VACUUM ARC DEPOSITION OF DECORATIVE AND PROTECTIVE COATINGS ON THE LARGE-AREA GLASS AND STEEL SUBSTRATES

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An industrial installation for vacuum arc deposition is presented. Its potential in the field of decorative coatings for large area glass and steel sheets is demonstrated. Particularly it is possible to deposit patterned coatings through a textile polymeric mask. TiN, TiO_2 and mutilayer TiN/TiO_2 coatings have been characterized. The depth profiling was made with the aid of Auger electron spectroscopy. The corrosion resistance of TiN coatings is higher than the corrosion resistance of TiO_2. The corrosion resistance of vacuum arc deposited TiN coatings on glass proves to be higher than that of TiN coatings produced by direct current reactive sputtering and plasma assisted chemical vapour deposition. Patterned TiN coatings do not show any signs of an accelerated corrosion along the border between the coated and uncoated glass.

INTRODUCTION

Vacuum arc deposition is an effective and environmental friendly technique for the production of decoration coatings on architectural glass and steel. This robust and inexpensive process allows to produce coated materials for building and construction which are cheap enough to be able to compete with materials prepared in a traditional metallurgical way. Particularly, in the last years stainless steel strips and rods coated with TiN in SONG Ltd. were used by building companies in Moscow for the rebuilding of the Cathedral of Christ The Saviour (2 m long elements for the chains fixing the crosses on the domes), for the construction of the monument for Emperor Peter the Great and of the new roof for the Moscow Luzhniki Olympic Stadion (altogether about 2000 m^2, 1x2 m coated strips are used) and for the reconstruction of the roof of the Great Kremlin Palace (about 200 m long decorative grating, made of laser patterned and TiN coated 1x2 m strips). Vacuum arc process allows one to deposit very uniform coatings on the three-dimensional parts having complicated form. 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 substrates. This allows in particular to have 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.

EXPERIMENTAL OUTLINE

The industrial scale set-up "Nikolay" used for the deposition of coatings on the large-area architectural glasses and steel strips has the following characteristics: size 6000×3000×3000 mm, mass 15500 kg, maximum power consumed 75 kW, ultimate vacuum 5×10^{-4} Pa, maximum size of substrates 2100×1300×8 mm, output capacity 30 sheets 2100×1300×5 mm in a 8 h cycle, up to 1000 m^2/month. A standard procedure for decorative coating includes three steps. The strip before being loaded into the machine is precleaned using hot distilled water. After precleaning, the sheets are mounted on metallic frames and placed in the machine vacuum chamber. Each frame contains two 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]. 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 [2] 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, TiO$_2$ and multilayers of TiN/TiO$_2$. 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, TiO$_2$ and TiN/TiO$_2$ coated silicate glass samples were cut from large glass sheets and analysed regarding surface morphology, composition and corrosion resistance.

The composition depth profile of TiN/TiO$_2$ coated silicate glass was made by Auger electron spectroscopy (AES). The specimens were mounted in the loaders of the spectrometer carrousel 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 μA 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 SiO_2.

