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Corrosion behaviour of the protective and decorative TiN coatings on large area steel strips

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Abstract

Decorative and protective TiN coatings were vacuum arc deposited in an industrial installation 'Nikolay' allowing coating of strips with maximum size 2100 × 1300 × 8 mm. Titanium nitride (TiN) coatings on stainless steel strips have been characterized in terms of microstructure and corrosion resistance. The vacuum arc deposited TiN coatings have a higher corrosion resistance compared with TiN coatings on steel produced by plasma assisted chemical vapour deposition, glow discharge deposition, direct current magnetron sputtering or magnetron sputter deposition. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Corrosion resistance; Titanium nitride; Vacuum arc deposition

1. Introduction

TiN coatings are widely used due to their high hardness and wear resistance. Their goldish appearance makes them very attractive for decorative purposes. One of the most reliable technologies for the production of TiN coatings, together with magnetron sputtering, is vacuum arc deposition [1]. This technology has been applied since the 1970s for the production of coated tools, medical implants, furniture pieces, etc. [2]. Recently, a reliable vacuum arc deposition technology was developed for the coating of large-area substrates [3]. This robust and inexpensive process allows the production of coated materials for building and construction which are cheap enough to compete with materials prepared in a traditional metallurgical way. Particularly, in recent years stainless steel strips and rods coated with TiN by 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, for the new roof for the Moscow Luzhniki Olympic Stadion (altogether about 2000 m^2, 1 × 2 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 1 × 2 m strips).

Recently, the technology of vacuum arc deposition of TiO_2 coatings with interference colours (red, pink, green, etc.) was also developed for large-area glass substrates [4]. The transfer of this technology to steel substrates will allow the production of materials with very attractive decorative appearance for architectural needs.

This new outdoor application is a big challenge to the area of materials science and technology, because the coated metallic parts are exposed to the aggressive atmosphere of a northern megalopolis with 10 million inhabitants and 5 million cars. For about 6 months a year they are covered by (repeatedly melting) snow. Though TiN has a very high intrinsic corrosion resistance [5,6], the combination with electrochemically less positive substrates can, in principle, lead to an increase

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of the corrosion rate in comparison with an uncoated substrate [7]. High corrosion resistance of laser ablated TiO_2 coatings on steel was reported recently [8]. The aim of this work is to present data on the properties of vacuum arc deposited decorative coatings on steel substrates, which are important for their outdoor applications.

2. Experimental

The industrial scale setup 'Nikolay' (Fig. 1) 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 = 5×10^{-4} Pa; maximum size of treated strips = 2100 × 1300 × 8 mm; output capacity for steel = 30 steel strips 2100 × 1300 × 5 mm in an 8 h cycle, 1000 m^2/month.

The standard procedure for decorative steel coating consisted of three steps. Before being loaded into the machine, the steel strip was precleaned using hot distilled water. After precleaning, the steel strips were mounted on metallic frames and placed in the vacuum chamber. Each frame held two steel strips, mounted back to back. The frame wass inserted into a slot (15 slots are available) and allowed to move independently inside the deposition chamber. The displacement velocity of the frame was monitored and could be controlled. Each frame received, in turn, a cleaning treatment followed immediately by the coating process in order to prevent recontamination. The complete treatment involved one return of the frame for cleaning and another return for coating. Cleaning was performed using a large aperture Hall current accelerator [9] providing high energetic ions which impact and sputter the substrate surface. Coating in the industrial setup was performed using four circular targets of 200 mm diameter. Three sources were placed on each side of the installation. Only two sources were normally used during the deposition. A reactive gas (oxygen) was introduced at 0.05 Pa if oxide coating was to be formed. TiN coating was obtained by introducing nitrogen at a pressure of about 0.05 Pa. Because microdroplets are ejected at small angles [10] with respect to the target surface, this configuration provided shielding and only a very small number of microparticles was present in the coating (Fig. 2). These microparticles do not disturb the optical appearance of the decorative coatings. The TiN coatings studied in this work were deposited on H18N10T (18% Cr, 9% Ni, 0.5% Ti) stainless steel without an intermediate layer.

