

CORROSION PERFORMANCE OF TITANIUM-BASED COMPOSITE COATINGS DEPOSITED BY PHYSICAL VAPOUR DEPOSITION

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Abstract. Titanium-based coatings deposited by physical vapour deposition (PVD) techniques are used routinely to improve the wear and corrosion resistance of a surface. TiN-coated stainless steel shows good corrosion resistance. Further improvement of the corrosion behaviour can be achieved by the deposition of multilayer coatings, including an intermediate layer with isolator properties or another type of conductivity. The investigated single- and multilayer coatings show high values of polarisation resistance. The coatings deposited within the Ti–N, Ti–Cr–O–N and Ti–O–N systems onto austenitic stainless steel substrates (AISI 321) significantly decrease the density of the corrosion current and move the corrosion potential of coated specimens to the passivity zone of the substrate. At the same time, there is no significant difference in the corrosion behaviour of single-layer and multilayer coatings. The factors of structure perfection predominate over those of the electron properties of the coating materials.

Key words: titanium-based coating, arc ion plating, PVD, corrosion performance, stainless steel AISI 321, single-layer coating, multilayer coating.

1. INTRODUCTION

Hard coatings deposited by physical vapour deposition (PVD) are commonly used for lifetime enhancement of cutting tools, improving the heat and wear resistance of a surface, the corrosion protection, and for other purposes. Transition metals (Me) of IV–V groups of the periodical table, when combined with nitrogen, carbon or oxygen, exhibit high melting points, excellent mechanical properties and a low coefficient of

friction. High physical properties, as defined in many papers, ensure high wear resistance and corrosion behaviour of the Me-N, Me-C and Me-O systems in different combinations.

Titanium nitride (TiN) films are widely used in manufacturing. Their excellent wear resistance in friction pairs, particularly in those of TiN-grey cast and TiN-carbon steel, is well known.

But the corrosion behaviour of TiN has not been defined clearly. Erdemir et al. [1, 2] describe dense well-deposited TiN films as layers with very good corrosion resistance. Elsner *et al.* [3, 4] studied the corrosion resistance of TiN deposited onto different substrates and found that TiN coatings can be applied successfully only on substrates that passivate easily. Forsén et al. [5] obtained the same results for a substrate of austenitic stainless steel AISI 316.

Composite coatings, both multicomponent and multilayer [4], are much more attractive for reliable protection against combined corrosion and wear attack.

1.1. Thermodynamic stability of TiN

Thermodynamic stability of TiN in water has been studied by Gorbachev [6] and Tavi [7]. The thermodynamically stable area of TiN is large (Fig. 1). All the chemical compounds on the diagram are linked to the reactions of the TiN-H₂O system. The principal oxidation-reduction reactions for the TiN-H₂O and Ti-H₂O systems (Table 1) were borrowed from [6, 8, 9]. Titanium nitride is thermodynamically stable in any acid media below -200 mV. The area of thermodynamic stability depends on the equilibrium potentials of the reactions (1) and (2). From the values of negative potentials, this area is bounded by the reaction (4).

As shown on the diagram (Fig. 1), the most significant peculiarity is the change of oxidising behaviour at pH = 1. TiN oxidises to Ti³⁺ according to Eq. (1) towards the negative values of pH, and Ti(OH)₃ according to Eq. (2) to increase the values of pH. Piippo [10] suggests that corrosion behaviour changes at pH = 2.

At the same time, the region of thermodynamical existence of Ti(OH)₃ is limited by the reaction (3). Ti(OH)₃ transforms to TiO₂ × H₂O lower than TiN does to Ti(OH)₃ by the reaction (2). The existence of Ti³⁺ ions is limited by the reaction (5), where Ti³⁺ transforms to TiO²⁺.

The equilibrium potentials of the reactions (1) and (2) are more negative than the equilibrium potentials of water with hydrogen and oxygen. Corrosion of titanium nitride in an aqueous solution is therefore thermodynamically possible both with hydrogen and oxygen depolarisation. However, the difference of equilibrium potentials of the reaction (2) and evolution of hydrogen is about 0.1 V and ionisation of oxygen about 1.2 V. As a result, oxidation reaction with oxygen depolarisation is preferable.

