

Corrosion resistance of the vacuum arc deposited Ti, TiN and TiO₂ coatings on large area glass substrates

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Abstract

An industrial installation for vacuum arc deposition is presented. Its potential in the field of decorative coatings for large area glass sheets is demonstrated. In particular it is possible to deposit patterned coatings through a polymeric textile mask. The ability to deposit uniform multilayer coatings having interference colours onto large silicate glass sheets is shown. Titanium, titanium nitride and titanium dioxide coatings on silicate glass have been characterized in terms of composition and corrosion resistance. Depth profiling was achieved with the aid of Auger electron spectroscopy. The corrosion resistance of TiN coatings is higher than that of TiO₂. The corrosion resistance of vacuum arc deposited TiN coatings on glass was higher than that of TiN coatings produced by direct current reactive sputtering and plasma assisted chemical vapour deposition. Mask-deposited TiN coatings do not show any signs of accelerated corrosion along the border between the coated and uncoated glass. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

During recent years, the physical vacuum deposition technologies originally developed for microelectronics and optics have penetrated into the areas of low cost and large area coated products traditionally produced by metallurgical methods. This trend is strongly supported by the decrease in the cost of vacuum equipment and by the development of robust and inexpensive coating technologies. One such method is vacuum arc deposition [1]. The vacuum arc process became prominent since the technology of TiN deposition was developed in the 1970s. It is widely used for the deposition of hard and wear resistant coatings on tools, medical prostheses, etc. [2–4]. Another important application of

vacuum arc deposition is for diamond-like coatings on video recorder heads [5]. In both of these applications, the dimensions of the parts to be coated is rather small. The next step in the development of vacuum arc deposition was the development of equipment able to coat large area substrates of complicated form [6]. This opened the way for marketing materials for architectural applications. A very important sector of this market is coated glasses. They are used for glazing (with semi-transparent coatings), decoration (mirrors), etc. Vacuum arc deposition has several advantages in this area, particularly:

- a high deposition rate which does not depend on the sputter coefficient of the target material [7];
- the weak dependence of the deposition rate on the orientation of substrate and the distance between target and substrate, which allows easy coating of three-dimensional parts of complicated form [8];
- the possibility of coating non-conductive substrates; and

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- low temperature of the substrate during deposition [6].

These advantages facilitated the development of new coated glass products for architectural applications which is described in this paper.

Architectural outdoor application of these new glass products needs data concerning their corrosion resistance because the coated glasses are exposed to the aggressive atmosphere of a modern megalopolis. High corrosion resistance of TiN and TiO₂ coatings on steel and brass substrates is well documented [9,10]. Nevertheless, the corrosion properties of a system containing a substrate and a coating depend strongly on the electrochemical properties of both components. Unfortunately, data on corrosion resistance of TiN and TiO₂ coatings on electrochemical inert surfaces, such as glass, are very scarce and do not relate to vacuum arc deposited coatings [11,12]. The aim of this work is to present data on the properties of vacuum arc deposited decorative coatings on glass substrates which are important for outdoor applications.

2. Experimental

The 'Nikolay' industrial scale system used for the deposition of coatings on large area architectural glasses 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 treated glass: 2100 × 1300 × 8 mm; output capacity: 30 glass sheets 2100 × 1300 × 5 mm in an 8 h cycle, up to 1000 m²/month. The standard procedure for glass decorative coating included three steps. Before being loaded into the machine the glass sheet was precleaned using hot distilled water. After this precleaning, the glass sheets were mounted on metallic frames and placed in the vacuum chamber. Each frame held two glass sheets, mounted back to back. The frames were inserted into a slot (15 slots were available) and allowed to move independently inside the machine in order to receive different treatment operations. The displacement velocity of the frame was monitored and could be controlled. Each pair of glass sheets was sputter cleaned immediately before coating using a Hall discharge accelerator having a form of a large elongated loop [13]. A twin aperture had two slots, 55 mm away from one another. Two juxtaposed permanent magnets acted as a cathode. The water cooled anode had a tubular shape and ran inside the groove made by the cathode. The whole apparatus was set under vacuum in the presence of a sputter gas (usually argon or oxygen; the gas inlet was directly in the source). Gas ionization and subsequent ion acceleration was achieved by crossed electric and magnetic fields. Sheets to be treated were successively transported under the Hall discharge accelerator at a given translation