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 corrosion behaviour of TiN coatings on the H18N10T stainless steel was characterized. The standard accelerated tests on atmospheric corrosion were carried out according to the Russian standards RST 9.303-84 and 9.302-88 over 2 months by complete immersion in solution and in the humid atmosphere above the solution (humidity 96–98%). Two different solutions were used for these tests: (1) 30 g NaCl + 30 g NH_4Cl + 1 ml HCl; and (2) 30 g NaCl + 10 g Na_2S + 30 g NH_4Cl + 1 ml H_2SO_4 for 1000 cm^3 of aqueous solution. Electrochemical tests were carried out in two aqueous solutions: (3) 30 g NaCl; and (4) 30 g NH_4Cl for 1000 cm^3 of solution. The pH value was varied from 2.0 to 8.0 The correction of the pH value of the solutions was carried out by addition of 0.05 mol

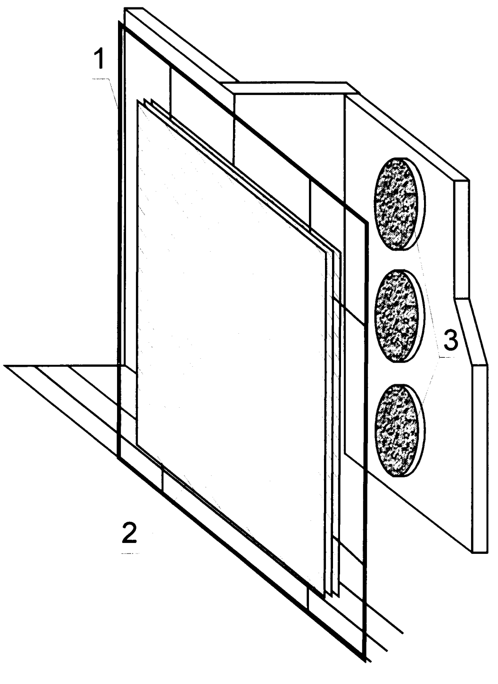

Fig. 1. Scheme of the 'Nikolai' apparatus for vacuum arc deposition on large-area substrates: (1) glass sheets mounted back to back; (2) mobile frame; (3) metallic cathodes.

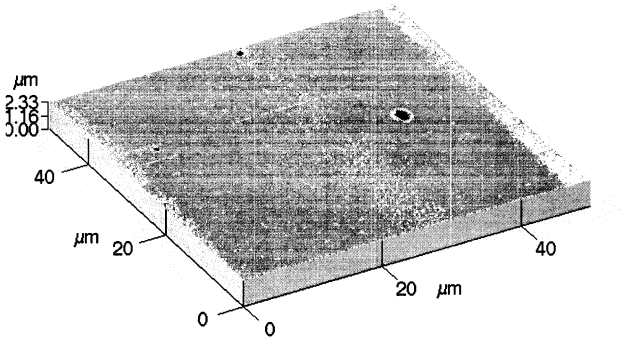

Fig. 2. AFM micrograph of a TiN coating showing Ti microparticles and point defects remaining after decohesion of the microparticles.

of HCl or NH_4OH (to the solutions containing NH_4Cl), and by addition of 0.05 mol of NaOH (to the solutions without NH_4Cl). The solution was prepared from reagent grade chemicals and distilled water. The area exposed to solution was 1 cm^2, the rest of the samples' surface was isolated by a varnish layer. The test temperature was 22–25°C. The pH value of a solution was controlled by a 'pH-121' meter. 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 on the hydrogen electrode scale). The scanning rate was 1 mVs^{-1}. The polarization was changed from -1.3 to $+0.5$ V. Before potentiodynamic measurements, the corrosion potential E_c was monitored for 0.5 h.

3. Results and discussion

During the accelerated corrosion tests a coated sample immersed into solution 2 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 after 8 days and 2 weeks: only after 2 months did the first signs of damage appear, 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. The AFM micrograph (Fig. 2) shows that such pores can exist in regions close to the Ti microdroplets.