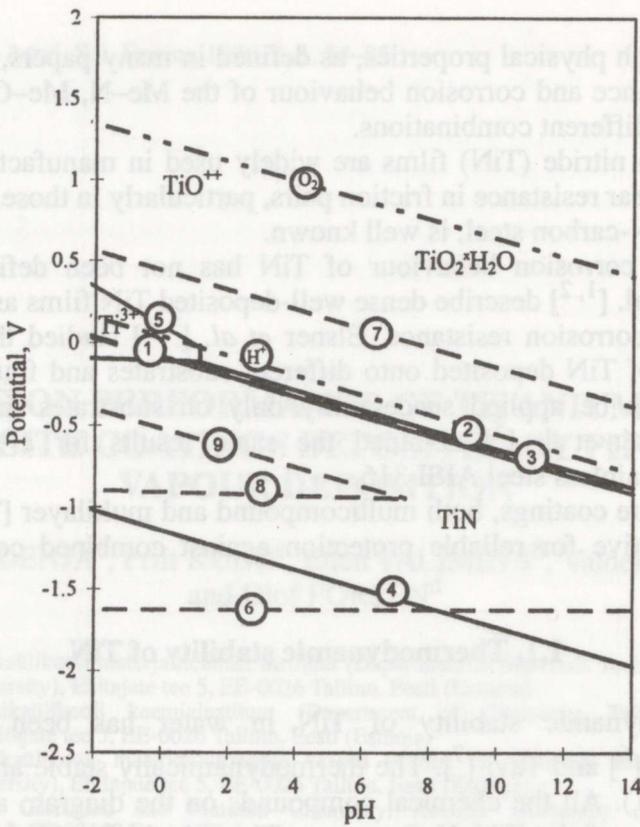


Fig. 1. E-pH diagram for TiN-H₂O and Ti-H₂O (dashed lines) systems at 25°C (hydrated form of oxides).

Table 1

Possible oxidation-reduction reactions in the TiN-H₂O system at 25°C and principal reactions in the Ti-H₂O system

Electrode reaction	Equilibrium potential (vs SHE, V)
System TiN-H ₂ O	
$\text{TiN} \rightleftharpoons \text{Ti}^{3+} + 1/2\text{N}_2 + 3\text{e}^-$	(1) $-0.14 + 0.0197 \log a_{\text{Ti}^{3+}} + 0.0098 \log P_{\text{N}_2}$
$\text{TiN} + 3\text{H}_2\text{O} \rightleftharpoons \text{Ti}(\text{OH})_3 + 3\text{H}^+ + \text{N}_2 + 3\text{e}^-$	(2) $-0.099 - 0.0591\text{pH} + 0.0098 \log P_{\text{N}_2}$
$\text{Ti}(\text{OH})_3 \rightleftharpoons \text{TiO}_2 \cdot \text{H}_2\text{O} + \text{H}^+ + \text{e}^-$	(3) $-0.092 - 0.0591\text{pH}$
$\text{TiN} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{TiH}_2 + 1/2\text{N}_2$	(4) $-1.44 - 0.0591\text{pH} + 0.0145 P_{\text{N}_2}$
$\text{Ti}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{TiO}^{2+} + 2\text{H}^+ + \text{e}^-$	(5) $0.100 - 0.1182\text{pH}$
System Ti-H ₂ O	
$\text{Ti} \rightleftharpoons \text{Ti}^{2+} + 2\text{e}^-$	(6) -1.63
$\text{TiH}_2 \rightleftharpoons \text{Ti} + 2\text{H}^+ + 2\text{e}^-$	(7) $0.44 - 0.591\text{pH}$
$\text{TiH}_2 \rightleftharpoons \text{Ti}^{3+} + \text{H}_2 + 3\text{e}^-$	(8) $-0.91 - 0.0197 \log P_{\text{H}_2}$
$2\text{TiH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ti}_2\text{O}_3 \cdot n\text{H}_2\text{O} + 10\text{H}^+ + 10\text{e}^-$	(9) $-0.52 - 0.0591\text{pH}$
$\text{Ti}_2\text{O}_3 \cdot n\text{H}_2\text{O} + \text{H}_2\text{O} = 2\text{TiO}_2 \cdot \text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^-$	(10) $-0.088 - 0.0591\text{pH}$

1.2. Thermodynamic stability of pure Ti

The diagram for pure titanium (Fig.1) and those in [6, 7, 10] are different in principle. Pure titanium reacts chemically with hydrogen above -1.63 V [9]. This influences further electrochemical behaviour of titanium. The concurrent forming-dissolution process of titanium hydride exists.

