

## PROTECTIVE PROPERTIES OF THE VACUUM ARC DEPOSITED DECORATIVE TiN AND TiO<sub>2</sub> COATINGS ON STAINLESS STEEL

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### ABSTRACT

Recently, the vacuum arc technology was developed for the deposition of the decorative and protective titanium nitride and titanium dioxide coatings on large area substrates. An industrial installation "Nikolay" for vacuum arc deposition of decorative and protective coatings is presented. It has the following parameters: size 6000×3000×3000 mm, mass 15500 kg, maximum power consumed 75 kW, ultimate vacuum  $5 \times 10^{-4}$  Pa, maximum size of treated strips 2100×1300×8 mm, output capacity for 30 strips 2100×1300×5 mm in a cycle and up to 1000 m<sup>2</sup>/month. It allows to deposit titanium nitride coatings having natural golden colour and titanium dioxide coatings having highly uniform interference colours. The morphology and microstructure of the coatings were studied with the aid of atomic force microscopy. Both accelerated tests on atmospheric corrosion and electrochemical tests of titanium nitride and titanium dioxide coatings on the stainless steel substrates were carried out. Hard coatings of refractory metal compounds (Ti, Zr, Cr, Mo, etc.) have more noble properties than steel substrates in an electrochemical sense. Therefore, the deposition of highly-porous nonuniform coatings can even accelerate the corrosion process caused by the formation of a galvanic couple of coating and substrate. It has been shown that the deposited coatings are very dense and have only very scarce individual pores due to the remaining Ti droplets. As a result, the highly decorative and biocompatible TiN and TiO<sub>2</sub> coatings do not deteriorate the corrosion resistance of stainless steel substrates.

### INTRODUCTION

In some cases (for example, in hospitals and medical or food industry) the number of allowable materials for decoration and construction is very restricted. The safety conditions limit a lot the architects who possess only a very poor spectrum of colours and materials. Therefore, novel methods for deposition of decorative biocompatible coatings on stainless steel find a great interest on the market. Titanium nitride and dioxide are biocompatible and offer a good opportunity for the deposition of decorative coatings. Titanium nitride hard coatings are widely used to increase the lifetime of cutting tools and improve their surface finish. The gold coloured TiN coating is also applied as a decorative coating on consumer goods. The very attractive yellow colour of TiN can be changed by changing the nitrogen content. Titanium dioxide has a high refractive index allowing one to deposit the coatings with various very bright interference colours. Though TiN has a very high intrinsic corrosion resistance [1, 2], the combination with electrochemically less positive substrates can in principle lead to the increase of the corrosion rate in comparison with an uncoated substrate [3]. A high corrosion resistance of laser ablated TiO<sub>2</sub> coatings on steel was reported recently [4]. The aim of this work is to present data on the properties of vacuum arc deposited decorative coatings on steel substrates important for their outdoor applications.

### EXPERIMENTAL

The industrial scale set-up "Nikolay" used for the deposition of coatings on large-area stainless steel strips has the following characteristics: size 6000×3000×3000 mm, maximum power consumed 75 kW, ultimate vacuum  $5 \times 10^{-4}$  Pa, maximum size of treated strips 2100×1300×8 mm, output capacity for steel 30 steel strips 2100×1300×5 mm in a 8 h cycle and up to 1000 m<sup>2</sup>/month. A standard procedure for decorative steel coatings includes three steps. The steel strip before being loaded into the machine is precleaned using hot distilled water. After precleaning, the steel strips are mounted on metallic frames and placed in the vacuum chamber. Each frame contains two steel strips, mounted back to back. The frame is inserted into a slot (15 slots are available) and allowed to move independently inside the deposition chamber. The displacement velocity of the frame is monitored and can be controlled. Each strip is ionically etched just before the coating process in order to prevent recontamination. The complete treatment involves one return of the frame for cleaning and another return for coating. The cleaning is performed using a large aperture Hall current accelerator [5], providing high energetic ions which impact and sputter the substrate surface. 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 for oxide or nitrogen for nitride coatings) is introduced at 0.05 Pa. The construction of the plant enables shielding, and only a very small number of microparticles is present in the coating. These microparticles do not disturb the optical appearance of the decorative coatings. The TiN coatings studied in this work were deposited on 12H18N9T (0.11% C, 17 % Cr, 8.8 % Ni, 0.35 % Ti) stainless steel and the coloured (blue) TiO<sub>2</sub> coating on H18N10 (18 % Cr, 9 % Ni) stainless steel without any intermediate layer.