speed, the substrate surface being perpendicular to the ionic flux axis. By changing the speed and accelerator power, we could control the sputter dose received by the substrate. Two Hall current accelerators were mounted in the machine. They were placed on both sides of the machine in order to clean the two sheets in the frame simultaneously. For Ar, the sputter voltage was typically 5 kV, the sputter current could vary from 1 to 6 A. The high power (up to 10 kW) provides sufficient cleaning of both surfaces in any circumstances.

Three sources with flat round targets of diameter 200 mm were placed on each side of the installation. The surfaces of the targets were parallel to the glass substrates. Only two sources were normally used during the deposition. Arc voltage was constant at $U=22$ V while the discharge current I on each source could be varied from 100 to 300 A. No bias was applied to the substrate. A reactive gas (oxygen or nitrogen) was introduced at a pressure of 0.05 Pa if an oxide or nitride coating was to be formed. The arc generation was continuous and random. The arc sources were placed a rather large distance (about 800 mm) from the sheets to be coated. The configuration of the machine provided shielding and increased the charged particle part of the beam using the fact that the microdroplets were ejected at small angles with respect to the target surface [14]. The distance of the glass sheet from the target depended on the position of a frame. Therefore, the thickness of the deposited layer was controlled by varying the translation speed of the frame. The translation speed varied from 0.5 to 3 m/min depending on the thickness of a coating (typically 300 to 500 nm). When decorative patterns had to be produced, light nylon patterned sheets were used to provide masking. Various colours can be produced depending on the gas and deposition parameters used. In this study Ti, TiN and TiO₂ coated silicate glass samples were cut from large glass sheets and the surface morphology, composition and corrosion resistance were analysed.

The microstructure of the TiN and TiO₂ coatings was studied using scanning electron microscopy (SEM) using the JEOL JSM-6300F with an electron beam microanalysis facility. The composition depth profile of TiN/TiO₂ coated silicate glass was performed by Auger electron spectroscopy (AES) on a Physical Electronics PHI-551 spectrometer with a double-pass cylindrical mirror analyzer. 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 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 to the sample. The peak-to-peak modulation was 3 V. 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 for SiO_2 were determined to be 25 nm/min. AES studies of the Ti-N system are complicated by the fact that the main Auger $\text{KL}_{2,3}\text{L}_{2,3}$ transition for nitrogen (379 eV) overlaps the titanium $\text{L}_3\text{M}_{2,3}\text{M}_{2,3}$ transition (383 eV) to produce a single peak at 385 eV [15]. Auger spectra of titanium nitride coatings hence include two peaks, one corresponding to the Ti $\text{L}_3\text{M}_{2,3}\text{M}_{4,5}$ transition (418 eV) and the TiN peak resulting from overlapping (385 eV). For quantitative analysis, one must be able to resolve the nitrogen peak by removing the titanium contribution to the 385 eV peak. This was performed using the method described previously [16] where the approach [15] was improved. The reflectivity, R , of coloured coatings was measured with standard lock-in techniques. White light from a halogen lamp was focussed on the entrance slit of a Jovin-Yvon H25 monochromator (with a 1200 grooves/mm grating) and monochromatic light was focused onto a silicon diode after reflecting on the sample. The signal was compared to the reflection of a high-reflectivity ($R=0.98$ at 500 nm) mirror in order to give the reflectance in absolute units.