Pure titanium has good corrosion performance in acidic media. Pure titanium can dissolve above the line of reaction (6). The process of dissolution is strongly limited by the formation of passive TiH_2 hydride film. This process proceeds up to the reaction (7). As shown in Fig. 1, the hydride film TiH_2 saves thermodynamical stability practically in the whole field between the reactions (6) and (7). A single domain of the anodic dissolution of TiH_2 resides between the reactions (8) and (9). This domain is a region of "active state of titanium", but even in this area, the metal has no contact with the solution. Titanium and solution have always been separated by a hydride film. Sukhotin [9, 11] presumes that the ratio of TiH_2 formation by the reaction (7) has never been less than the dissociation ratio by the reaction (6). In this region, TiH_2 coating by the passive $\text{Ti}_2\text{O}_3 \times n\text{H}_2\text{O}$ film starts. However, it achieves a full thermodynamical stability above the region of the reaction (9) and transforms to $\text{TiO}_2 \times \text{H}_2\text{O}$ according to the reaction (10).

1.3. Multilayer coatings for corrosion protection

The coatings of transition metal compounds, as a rule, demonstrate semiconductive electrical properties with different types of conductivity. However, a small group has the properties of isolators. Multilayer coatings with intermediate layers of different types of conductivity can be used to reduce diffusion of such carriers as electrons and protons.

2. EXPERIMENTAL DETAILS

Titanium-based coatings were deposited by the arc ion plating technique [12]. The coatings used were both single-layer and multilayer films within the Ti-N, Ti-Cr-O-N and Ti-O-N systems. Austenitic stainless steel plates AISI 321, preliminarily polished, were used as the substrate material, with roughness of $1 \mu\text{m}$. All substrates were sputter cleaned before deposition. The substrate for the so-called TiN Cr-beam etched coating was treated by low-energy chromium-ion beam before deposition.

The deposition system consisted of an arc evaporator with crossed electrical and magnetic fields, a focusing magnetic field, a chamber, a substrate connected with a negative bias unit, and a system of reactive gas underflooding.

The arc current was $I_a = 80$ A, negative bias at the substrate $U_{\text{sub}} = 300$ V, substrate current $I_{\text{sub}} = 1$ A, reactive gas pressure $- 4 \times 10^{-3}$ torr

and temperature of deposition – 300°C. Technically pure titanium (Ti content 99.8%) and chromium (Cr content 99.99%) were used as cathode materials.

Table 2

Thickness of coatings, μm

Coating			
TiN	Ti–O–N composite	Ti–Cr–O–N composite	Ti–N alloyed Si
Single-layer	3-layers, TiN + TiO ₂ + TiN	5-layers, TiN + (Ti,Cr)O + Cr ₂ O ₃ + (Ti,Cr)O + TiN	Single-layer
2.0	3.0	3.0	3.0

Electrochemical measurements were made with a computer-controlled measurement system developed at the Helsinki University of Technology [13]. The system incorporates an Olivetti M28 microcomputer and digital measurement units, an NF2000 potentiostat and a NF5050 frequency response analyzer. First, the corrosion potential E_{corr} was measured, then the polarisation resistance R_p was obtained by linear polarisation. Impedance spectra were measured at the corrosion potential, using logarithmic sweep at a frequency range of 0.6 mHz to 100 kHz. The amplitude of the excitation voltage signal was 10 mV with five measuring points per decade. Finally, the anodic polarisation measurements were made.