The sample 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 a nominal radius of curvature of the tip less than 20 nm. The corrosion behaviour of TiN and coloured (blue) TiO<sub>2</sub> coatings on stainless steel strips was characterized. Both accelerated tests on atmospheric corrosion and electrochemical tests were carried out. In the accelerated tests on atmospheric corrosion two different solutions were used: (1) 30 g NaCl + 30 g NH<sub>4</sub>Cl + 1 ml HCl and (2) 30 g NaCl + 10 g Na<sub>2</sub>S + 30 g NH<sub>4</sub>Cl + 1 ml H<sub>2</sub>SO<sub>4</sub> for 1000 cm<sup>3</sup> of aqueous solution. Electrochemical tests were carried out in two aqueous solutions: (3) 30 g NaCl and (4) 30 g NH<sub>4</sub>Cl for 1000 cm<sup>3</sup> of solution. The pH value was varied from 2.0 to 8.0 in case of TiN coatings and was 6.0 in case of TiO<sub>2</sub> coatings. The correction of the pH value of the solutions was carried out by addition of 0.05 mole of HCl or NH<sub>4</sub>OH (to the solutions containing NH<sub>4</sub>Cl) and by addition of 0.05 mole of NaOH (to the solutions without NH<sub>4</sub>Cl). The solution was prepared from reagent-grade chemicals and distilled water. The area exposed to solution was 8 cm<sup>2</sup> in the atmospheric corrosion tests and 0.3 to 1 cm<sup>2</sup> in electrochemical tests. The residual surface of the samples was isolated by a varnish layer. The samples were degreased before the tests in the humid mixture of MgO and K<sub>2</sub>CO<sub>3</sub> and washed out with water. The test temperature was 22–25 °C. The standard accelerated tests on atmospheric corrosion were carried out according to the Russian standards RST 9.303-84 and 9.302-88 during 2 months by complete immersion in the solution and in the humid atmosphere above this solution (humidity 96–98%). The prepared samples were positioned in a closed glass container half-filled with the test solution. One sample was completely immersed in the solution. Another sample was positioned above the solution in the humid atmosphere. The corrosion behaviour was studied visually. The time of the appearance of the first corrosion damage was measured. Afterwards the ratio of the damaged to intact area was estimated. The electrochemical measurements were performed in a three-electrode cell with separated volumes in air at the ambient temperature. The pH value of a solution was controlled by a pH-meter "pH-121". Before the beginning of the measurements, the samples were washed out in the solution for the tests. The polarization behaviour was measured potentiodynamically with the aid of a potentiostatic apparatus PI-50-1/PR8. All the potentials were measured with an Ag/AgCl reference electrode ( $E_{\text{Ag}/\text{AgCl}} = 0$  corresponds to – 200 mV in the hydrogen electrode scale). The scanning rate was 1 mVs<sup>-1</sup>. The polarization was changed from – 1.3 V to + 0.5 V. Before the potentiodynamic measurements, the corrosion potential  $E_c$  was monitored for 0.5 h. The porosity of the samples was estimated with the aid of metallography and chemical methods. In the chemical method the sample was immersed during 5 min into the aqueous solution containing 40 g/l K<sub>3</sub>[Fe(CN)<sub>6</sub>] and 15 g/l Na<sub>2</sub>SO<sub>4</sub>. Afterwards, the number of points marked with blue corrosion products was counted and used for the characterization of the porosity.

## RESULTS

The studied vacuum arc coated architectural stainless steel (with standard dimensions of 1000×2000 mm) has the following coatings:

- (1) Thick nontransparent TiN coatings (the thickness was about 0.5 to 0.8 μm). The colour of these coatings was determined mainly by the composition of TiN.
- (2) TiO<sub>2</sub> coatings having interferential colours defined by the thickness of the coating (below 1 μm). The TiO<sub>2</sub> coatings with blue colour were characterized.

### *TiN coatings*

During the accelerated corrosion tests a coated sample immersed into solution 2 (NaCl + Na<sub>2</sub>S + NH<sub>4</sub>Cl + H<sub>2</sub>SO<sub>4</sub>) revealed the first signs of corrosion damage after 8 days. After 2 weeks about 32 % of the surface area was corroded and after 2 months almost all the surface was corroded. No damage appeared on the sample immersed in solution 1 (NaCl + NH<sub>4</sub>Cl + HCl) after 8 days and 2 weeks. Only after 2 months the first signs of damage appeared, similar to the damage of the sample tested in the atmosphere above solution 2. The observed corrosion behaviour reveals the presence of pores in the coating. Especially dangerous are the regions where the large microdroplets delaminated from the substrate (see AFM micrograph in Fig. 1). Such pores can exist in the regions close to the Ti microdroplets. The corrosive properties of the cathodic coatings are greatly affected by