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 the influence of gaseous chlorides, NH_3 and SO_2). Accelerated tests in 3.5% NaCl solution at 22–25°C under both full and partial immersion were also carried out. Both uniform and mask-deposited TiN coatings were studied because on the border 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 of MSNP. All potential values are given versus an Ag/AgCl electrode ($E_{\text{Ag}/\text{AgCl}}=0$ corresponds to -200 mV on the hydrogen electrode scale). The scanning rate was 1 mV s^{-1} . The polarization was changed from -0.8 to $+1.5$ V. Before the potentiodynamic measurements, the corrosion potential E_c was monitored for 0.5 h. The measurements were carried out in the electrolytes 3.0% NaCl solution, and 3.0% NaCl + 3.0% NH_4Cl solution with pH=4 and 2. The pH of the solutions was corrected by adding 0.05 mol of NH_4OH to the solutions containing NH_4Cl and by adding 0.05 mol of NaOH to the solutions without NH_4Cl . The pH value of the solution was controlled by a 'pH-121' pH-meter of MSNP. The solution was prepared from reagent-grade chemicals and distilled water.

The area exposed to the solution was 1 cm^2 , the remaining surface of the samples was isolated by a varnish layer. The test temperature was 22–25°C.

3. Results and discussion

Vacuum arc deposition produced architectural glass (with standard dimensions of 1300×1600 mm) has the following coatings:

1. Thin semitransparent TiN coatings for glazing or thick non-transparent for mirrors. The colour of these coatings was determined mainly by the composition of TiN.
2. TiN patterned coatings. In this case the light polymeric mask was positioned between the vacuum arc source and the substrate. An example of a mask deposited coating is shown in Fig. 1. The natural coloured TiN coating was combined with uncoated transparent glass.
3. TiO_2 coatings having interferential colours defined by the thickness of the coating. TiO_2 coatings of three different thicknesses were characterized (blue, green and red). Reflectivity spectra for wavelength



Fig. 1. Detail of a decorative pattern obtained by masking during TiN arc deposition on silicate glass.

from 400 to 800 nm (Fig. 2) characterized quantitatively the green and blue colours of the TiO₂ coatings.

4. TiN patterned coating deposited on an intermediate coloured TiO₂ coating. In this case the TiN coating of natural colour (goldish or yellow) was combined with a red, blue or green TiO₂ coating.

The depth concentration profile obtained from the AES for the TiN coating on silicate glass is shown in Fig. 3. The peak characteristics for titanium, nitrogen, oxygen, carbon and oxygen appeared in the spectra. The decreasing concentration of titanium and increasing concentration of Si mark the transition from the coating to the substrate. The nitrogen and oxygen content in the TiN coating was uniform except in the thin oxygen-rich layer close to the glass substrate (deliverably deposited for the better adhesion of TiN to the SiO₂ substrate). Quantitative analysis revealed that the Ti to N ratio in the TiN layer is about 1.2, very close to stoichiometric. The carbon concentration is nearly uniform in the whole coating (about 10 at.%). The uniformity of the composition of the TiN layer, which does not change significantly with depth, is comparable with that of TiN coatings obtained with the aid of the chemical vapor deposition (CVD) technique [17]. The TiN composition was similar to that obtained using plasma-assisted CVD (PACVD) deposited at 430°C substrate temperature, 60 W radio frequency power by Kim et al. [18]. They detected the stoichiometric composition for substrate temperatures

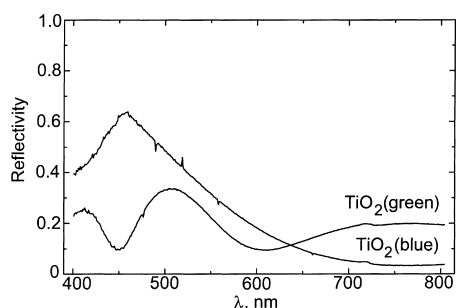


Fig. 2. Reflectivity spectra of green and blue TiO₂ coatings on silicate glass.