Before electrochemical measurement, provisions were made for the samples to reach an equilibrium potential. Stainless steel specimens reached this potential after 30 min and the coated ones in 120–180 min. The potential varied less than ± 2 mV in 5 min. Polarisation resistance was determined in the potential domain $E_{corr} \pm 10$ mV, using alternating anodic and cathodic polarisation.

Tests were carried out using a three-electrode cell, which contained a diluted aqueous solution of sulphuric acid with hydrochloric acid. The solutions of concentration 0.1 M H₂SO₄ + 0.05 M HCl and 0.5 M H₂SO₄ + 0.5 M HCl were used at 298 K. All potentials were measured with respect to a saturated calomel electrode (SCE), whereas a platinum plate was applied as a counterelectrode. The potential used in potentiostatic measurements was selected on the basis of anodic potential measurements.

3. RESULTS

3.1. Polarisation resistance

The polarisation resistance R_p obtained by linear polarisation is illustrated in Fig. 2 (Table 3).

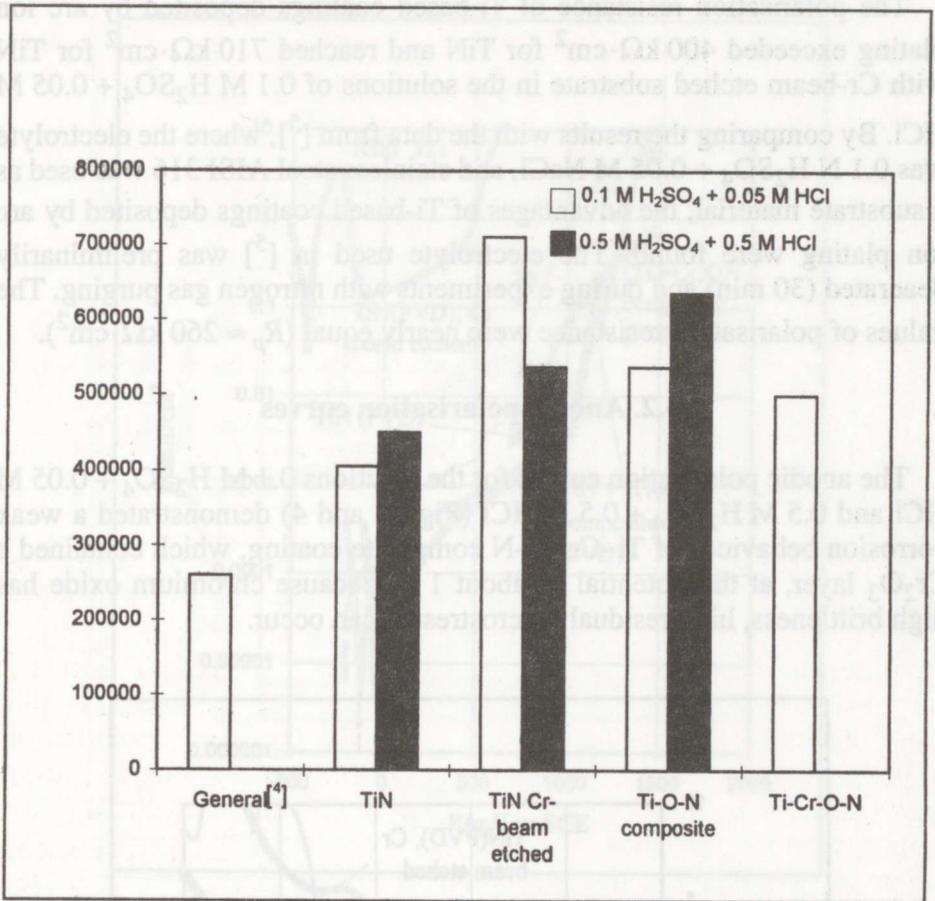


Fig. 2. Polarisation resistance of different types of coatings in the solutions 0.1 M H₂SO₄ + 0.05 M HCl and 0.5 M H₂SO₄ + 0.5 M HCl.