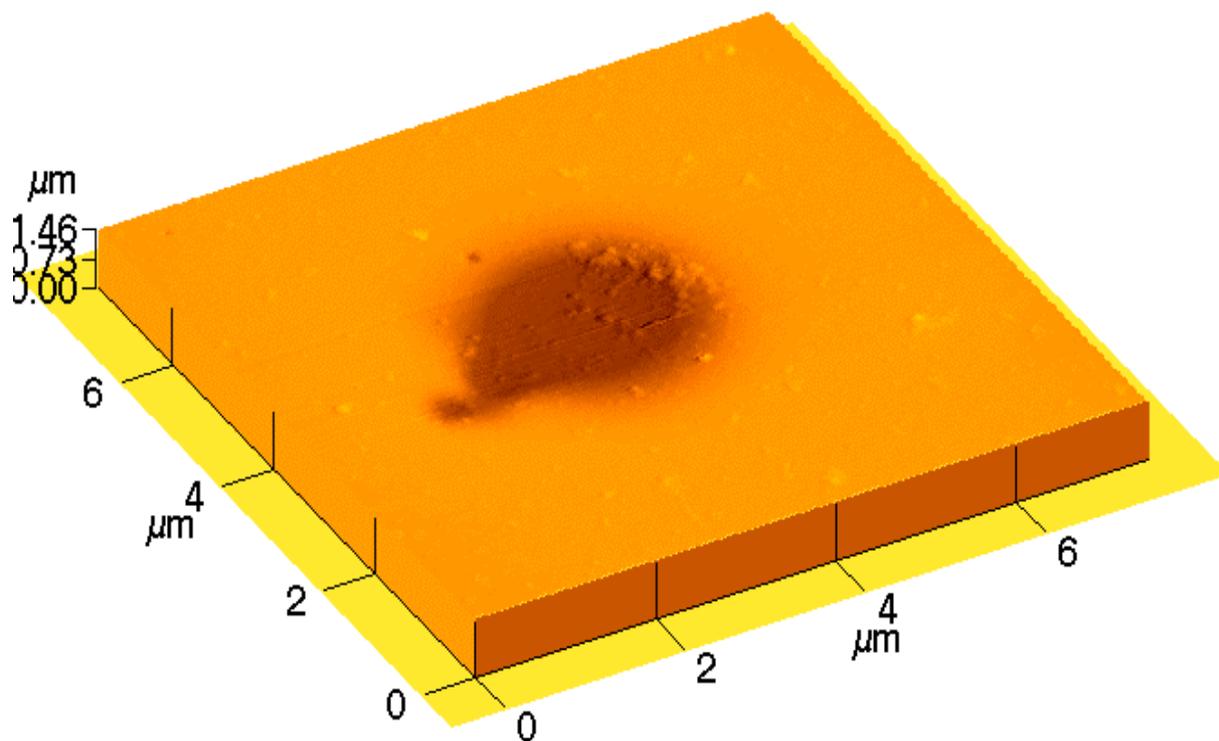


Fig. 1 AFM micrograph of the vacuum arc deposited TiN coating. The area around the delaminated large Ti droplet is shown. Small Ti droplets are also visible

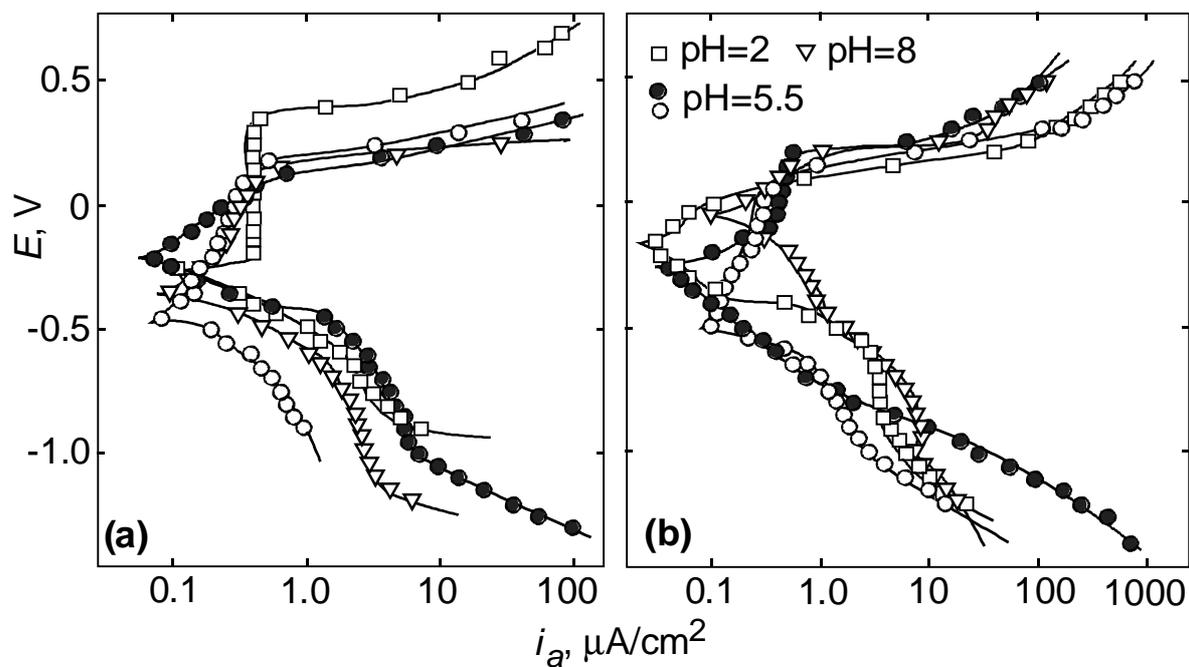
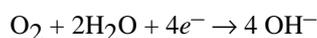