The data from the electrochemical tests for coated and uncoated samples in solutions 3 (NaCl) and 4 (NH_4Cl) with various pH values are shown in Figs. 3 and 4, 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 NaCl solutions proceeds with the oxygen depolarisation. This follows from the form of the cathode curves at various pH values (Fig. 3). It means that the corrosion rate is controlled by the oxygen concentration in the solution and by the rate of the reaction:

$$O_2+2H_2O+4e^- \rightarrow 4\ OH^-.$$

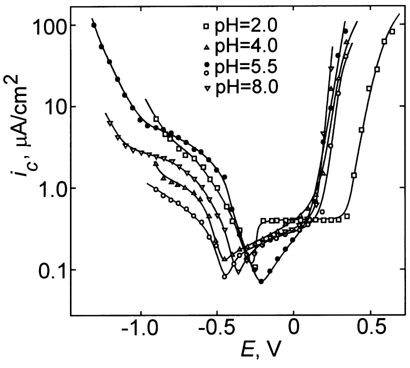

Fig. 3. The dependence of the corrosion current i_c on the polarisation voltage E in 3.0 at.% NaCl solution at various pH values for H18N10T stainless steel vacuum arc coated with a TiN layer (open symbols) and uncoated (full symbols). The lines are guides for the eye.

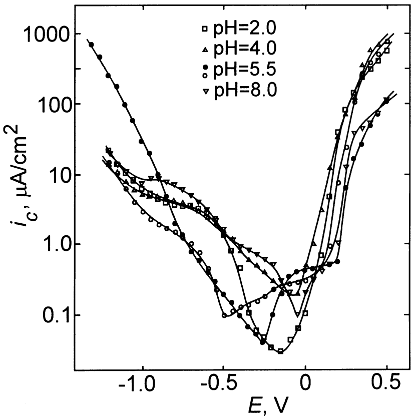

Fig. 4. The dependence of the corrosion current i_c on the polarisation voltage E in 3.0 at.% NH_4Cl solution at various pH values for H18N10T stainless steel vacuum arc coated with a TiN layer (open symbols) and uncoated (full symbols). The lines are guides for the eye.

Additionally, it is confirmed by the fact that the anodic polarization curves practically do not change by varying the pH value. Only at pH = 2 in NaCl solution does the rate of the active dissolution increase by about 1.5 times, but the repassivation potential (+0.35 V) is about 0.2 V higher than for other pH values studied. The value of the repassivation potential (+0.15 V) and the rapid increase of the anodic current are typical of 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 NH_4Cl solutions practically does not depend on the pH value. The rate of the anodic dissolution increases slightly (about 10–15%) with increasing pH, and the repassivation potential at all pH values studied is $+0.15\pm0.05$ V. The stainless steel without a coating has similar behaviour. The corrosion in NH_4Cl solutions proceeds with oxygen depolarization, similar to the NaCl solutions. It means that the oxygen solubility in NH_4Cl solution practically does not depend on the pH value. The corrosion current estimated with the aid of the Tafel equation decreases by about one order of magnitude with increasing pH (Fig. 4). 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 uniform corrosion is more likely. 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 susbtrates (silicate glass, Al_2O_3) [3–6] and also very close to that of uncoated stainless steel. The vacuum arc deposited TiN coating on stainless steel is cathodic and ensures higher corrosion resistance only in the absence of pores. The stainless steel coated with TiN studied 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 environments contain sulphur, the multilayer coating must be used with additional intermediate layers (Ti, Ni) preventing contact with the substrate [11].

T. Wierzhon et al. [12] investigated TiN coatings 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 five times lower than that obtained in [12] in 0.5 M NaCl neutral aqueous solution. In [6] 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 [6] in acidic solution (H_3PO_4). In [6] TiN coatings were deposited on M50 bearing steel with the aid of: (1) 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 four to five 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 stainless steel. These facts reveal that vacuum arc deposition allows reaching a higher corrosion resistance of the TiN coating compared to other methods such as PACVD, glow discharge deposition, d.c. magnetron sputtering or magnetron sputter deposition.

Acknowledgements

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