Table 3

Polarisation resistance of titanium-based coatings for two solutions, kΩ·cm²

Coating, type				
Ti-O-N composite	AISI 321	TiN	TiN Cr-beam etched	Ti-Cr-O-N composite
0.1 M H ₂ SO ₄ + 0.05 M HCl				
537	559 × 10 ⁻³	405	711	500
0.5 M H ₂ SO ₄ + 0.5 M HCl				
636	82 × 10 ⁻³	450	537	-

The polarisation resistance of Ti-based coatings deposited by arc ion plating exceeded $400 \text{ k}\Omega \cdot \text{cm}^2$ for TiN and reached $710 \text{ k}\Omega \cdot \text{cm}^2$ for TiN with Cr-beam etched substrate in the solutions of $0.1 \text{ M H}_2\text{SO}_4 + 0.05 \text{ M HCl}$. By comparing the results with the data from [5], where the electrolyte was $0.1 \text{ N H}_2\text{SO}_4 + 0.05 \text{ M NaCl}$, and stainless steel AISI 316 was used as a substrate material, the advantages of Ti-based coatings deposited by arc ion plating were found. The electrolyte used in [5] was preliminarily deaerated (30 min) and during experiments with nitrogen gas purging. The values of polarisation resistance were nearly equal ($R_p \approx 260 \text{ k}\Omega \cdot \text{cm}^2$).

3.2. Anodic polarisation curves

The anodic polarisation curves for the solutions $0.1 \text{ M H}_2\text{SO}_4 + 0.05 \text{ M HCl}$ and $0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M HCl}$ (Figs. 3 and 4) demonstrated a weak corrosion behaviour of Ti–Cr–O–N composite coating, which contained a Cr_2O_3 layer, at the potential of about 1 V. Because chromium oxide has high brittleness, high residual macrostresses can occur.

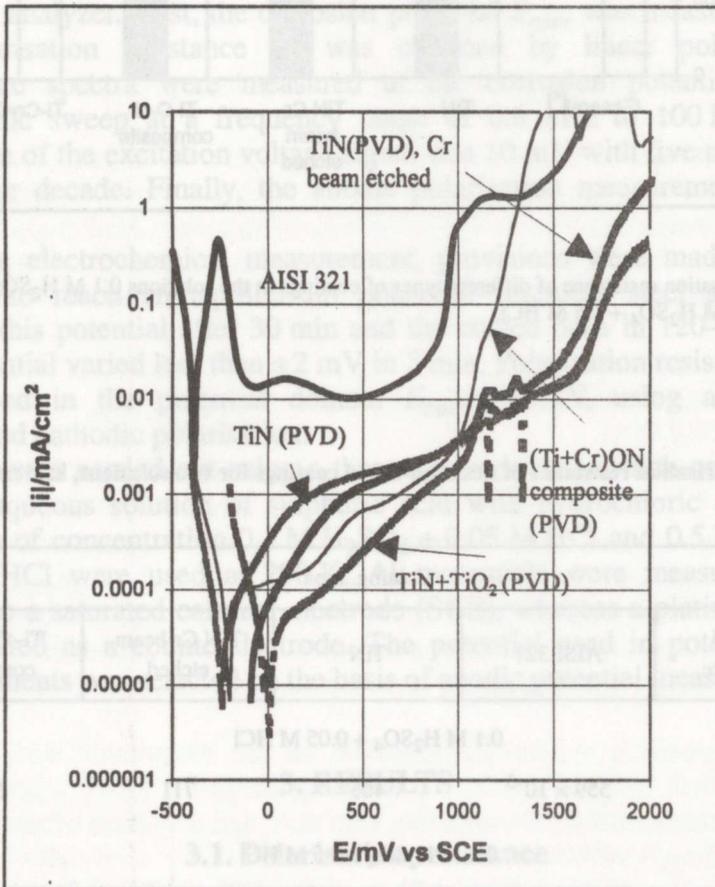


Fig. 3. Anodic polarisation curves for AISI 321 in the solution $0.1 \text{ M H}_2\text{SO}_4 + 0.05 \text{ M HCl}$.