Fig. 2 The dependence of the corrosion current  $i_c$  on the polarisation voltage  $E$  at various pH values for the vacuum arc deposited TiN coatings on stainless steel is shown. The full circles denote the corrosion behaviour of the uncoated substrate. (a) 3.0 at.% NaCl solution, (b) 3.0 at.%  $\text{NH}_4\text{Cl}$  solution

the porosity, therefore, the evaluation of the amount of porosity in the coatings is essential. Milosev [6] studied the microporosity of the TiN coatings on CRK 34, ASP 29, and AISI 293 substrates by multisweep experiments in acetate buffer solutions, and concluded that this method is suitable only when the substrate is actively corroded in the potential range investigated. Arata et al. [7] measured the current density ratio of the ceramics-sprayed coating and substrate, using anodic polarization curves in NaCl solution, and utilized this ratio to select the optimum spraying conditions. Celis et al. [8] proposed a modified electrochemical method to determine the porosity of coatings in a qualitative way. They made coulometric measurements in HCl solution on the coated samples, on the bare substrate material, and artificial through-coating holes of known area were created in the coatings to evaluate the unknown porosity. Konyashin et al. [9] applied electrochemical techniques for the quantitative measurements of the porosity of physical and chemical vapour deposited coatings in acidic  $K_2SO_4$  solution. The rate of the anodic dissolution of uncoated and coated substrate was compared using current data from potentiodynamic and chrono-amperometric measurements. These studies unambiguously indicate that microscopic defects which expose the substrate to the corrosive media are the main problem of the cathodic coatings.

The data of the electrochemical tests for coated and uncoated samples in the solutions 3 (NaCl) and 4 ( $NH_4Cl$ ) with various pH values are shown in Figs. 2a and b, respectively. Generally, the pH value of a solution essentially influences the kinetics of the anode and cathode processes and the corrosion rate. The corrosion process in the NaCl solutions proceeds with the oxygen depolarisation. This follows from the form of the cathode curves at various pH values (Fig. 2a). It means that the corrosion rate is controlled by the oxygen concentration in the solution and by the rate of the reaction



Additionally, it is confirmed by the fact that the anodic polarization curves practically do not change by varying of the pH value. Only at pH = 2 in the NaCl solution the rate of the active dissolution increases about 1.5 times, but the repassivation potential (+ 0.35 V) is about 0.2 V higher than for the other pH values studied. The value of the repassivation potential (+ 0.15 V) and the quick increase of the anodic current are typical for the local activation corrosion mechanism. It means that the coating is porous, and the steel surface is activated in the pores by anodic polarization. This fact is supported by the form of the anodic curve for the uncoated steel. The anodic behaviour of the samples in the  $NH_4Cl$  solutions practically does not depend on the pH value (Fig. 2b). The rate of the anodic dissolution increases slightly (about 10–15%) with increasing pH, and the repassivation potential at all pH values studied is + 0.15±0.05 V. The stainless steel without coating has similar behaviour. The corrosion in the  $NH_4Cl$  solutions proceeds with oxygen depolarization, similar to the NaCl solutions. It means that the oxygen solubility in the  $NH_4Cl$  solution practically does not depend on the pH value. The corrosion current estimated with the aid of the Tafel equation decreases about one order of magnitude with increasing pH. The minimal corrosion rate corresponds to the neutral solution. The data obtained reveal that both coated and uncoated steel is inclined to the pitting corrosion in an acidic environment (pH < 4). At high pH values more likely is the uniform corrosion. The corrosion resistance of the TiN coating on stainless steel around  $E = 0$  V is comparable with the «intrinsic» corrosion behaviour of TiN on electrochemically inert substrates (silicate glass,  $Al_2O_3$ ) [1, 2, 10, 11] and also very close to that of uncoated stainless steel. The vacuum arc deposited TiN coating on stainless steel is cathodic and ensures a higher corrosion resistance only in the absence of pores. The studied stainless steel coated with TiN can be used under atmospheric conditions. The TiN coating conserves its decorative properties under normal atmospheric conditions, but does not enhance the corrosion resistance of stainless steel. If the environment contains sulphur, a multilayer coating must be used with additional intermediate layers (Ti, Ni) preventing the contact to the substrate [12].