The corrosion behaviour of both TiN and TiO_2 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 SO_2). 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
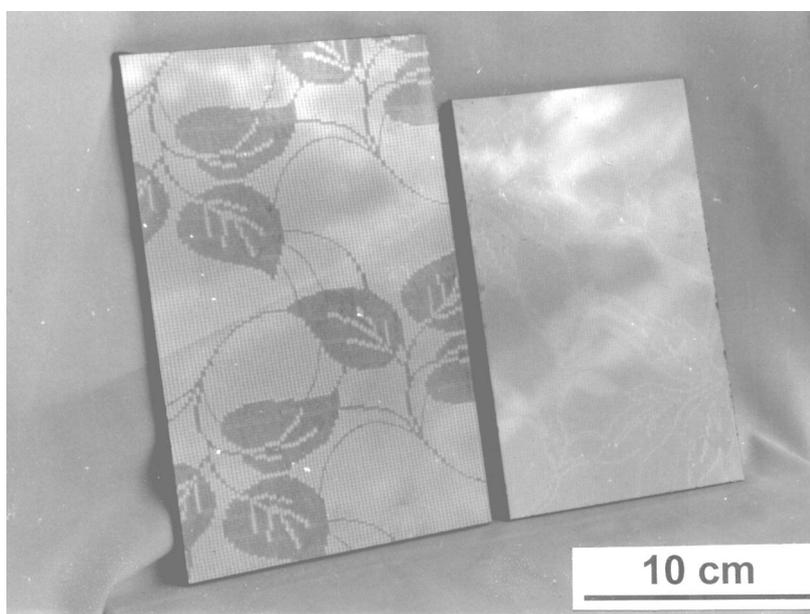
Fig. 1. Patterned TiN/TiO$_2$ coating vacuum arc deposited on silicate glass through polymeric mask (left-hand sample) and uniform TiN coating deposited without mask (right-hand sample).
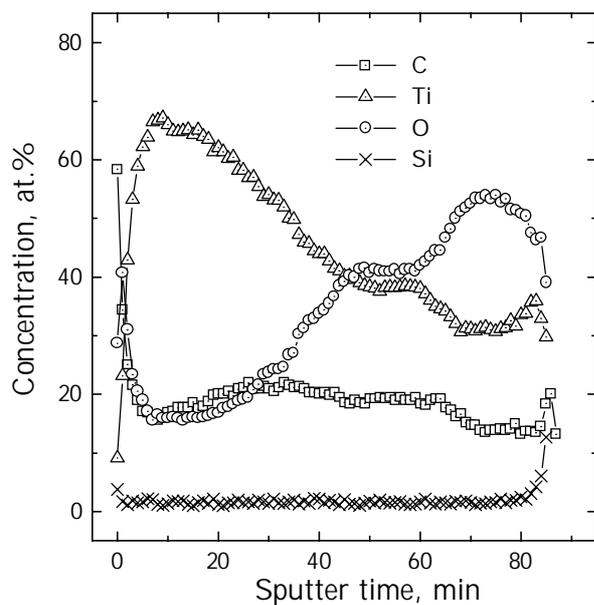
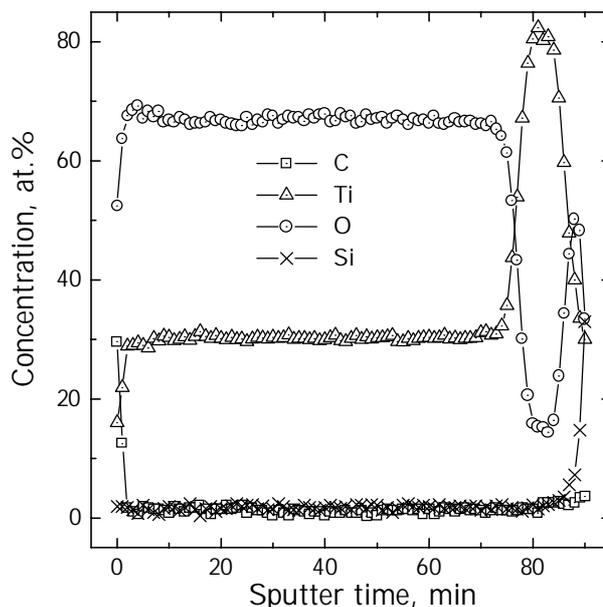*Fig. 2*. AES spectra for the Ti coating on silicate glass.

Fig. 3. AES spectra for the TiO$_2$ coating on silicate glass.

+ 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% NH$_4$Cl solution with pH = 6. The correction of the pH of the solutions was carried out by addition of 0.05 mole of NH$_4$OH (to the solutions containing NH$_4$Cl) and by addition of 0.05 mole of NaOH (to the solutions without NH$_4$Cl). 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 cm^2, the rest surface of the samples was isolated by a varnish layer. The test temperature was 22–25 °C.