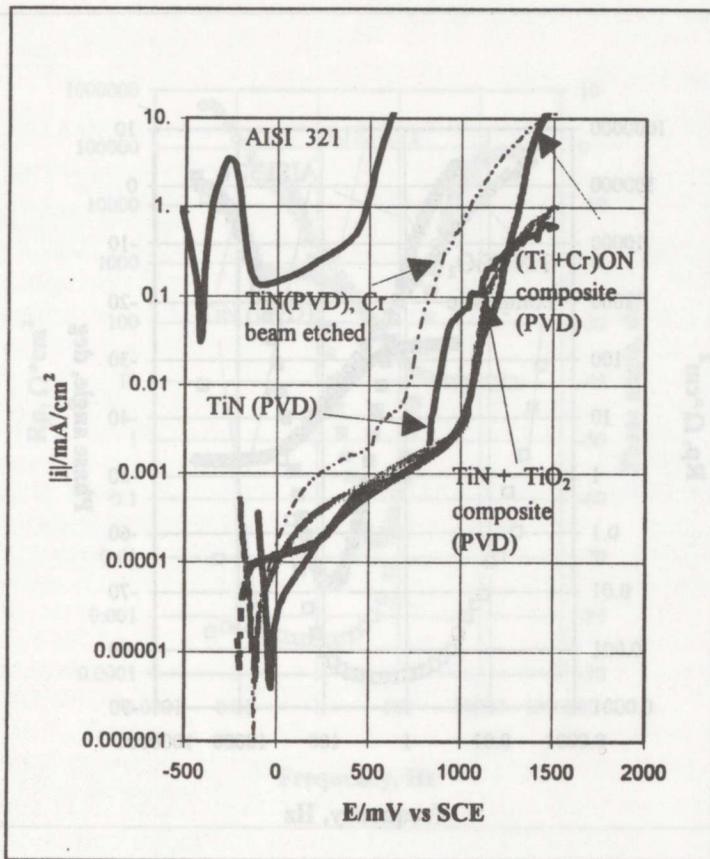


Fig. 4. Anodic polarisation curves, stainless steel AISI 321 in the 0.5 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M HCl}$ solution.

All the other coatings have good corrosion behaviour. Thus they move corrosion potential of coated specimens to the zone of substrate passivity and decrease the density of corrosion current for one decade (for 0.1 M $\text{H}_2\text{SO}_4 + 0.05 \text{ M HCl}$) and for two or three decades (for 0.5 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M HCl}$) in logarithmic coordinates. No significant differences were found in the corrosion behaviour of the TiN, Ti-O-N coating system and the TiN Cr-beam etched system.

The coatings had a wide range of passivity up to 1.2 V for the 0.1 M $\text{H}_2\text{SO}_4 + 0.05 \text{ M HCl}$ solution and up to 1 V for 0.5 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M HCl}$, then the corrosion current density started to rise.

3.3. Impedance measurement

The impedance spectra (Figs. 5 and 6) show that the polarisation resistance does not reach a maximum value. At frequencies less than 1 MHz, points of spectra start to disperse noticeably, and the value of polarisation resistance drops. The reduction of the corrosion rate at the corrosion potential of coatings is clearly defined.