By Wierzhon et al. [13] TiN coatings were deposited on 1H18N10T stainless steel (very similar to that studied in the present work) with the aid of glow discharge. The corrosion current  $i_a$  in our experiments is about 5 times lower than that obtained in [13] in 0.5 m NaCl neutral aqueous solution. In [2] TiN coatings were deposited on tool steel with the aid of the plasma assisted chemical vapour deposition process (PACVD). The corrosion current  $i_a$  in our experiments is more than one order of magnitude lower than that obtained in [13] in acidic solution ( $H_3PO_4$ ). In [2] TiN coatings were deposited on M50 bearing steel with the aid of (1) the direct current (d.c.) magnetron sputtering, (2) magnetron sputter deposition, and (3) vacuum arc deposition. The samples were tested in 1 N acidic solution ( $H_2SO_4$ ). The corrosion current  $i_a$  for coatings (1) and (2) is 4 to 5 orders of magnitude higher than in our experiments. But the corrosion curve for the vacuum arc deposited coatings is very similar to our curves for the vacuum arc deposited TiN on the stainless steel. These facts reveal that the vacuum arc deposition permits to reach a higher corrosion resistance of the TiN coating in comparison



Fig. 3 New roof for the Moscow Luzhniki Olympic Stadion



Fig. 4 The individual element (1×2 m TiN coated stainless steel strip) of the new roof for the Moscow Luzhniki Olympic Stadion.



Fig. 5 Decorative grating for the reconstructed roof of the Great Kremlin Palace in Moscow (about 200 m long, made of laser patterned and TiN coated 1×2 m strips)



Fig. 6 Decorative grating for the reconstructed roof of the Great Kremlin Palace in Moscow. The individual elements (laser patterned and TiN coated 1×2 m stainless steelstrips) are visible

with other methods like PACVD, glow discharge deposition, d.c. magnetron sputtering or magnetron sputter deposition. Rudenja et al. studied the so-called duplex coatings [14, 15]. The 5  $\mu\text{m}$  thick TiN coatings were vacuum arc deposited onto AISI 304 stainless steel in the Bulat-6 vacuum arc installation after plasma pre-nitriding of the substrate. The comparison with data obtained by us shows that the corrosion resistance of the vacuum arc deposited TiN coatings (without pre-nitriding) is very similar to that obtained in the Bulat-6 set-up. Moreover, the next-generation vacuum arc machine used in this work ensures not only the coating of large-area substrates, but allows to reach a similar corrosion protection by 5-10 times thinner TiN layers. Nevertheless, the corrosion resistance of the so-called duplex coatings which consist of TiN deposited onto the pre-nitrided steel substrates is always much higher in comparison with simple coatings [16–18]. The set-up used for the deposition includes also the Hall current accelerator which is used normally for the ionic cleaning. The same accelerator can be used for the low-energy (below 10 keV) high-current (about 1 mAcm<sup>-2</sup>) nitrogen implantation and, therefore, the deposition of TiN coatings on pre-nitrided substrates is possible. The properties of the duplex coatings produced with the Hall current accelerator and vacuum arc deposition will be studied in the future.

Therefore, the developed vacuum arc deposition technology for the coating of large-area substrates is reliable for the indoor and outdoor architectural applications. 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 with the aid of vacuum arc machine described in this work 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<sup>2</sup>, 1×2 m coated strips are used, see Figs. 3 and 4) 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 1×2 m strips, see Figs. 5 and 6).

### *TiO<sub>2</sub> coatings*

The corrosion of TiN coatings and TiO<sub>2</sub> layers are tightly interconnected. According to the thermodynamic E–pH diagram of TiN derived by Gorbachev [19], TiN is always separated from the aqueous solution by a passive TiO<sub>2</sub>·H<sub>2</sub>O film during anodic polarization. A different definition of the high stability of TiN up to 1.25 V vs. SHE in aqueous solution has been given by Heide and Schultze [20]. The high stability of nitridic layers was caused by anionic surfaces which shield the underlying titanium atoms from oxidation [21]. The Mott–Schottky plots obtained in [15] provide an indirect evidence of oxide film formation on the TiN surface. The observed donor density [15] is rather high compared with a typical value for passive or anodic TiO<sub>2</sub> films formed on titanium [22–25]. This high value of donor density implies a high concentration of oxygen vacancies or metal interstitials in the oxide film formed on TiN. This feature of the passive film on TiN facilitates ion transfer through the oxide film which may lead to further oxidation of TiN.