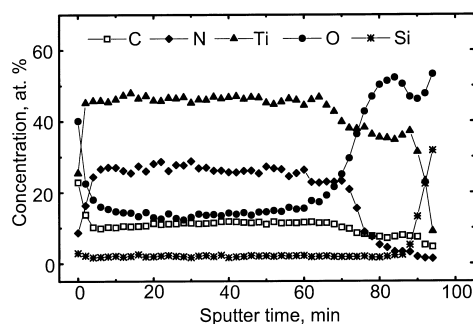


Fig. 3. AES depth profile for a TiN coating on silicate glass. The thickness was about 0.5 μm.

above 500°C. In our case, the substrate temperature was well below 100°C, which allowed the use of polymer masks for the deposition of patterned TiN and TiO₂ coatings. It was shown [19] that even a rather high residual carbon content did not drastically affect the properties of TiO₂. In our case, the vacuum arc deposited coatings possessed high corrosion resistance, and the carbon contamination was obviously not detrimental to corrosion resistance.

The most important structural feature of both TiN and TiO₂ coatings is the Ti microdroplets present in the coating [7]. These microdroplets are so small that they are not visible to a naked eye, do not disturb the appearance of coated glasses and, therefore, do not resurrect their applicability as architectural materials. Nevertheless, in the case of a less corrosion resistant substrate (stainless steel instead of glass) the small pores surrounding these droplets can feed the corrosive agent to the substrate and active corrosion starts [20]. Visual examination of TiN and TiO₂ coatings before and after electrochemical corrosion testing in neutral solution revealed differences in the corrosion mechanism. The corrosion of TiO₂ coatings started at low E values (both positive and negative) and formed dark corroded regions around the Ti microparticles. The number and area of corroded places uniformly increased with increasing E . The TiN coatings were stable against corrosion and did not reveal any visual signs of damage up to rather high positive and negative E values -0.8 V and $+0.7$ V. Above $E = +0.7$ V, multiple corroded areas suddenly appeared all over the surface, destroying the coating almost simultaneously everywhere.

After 12 months of exposure to atmospheric corrosion, with conditions which correspond to the most aggressive type of industrial atmosphere (temperature 22–25°C, humidity 96–98%, no water condensation, under influence of gaseous chlorides, NH₃ and SO₂) neither the mass nor appearance changed. Likewise, neither full nor partial immersion in NaCl solution for 8 months produced any changes. The first signs of corrosion in these tests appeared only after 11 months. This high corrosion resistance is comparable with the properties of vacuum arc deposited TiN coatings on steel and brass substrates [10]. The mask-deposited TiN coatings did not show any signs of accelerated corrosion along the border between coated and uncoated glass. The data from electrochemical tests are displayed in Fig. 4 (NaCl solution, pH=4) and Fig. 5 (NaCl+NH₄Cl solution, pH=2). The dependence of the corrosion current i_c on the polarisation voltage E is shown for Ti, TiN and two different TiO₂ coatings of various thickness having red and green colours. Both TiN and TiO₂ were self-passivated. The corrosion potentials are given in Table 1. This data show that at a low pH value the corrosion resistance of TiN is much higher than that of Ti and TiO₂ in both solutions studied.

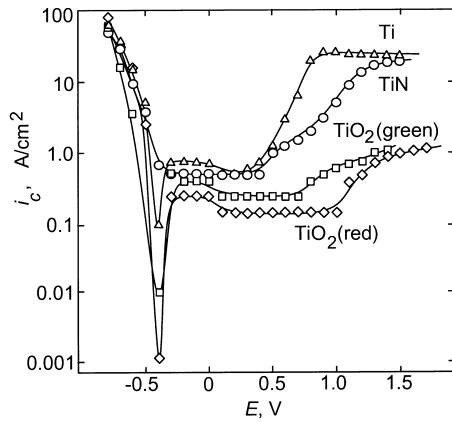


Fig. 4. The dependence of the corrosion current i_c on the polarisation voltage E in 3.0 at.% NaCl solution with pH=4.