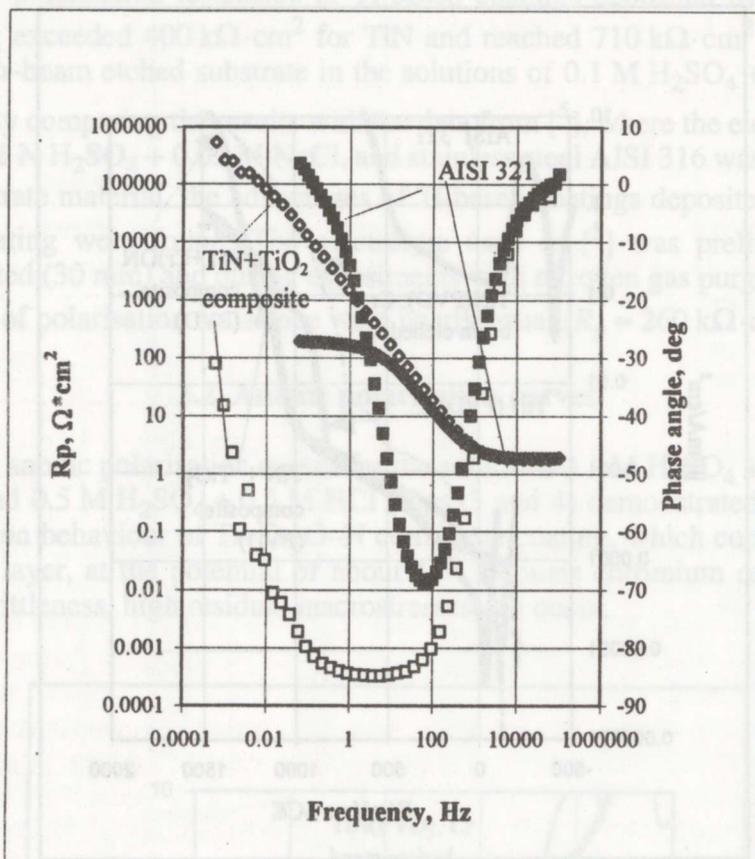


Fig. 5. Electrochemical impedance for stainless steel AISI 321-coated TiN + TiO₂ composite in the 0.5 M H₂SO₄ + 0.5 M HCl solution.

4. DISCUSSION

A simple single-layer coating, such as TiN *in situ*, is a composite. It has a pure titanium underlayer, which was indented to the coating to improve adhesion and enhance service lifetime.

Wiiala et al. [14] showed that deposition of an intermediate metal layer between the substrate and the coating improves corrosion resistance.

The values of polarisation resistance by the investigated coatings (Fig. 2) imply that these coatings have no pores to facilitate direct penetration of acidic solution to the substrate. The process of diffusion continues to the substrate on the level of electrons and protons.

As shown in Fig. 1, the pure titanium reacts actively with hydrogen. Between the reactions (7) and (8), the surface of titanium is coated by a dense hydride film. Hydrogen ions well penetrating from the solution to the titanium form the titanium hydride. The structure of the titanium underlayer has less microdefects because of lower residual stresses and more favourable deposition conditions.

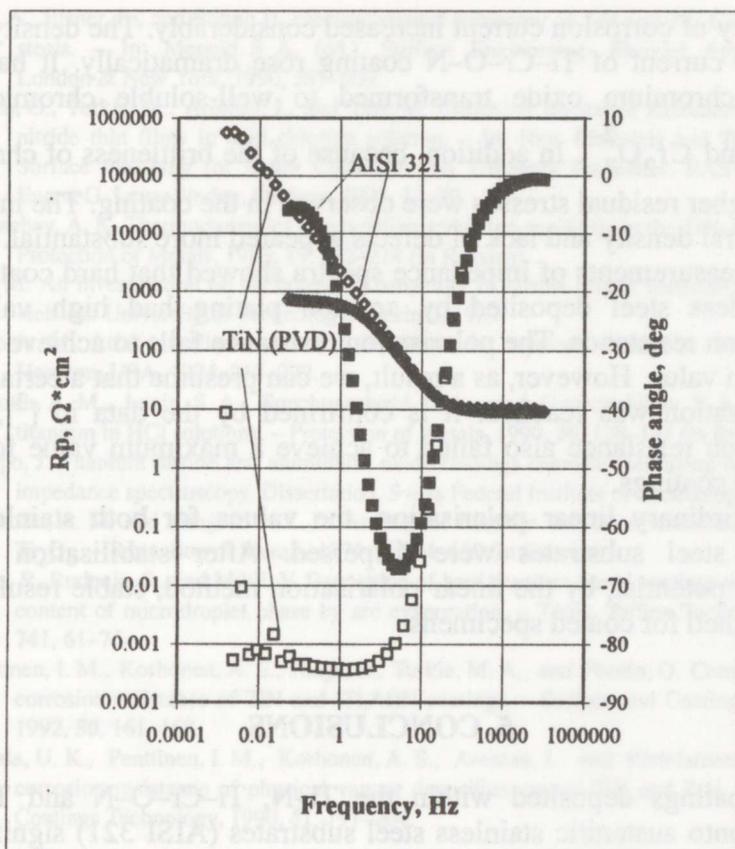


Fig. 6. Electrochemical impedance for stainless steel AISI 321-coated TiN in the 0.1 M H_2SO_4 + 0.05 M HCl solution.