The results of both chemical and metallographical measurements of the porosity of blue interferentially coloured TiO<sub>2</sub> coatings practically coincide. On all samples about 5 to 10 active pores on 100 cm<sup>2</sup> are present. The results of AFM examination (Fig. 7) show the place where the big droplet Ti delaminated from the TiO<sub>2</sub> coating. The number of such big droplets is rather low and corresponds to the number of active pores in the coating. The TiO<sub>2</sub> film under a delaminated droplet is thinner, forming, therefore, a weak place in the coating for easy corrosion. The results of the accelerated corrosion tests show that in solution 2 (30 g NaCl + 10 g Na<sub>2</sub>S + 30 g NH<sub>4</sub>Cl + 1 ml H<sub>2</sub>SO<sub>4</sub> at pH = 2.4) the first signs of corrosion appeared after 5 months from the start of the tests. In the first 5 months no visible changes in the appearance of the coating were observed. After 140 days the brilliance of the coating started to decrease non-uniformly. After 160 days the first centre of corrosion damage appeared at the big pore close to the edge of the sample. During the next 20 days of the accelerated test this corroded area increased up to 0.36 cm<sup>2</sup>. Therefore, the corrosion protective properties of the vacuum arc deposited blue coloured coatings tested in solution 2 are much higher than those of TiN coatings.

The data of the electrochemical tests for TiO<sub>2</sub> coated and uncoated samples in solution 3 (NaCl) at pH = 6 are shown in Fig. 8. The corrosion behaviour of coated and uncoated samples differs a lot. The passivation ability of TiO<sub>2</sub> coated stainless steel is much higher than that of the uncoated due to the higher positive corrosion potential (+0.06 V) of coated steel in comparison with uncoated (0 V). The corrosion current density in the passive state of coated samples is 5 to 7 times lower than that of uncoated (0.11 and 0.86  $\mu\text{A}/\text{cm}^2$ , respectively).

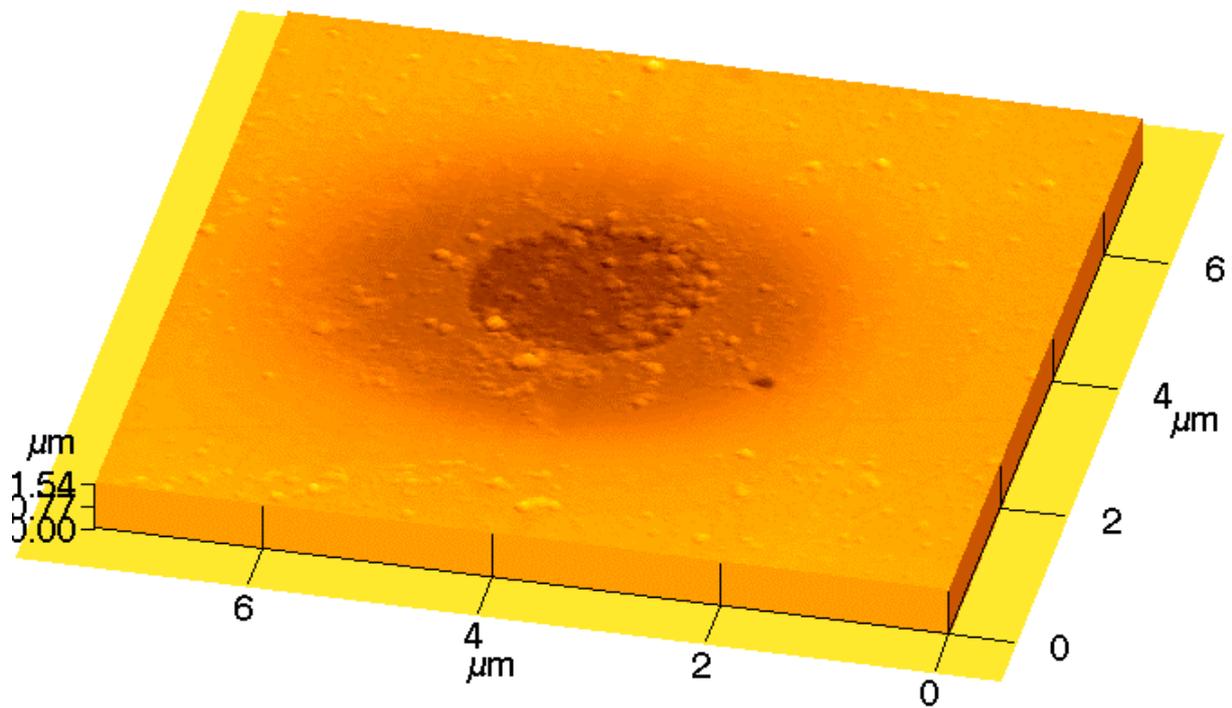


Fig. 7 AFM micrograph of the vacuum arc deposited TiO<sub>2</sub> coating. The area around the delaminated large Ti droplet is shown. Small Ti droplets are also visible

