of NaOH (to the solutions without NH₄Cl). The pH value of a solution was controlled by a pH-meter "pH-121". The solution was prepared from reagent-grade chemicals and distilled water. The area exposed to solution was 1 cm², the rest surface of the samples was isolated by a varnish layer. The test temperature was 22–25 °C.

The AFM-micrographs of the TiO₂ coating on silicate glass are shown in *Figures 1 and 2*. The coating contains small Ti particles formed from liquid droplets (Fig. 1) included in the smooth TiO₂ film formed as a result of reaction of individual titanium and oxygen ions (Fig. 2). The depth concentration profile obtained from the Auger spectra for Ti and TiO₂ coatings on silicate glass are shown in *Figures 3 and 4* respectively. The peaks characteristic for titanium, oxygen, carbon and silicon were analyzed. After about 3 min of sputtering, the surface contamination of carbon and oxygen disappear from the spectra. The increasing concentration of silicon marks the transition from the coating to substrate. The oxygen content in the Ti coating steadily increases towards the substrate. The oxygen content in the TiO₂ coating remains unchanged except the thin Ti-rich layer close to the glass substrate. Quantitative analysis reveals that the Ti to O ratio in the TiO₂ coating is about 1.95 being very close to the stoichimetical one. The carbon concentration is nearly constant in the whole coating (close to zero in the TiO₂ and slightly

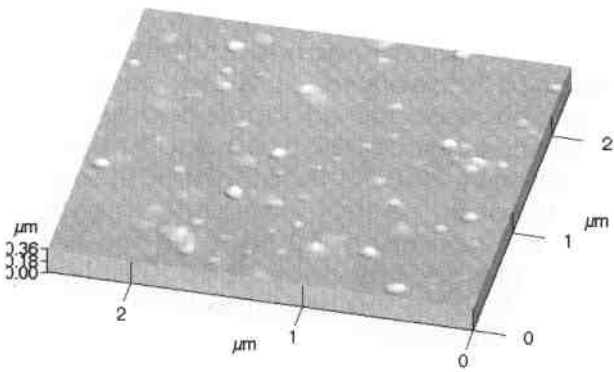


Figure 1. AFM micrograph of TiO_2 coating showing TiO_2 film containing Ti droplets.

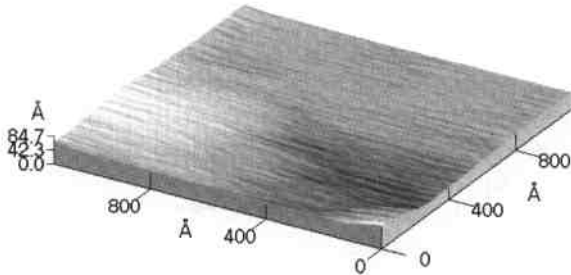


Figure 2. AFM micrograph of TiO_2 film between Ti droplets (high magnification).

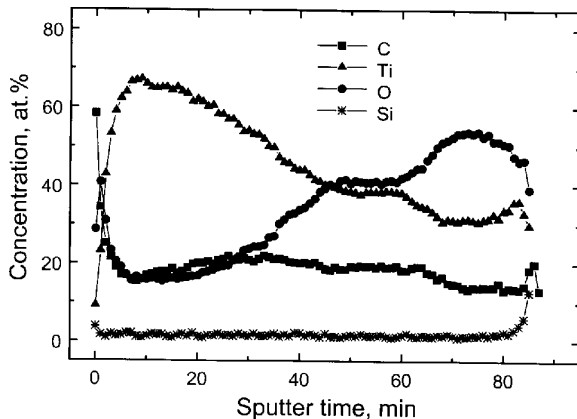


Figure 3. AES spectra for the Ti coating on silicate glass.

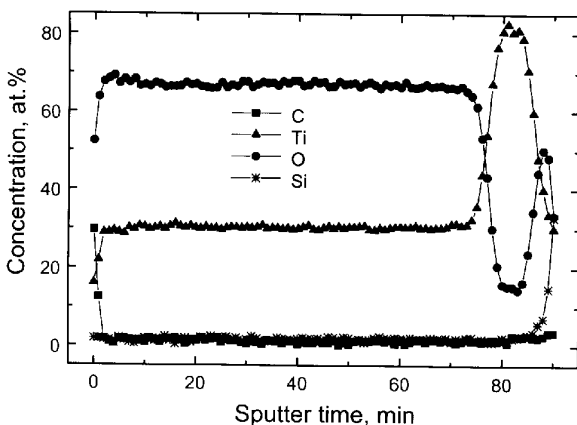


Figure 4. AES spectra for the TiO_2 coating on silicate glass.

below 20 at.% in Ti). At the coating/substrate interface the oxygen and silicon content climb up as the titanium content slightly falls down.

After 8 months of tests in atmospheric corrosion with conditions which correspond to the most aggressive part of the industrial atmosphere, no changes of mass and appearance in the characterized samples was monitored. It demonstrates the high resistance against atmospheric corrosion of the characterized TiN and TiO_2 coatings on silicate glass. The corrosion tests carried out in a NaCl solution during 8 months also showed no changes in the mass and appearance of the samples both by full immersion and by partial immersion in the zone of contact between solution and air. This high corrosion resistance is comparable with the properties of vacuum arc deposited TiN coatings on steel and brass substrates [4]. The mask-deposited TiN coatings do not show any signs of accelerated corrosion along the border between coated and uncoated glass.