Further diffusion of protons to the substrate is limited, i.e., the intermediate layer (underlayer) from pure titanium minimises the possibility of substrate corrosion by hydrogen depolarisation.

The Ti-N, TiN Cr-beam etched and Ti-O-N coatings substantially improve the corrosion behaviour of the substrate. They show high values of polarisation resistance (Fig. 2) and move corrosion potential of the coated specimens to the passivity region of the substrate. At the same time, a high value of polarisation resistance does not ensure better corrosion resistance. All the anodic polarisation curves show similar corrosion behaviour of the coated specimens (Figs. 3 and 4). The corrosion behaviour of the multilayer and single-layer coatings does not differ in principle. It means that both single- and multilayer coatings protect the substrate by the same corrosion mechanism of cathodic protection. The factors of structure perfection predominate over those of the electron properties of the coating materials. Therefore an additional intermediate layer of TiO_2 or Cr_2O_3 does not improve the corrosion performance of the coated substrate.

At the values of corrosion potential 1.2 V in the solution 0.1 M H_2SO_4 + 0.05 M HCl and 1 V in the solution 0.5 M H_2SO_4 + 0.5 M HCl

the density of corrosion current increased considerably. The density of the corrosion current of Ti–Cr–O–N coating rose dramatically. It happened because chromium oxide transformed to well-soluble chromic acids CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. In addition, because of the brittleness of chromium oxide, higher residual stresses were observed in the coating. The influence of structural density and lack of defects appeared more substantial.

The measurements of impedance spectra showed that hard coatings on the stainless steel deposited by arc ion plating had high values of polarisation resistance. The polarisation resistance fails to achieve a given maximum value. However, as a result, we can presume that a certain level of polarisation was reached. It is confirmed by the data in [3], where polarisation resistance also failed to achieve a maximum value for PVD and CVD coatings.

With ordinary linear polarisation, the values for both stainless and ordinary steel substrates were dispersed. After stabilisation of the corrosion potential, by the linear polarisation method, stable results were also obtained for coated specimens.

5. CONCLUSIONS

1. The coatings deposited within the Ti–N, Ti–Cr–O–N and Ti–O–N systems onto austenitic stainless steel substrates (AISI 321) significantly decrease the density of the corrosion current and move corrosion potential of coated specimens to the passive zone of the substrate.
2. The corrosion behaviour of single-layer and multilayer coatings does not differ in principle.
3. The factors of structure perfection predominate over those of the electron properties of the coating materials.

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FÜÜSIKALISTE MEETODITEGA AURUFAASIST SADESTATUD KÕVADE TITAANI BAASIL PINNETE KORROSIONIKINDLUS

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Füüsikaliste meetoditega aurufaasist sadestatud kõvad titaani baasil pinded on leidnud kasutust mitmesuguste detailide ning tööriistade kulumis- ja korrosioonikindluse tõstmisel. Roostevabale terasele AISI 321 (12CrNiTi18 10) sadestatud TiN pinded on hea korrosioonikindlusega, mille tõstmine on võimalik mitmekihiliste pinnete loomisega, kasutades pinde põhimaterjali omadest erinevate omadustega dielektrilisi või voolu juhtivaid vahepindeid.

Ühe- ja mitmekihiliste pinnete uurimine on näidanud nende kõrget polarisatsioonitakistust. Süsteemi TiN, Ti–Cr–O–N ja Ti–O–N sadestatud pinded roostevabal austeniitaterastel vähendavad märgatavalt korrosiooni voolutihedust ja nihutavad pinnatud detaili korrosioonipotentsiaali põhimaterjali passiivsuse tsooni. Samal ajal põhimõttelist vahet ühe- ja mitmekihiliste pinnete korrosioonis ei täheldatud. Pindmaterjali struktuuri täiuslikkus on olulisem kui selle elektroonsed omadused.