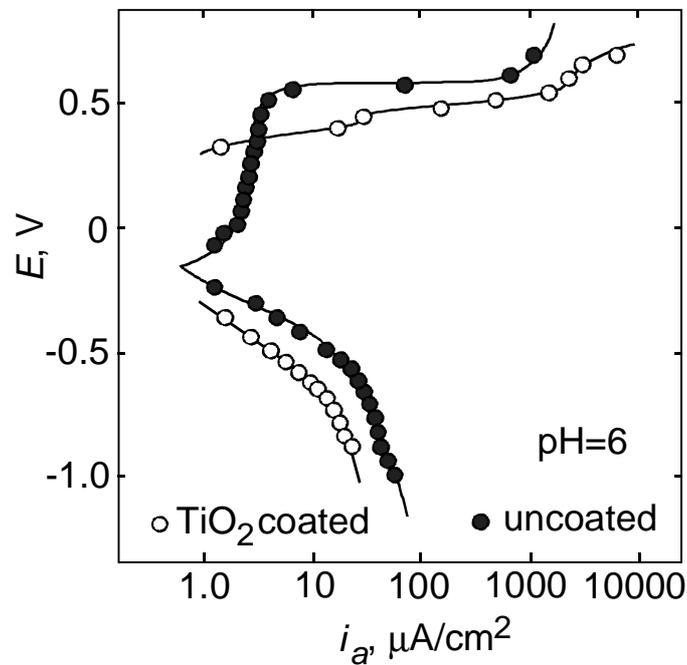


Fig. 8 The dependence of the corrosion current  $i_c$  on the polarisation voltage  $E$  for the vacuum arc deposited TiO<sub>2</sub> coatings on the stainless steel in 3.0 at.% NaCl solution is shown. Full circles denote the corrosion behaviour of the uncoated substrate

The increase of the cathodic polarization (about 100 to 150 mV) reveals also the increase of the corrosion resistance of TiO<sub>2</sub> coated substrates in comparison with intact stainless steel. The electrochemical corrosion curve for the stainless steel substrate used for the deposition of TiO<sub>2</sub> coatings is very similar to that of the stainless steel strips used for the deposition of TiN (cf. Figs. 2a and 8). In order to estimate the corrosion rate the method of the extrapolation of corrosion curves has been used. These estimations show that the corrosion rate of the uncoated steel is about 8 times higher than that of TiO<sub>2</sub> coated. However, the polarization curves show that the application of TiO<sub>2</sub> coated stainless steel in oxidative environments is undesirable because their oxidation-reduction potential is lower than the repassivation potential. Therefore, the results of corrosion tests reveal that the vacuum arc deposited TiO<sub>2</sub> coating is cathodic in contact with stainless steel and can ensure the long corrosion protection in the absence of active oxidation agents and external polarization. The corrosion damage is non-uniform and starts at the pores location. The TiO<sub>2</sub> coated stainless steel can be used, therefore, for the outdoor applications in the normal atmospheric conditions.

The big demand of the coloured stainless steel has driven the development of various technologies of coloration. The characteristics required for a coloured film are uniform interference colour, adherence and high corrosion resistance. Chemical colouring processes have been developed to produce a uniform and bright coloured film on stainless steel by the use of a hot solution containing chromic and sulphuric acids [26–29]. The transmission electron microscopy of stripped films showed that the film was rather porous. The porous coloured film could be furthermore improved by an electrolytic hardening treatment. The so-called INCO technique method was developed [28] which includes two steps, i.e. "chemical colouring" and "electrolytic hardening", which are carried out separately with individual solution compositions, temperatures and treatment conditions. However, a colour change inevitably accompanies the hardening treatment because the coloured film is continuously thickened. Recently, Sone et al. [30, 31] and Ogura et al. [32, 33] developed electrochemical colouring processes by using the alternating current (a.c.) and alternating potential pulse techniques, respectively. The a.c. electrolysis process simultaneously modulates colouring and then hardens the deposited film by a single solution-single step. In [34] the corrosion behaviour of coloured films on stainless steel formed by chemical, INCO and a.c. processes was investigated in HCl solution. It was shown that the corrosion resistance of coloured films deposited by INCO and a.c. processes is higher than that of chemically deposited films. If we compare the properties of vacuum arc deposited TiO<sub>2</sub> films tested in neutral NaCl solution (Fig. 8) with those of Cr-based golden coloured films tested in 1 M HCl solution [34]. We could see that the corrosion resistance of TiO<sub>2</sub> coatings is similar to that of films deposited by the a.c. process and also higher than that of chemically deposited Cr-based coloured films.