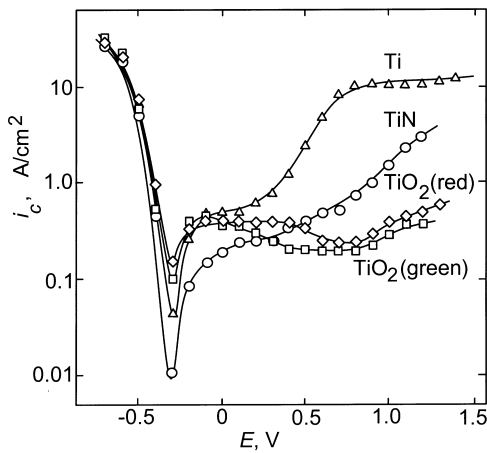


Fig. 5. The dependence of the corrosion current i_c on the polarisation voltage E in 3.0 at.% NaCl + 3.0 at.% NH_4Cl solution with pH=2.

Furthermore, the TiO_2 coating is more corrosion resistant than pure Ti. With increasing pH, E_c becomes more negative. Nevertheless, E_c in all cases remains more positive than the reduction potential for hydrogen. This indicates that the corrosion process for all coatings studied can proceed only with oxygen depolarization. The most negative E_c was measured for the Ti coatings, the most positive for TiN. It can be seen in Figs. 4 and 5 that both the cathodic and anodic processes are less pronounced on the surface of TiO_2 in comparison with TiN. The corrosion current i_c for TiN is smaller in the

NH_4Cl -containing solution. The values of i_c for Ti and TiO_2 remain at the same levels as those in NaCl solution without NH_4Cl . It is also important to mention that at anodic polarization voltages for TiO_2 , i_a oscillates. This reveals that the coating surface layer is repeatedly attacked and activated. The corrosion properties of a system containing a substrate and a coating depend strongly on the electrochemical properties of both components. To correctly discuss our results, we compare our data with the electrochemical properties of TiN deposited on electrochemically inert substrates (glass, Al_2O_3) by reactive direct current sputtering and PACVD [11,12]. The values of corrosion current density, i_c [11,12], are of the same order of magnitude as in this work. The corrosion potential E_c of TiN in NaCl solution with pH=6 in our work is about 0.09 mV more positive than E_c for nearly the same electrochemical conditions after results in [21]. For pH=1 [11], $E_c = -0.23$ V for sputtered films (recalculated for the Ag/AgCl electrode) and for pH=12, $E_c = -0.33$ V, which is much lower than both values obtained in this work. A pronounced anodic peak was present in all potentiodynamic curves [12]. In our work the coatings were self-passivated. Therefore, the corrosion resistance of TiN deposited by vacuum arc process is definitely higher than that of TiN coatings deposited on silicate glass substrates by reactive d.c. sputtering [12] and on Al_2O_3 substrates by PACVD [11].

The vacuum arc deposited naturally coloured Ti and TiN coatings, interferentially coloured TiO_2 coatings, and patterned TiN and TiN/ TiO_2 coatings on large area glass substrates were very uniform and exhibited high corrosion resistance. These properties, together with the unusual appearance, make vacuum arc coated glass very attractive for architectural applications.

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Table 1
Corrosion potentials E_c (V) for Ti, TiN and TiO_2 coatings vacuum arc deposited on silicate glass

Solution	3.0 at.% NaCl			3.0 at.% NaCl + 3.0 at.% NH_4Cl		
	pH=4	pH=6	pH=8	pH=2	pH=4	pH=6
Ti	-0.10	-0.22	-0.12	+0.05	-0.25	-0.26
TiO_2 (red)	+0.16	-0.10	-0.10	+0.23	0	-0.10
TiO_2 (green)	+0.10	-0.14	-0.07	+0.25	-0.05	-0.05
TiN	+0.28	+0.05	0	+0.35	+0.20	+0.15

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