The data of electrochemical tests are displayed in Figure 5 (NaCl solution) and Figure 6 (NaCl + NH_4Cl solution) both at pH = 6. The dependence of corrosion current i_c on the polarisation voltage E is shown for Ti, TiN coatings and for two different TiO_2 coatings of various thickness having red and green colours. For both TiN and TiO_2 no active peaks are present and the coatings are in the self-passivated state. For NaCl solution $E_c(\text{Ti}) = -0.22$ V, $E_c(\text{TiN}) = 0.05$ V, $E_c(\text{TiO}_2, \text{red}) = -0.1$ V and $E_c(\text{TiO}_2, \text{green}) = -0.14$ V. For NaCl + NH_4Cl solution $E_c(\text{Ti}) = -0.26$ V, $E_c(\text{TiN}) = 0.15$ V, $E_c(\text{TiO}_2, \text{red}) = -0.1$ V and $E_c(\text{TiO}_2, \text{green}) = -0.05$ V. This data show that corrosion resistance of TiN is much higher than that of Ti and TiO_2 in both solutions studied. Furthermore, the TiO_2 coating is more corrosion resistant than pure Ti. Nevertheless, E_c in all cases remains more positive than the reduction potential for hydrogen. This reveals that the corrosion process for all coatings studied can proceed only with oxygen depolarization. It can be seen in Figs. 5 and 6 that both cathodic and anodic processes are less pronounced on the surface of TiO_2 in comparison with TiN. In the presence of NH_4Cl i_a for TiN decreases in comparison to NaCl solution. i_a for Ti and TiO_2 remains on the same level, but the difference for TiO_2 coatings of different thickness increase. It is also important to mention that at voltages of anodic polarization of TiO_2 oscillations of i_a take place. These oscillations mean that the local repeated corrosion attack of the coating surface layer proceeds and that the surface is repeatedly activated.

Numerous papers report data on the electrochemical properties of TiN deposited on metallic substrates like tool steel [4-10]. The corrosion process of TiN/steel is rather

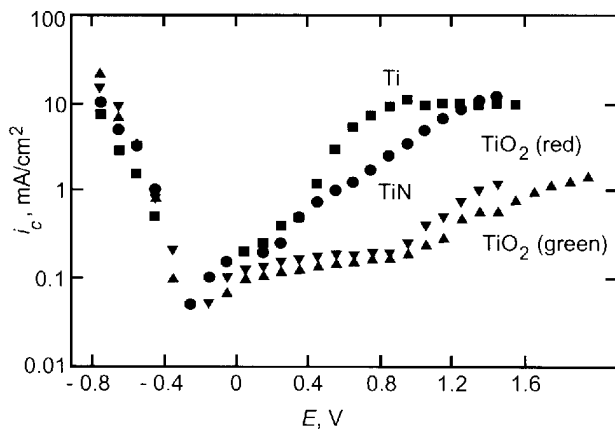


Figure 5. The dependence of corrosion current i_c on the polarisation voltage E in the 3.0 at. % NaCl solution at pH=6.

complicated and includes, together with corrosion of TiN, the corrosion of the steel substrate. It can be controlled by the penetration of the corrosion agents both along the interface between the coating and substrate and through defects in the coating. In order to discuss correctly our results, we should use the data on electrochemical properties of TiN deposited on glass by reactive d.c. sputtering [10] and on Al_2O_3 by PACVD [6]. Both glass and Al_2O_3 substrates are inert from the corrosion point of view. Therefore, these data characterize the intrinsic properties of TiN rather than a combination of corrosion processes of both substrate and coating. The values of corrosion current density, i_c (established as the current density on the cathodic polarization curve corresponding to the E_c) reported in [6, 10] are of the same order of magnitude as in our work. The corrosion potential E_c of TiN in a NaCl solution with pH = 6 in our work is about 0.09 mV more positive than E_c reported in [9] for nearly the same electrochemical conditions. In [6] the data are given for pH = 1 ($E_c = -0.23$ V, recalculated for the Ag/AgCl electrode) and pH = 12 ($E_c = -0.33$ V) which is much lower than both values obtained in this work. The pronounced anodic peak is present in all potentiodynamic curves presented in [10]. In this work coatings are in the self-passivated state. Therefore, the corrosion resistance of TiN deposited by the vacuum arc process is definitely higher than that of TiN coatings deposited on silicate glass substrates by reactive d.c. sputtering [10] and on Al_2O_3 substrates by PACVD [6].

Conclusions

The vacuum arc deposition process proved to be an industrially viable technique to provide a wide range of decorative coatings on large area substrates. The low substrate temperature and the coverage efficiency of vacuum arc deposition

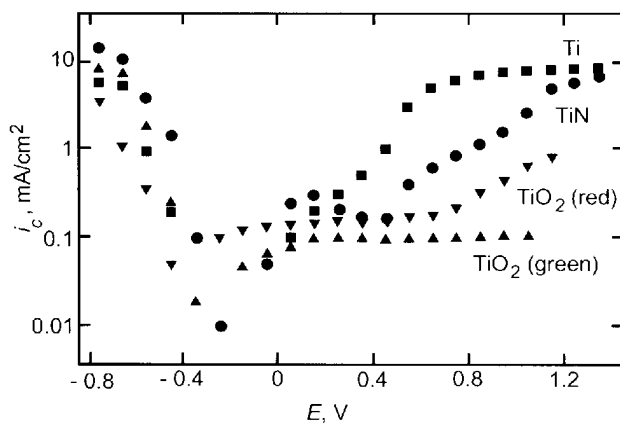


Figure 6. The dependence of corrosion current i_c on the polarisation voltage E in the 3.0 at. % NaCl + 3.0 at. % NH_4Cl solution at pH=6.

make it possible to coat plastics or use them as mask to create patterns. Due to the attractive properties, titanium has been deposited alone or in presence of a reactive gas (nitrogen, oxygen) to produce various coloured coatings. TiN, TiO_2 and TiN/ TiO_2 layers deposited on silicate glass have been investigated. TiN and TiO_2 layers exhibited a high corrosion resistance.

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