## CONCLUSIONS

A commercially reliable method for the vacuum arc deposition of coloured films on large-area strips of stainless steel was developed. The corrosion resistance allows to use these materials for indoor and outdoor architectural applications. The corrosion resistance of the TiO<sub>2</sub> coloured coatings is comparable with that of the Cr-based coloured coatings developed recently. The further development of this method basing on the additional low-energy high-current ionic pre-nitriding of the substrate is possible.

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## REFERENCES

- [1] Massiani Y, Medjahed A, Gravier P, Argème L, Fedrizzi L, *Thin Solid Films* **191** (1990) 305
- [2] Lunarska E, Michalsky J, *J. Mat. Sci.* **30** (1995) 4125
- [3] Uhlig HH, Revie RW, 'Corrosion and Corrosion Control', Wiley, (N. Y.) 1985
- [4] Giardini-Guidoni A, Marotta V, Teghil R, DiPalma TM, Beccaria AM, Chiaruttini L, *Surf. Coat. Technol.* **100–101** (1998) 437
- [5] Vershinin N, Straumal B, Filonov K, Dimitriou R, Gust W, Benmalek M, *Thin Solid Films* **351** (1999) 172
- [6] Milosev I, Navinsek B, *Surf. Coat. Technol.* **63** (1994) 173
- [7] Arata Y, Ohmori A, Li C-J, *Thin Solid Films* **156** (1988) 315
- [8] Celis P, Drees D, Maesen E, Roos JR, *Thin Solid Films* **224** (1993) 58
- [9] Konyashin IYu, Chukalovskaya TV, *Surf. Coat. Technol.* **88** (1996) 5
- [10] Straumal B, Vershinin N, Filonov K, Dimitriou R, Gust W, *Thin Solid Films* **351** (1999) 204
- [11] Vershinin N, Filonov K, Straumal B, Gust W, Dimitriou R, Kovalev A, Camacho J, *Surf. Coat. Techn.* **125** (1999) 228

- [12] Zabinski JS, Voevodin AA, J. Vac. Sci. Technol. A **16** (1998) 1890
- [13] Wierzhon T, Michalski J, Rudnicki J, Kulakovska B, Zyrinski N, J. Mater. Sci. **27** (1992) 771
- [14] Rudjena S, Kulu P, Talimets E, Mikli V, Straede C.A, Surf. Coat. Technol. **100/101** (1998) 247
- [15] Rudjenja S, Leygraf C, Pan J, Kulu P, Talimets E, Mikli V, Surf. Coat. Technol. **114** (1999) 129–136
- [16] Dingremont N, Bergmann E, Hans M, Collignon P, Surf. Coat. Technol. **76–77** (1995) 218
- [17] Höck K, Spies H-J, Larisch B, Leonhardt G, Buecken B, Surf. Coat. Technol. **88** (1996) 44
- [18] Dong H, Sun Y, Bell T, Surf. Coat. Technol. **90** (1997) 91
- [19] Gorbachev AK, Protect. Met. **19** (1983) 212
- [20] Heide N, Schultze JW, Nucl. Instr. Met. B **80/81** (1993) 467
- [21] Siemensmeyer B, Bade K, J.W. Schultze, Ber. Bunsenges. Phys. Chem. **95** (1991) 1461
- [22] Pan J, Leygraf C, Thierry D, Ektessabi AM, J. Biomed. Mater. Res **35** (1997) 309
- [23] Pan J, Thierry D, Leygraf C, J. Biomed. Mater. Res. **28** (1994) 113
- [24] Blackwood DJ, Peter LM, Electrochim. Acta (1989) 1505
- [25] Silva R, Barbosa MA, Rondot B, Cunha Belo M, Br. Corros. J. **25** (1990) 136
- [26] Naylor CE, Plating **37** (1950) 153
- [27] Evans TE, Hart AC, James H, Smith VA, Trans. Inst. Met. Finish. **50** (1972) 77
- [28] Evans TE, Hart AC, Skedgell AN, Trans. Inst. Met. Finish. **51** (1973) 108
- [29] Evans TE, Corros. Sci. **17** (1977) 105
- [30] Sone Y, Shimizu K, Kurahashi S, Ishii M, Hasuno S, Suznki S, Mater. Process. **1** (1988) 689
- [31] Sone Y, Wada K, Kurahashi H, Nakai Y, Narutani T, Suzuki S, US Pat. **4859287** (1989)
- [32] Ogura K, Tsujigo M, Sakurai K, Yano J, J. Electrochem. Soc. **140** (1993) 1311
- [34] Ogura K, Sakurai K, Uehara S, J. Electrochem. Soc. **141** (1994) 648
- [35] Wang JH, Duh JG, Shih HC, Surf. Coat. Technol. **78** (1996) 248