RESULTS AND DISCUSSION

The photographs of the patterned TiN/TiO$_2$ coating deposited on silicate glass through polymeric mask (left-hand sample) together with uniform coating (right-hand sample) are shown in Fig. 1. The depth concentration profile obtained from the Auger spectra for Ti and TiO$_2$ coatings on silicate glass are shown in Fig. 2 and 3 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
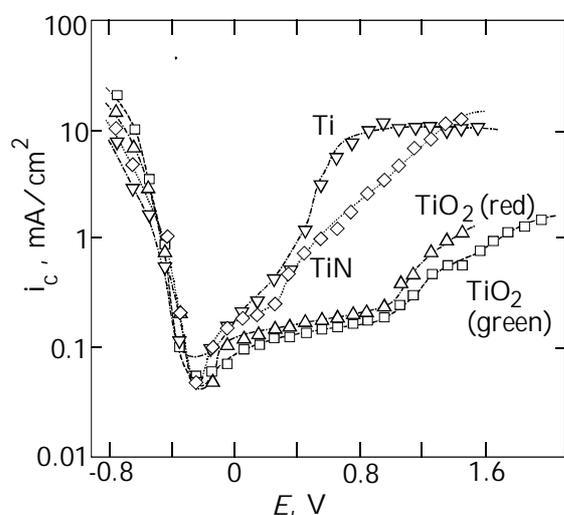
Fig. 4. The dependence of corrosion current i_c on the polarisation voltage E in the 3.0 at.% NaCl solution at pH=6.
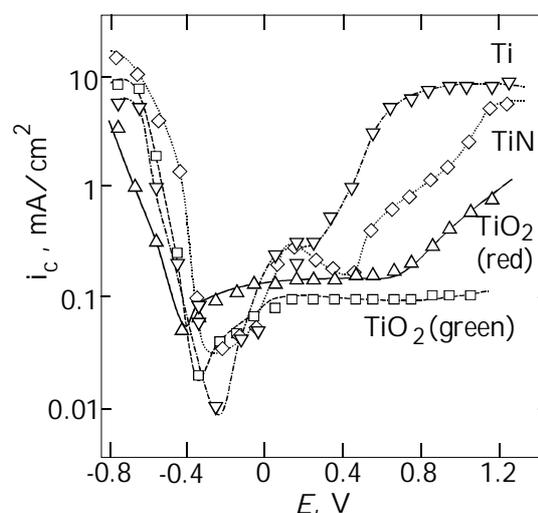
Fig. 5. The dependence of corrosion current i_c on the polarisation voltage E in the 3.0 at.% NaCl + 3.0 at. % NH_4Cl solution at pH=6.

increases towards the substrate. The oxygen content in the TiO_2 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 TiO_2 coating is about 1.95 being very close to the stoichimetrical one. The carbon concentration is nearly constant in the whole coating (close to zero in the TiO_2 and slightly 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 12 months of tests in atmospheric corrosion with conditions which correspond to the most aggressive art 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 12 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 [3]. 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 Fig. 4 (NaCl solution) and Fig. 5 (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 (Ti) = − 0.22 V, E_c (TiN) =

0.05 V, E_c (TiO$_2$, red) = $-$ 0.1 V and E_c (TiO$_2$, green) = $-$ 0.14 V. For NaCl + NH$_4$Cl solution E_c (Ti) = $-$ 0.26 V, E_c (TiN) = 0.15 V, E_c (TiO$_2$, red) = $-$ 0.1 V and E_c (TiO$_2$, green) = $-$ 0.05 V. This data show that the 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. 4 and 5 that both cathodic and anodic processes are less pronounced on the surface of TiO$_2$ in comparison with TiN. In the presence of NH$_4$Cl 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 [3–9]. The corrosion process of TiN/steel is rather 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 [9] and on Al$_2$O$_3$ by PACVD [5]. Both glass and Al$_2$O$_3$ 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 [5, 9] 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 [8] for nearly the same electrochemical conditions. In [5] 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 [9]. 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 [9] and on Al$_2$O$_3$ substrates by PACVD [5].

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