Testing effectiveness of coatings based on TiO_2 nanoparticles for corrosion protection of stainless steel

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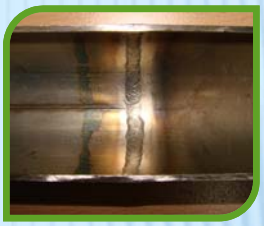
In corrosive atmospheric environments containing chlorides, widely utilized AISI 304 stainless steel does not exert sufficient resistance towards corrosion. On existing stainless steel structures, where replacement of constructional elements with those built of more resistant stainless steels is impossible or economically unviable, the surface of steel may additionally be protected by coatings. This study focuses on applicability of water-based coatings containing TiO2 nanoparticles for corrosion protection of AISI 304 stainless steel.

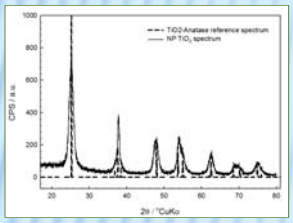
To produce titanium dioxide (TiO2) nanoparticle coatings, it is desirable that nanoparticles are dispersed into a liquid base so that the dispersion remains stable for a certain period of time. Controlling the dispersion and aggregation of the nanoparticles is crucial to exploiting the advantages of their nanometer-sized. For that purpose, the investigated coating formulations usually contain various organic and/or inorganic compounds in order to prevent the tendency of agglomeration of nanoparticles in aqueous medium.

In the present work, besides pure TiO2 dispersions in redistilled water or nitric acid of pH 2, dispersions containing sodium nitrate and a commercial dispersant were also tested. Dispersions were applied to samples by the technique of aerial spraying under pressure or by drop application to the surface. The measurements of: corrosion potential, cyclic polarization and electrochemical impedance spectroscopy were done in order to determine which of the dispersion formulations and methods of application provide a nanostructured coating with the best protective action against corrosion on AISI 304 stainless steel.

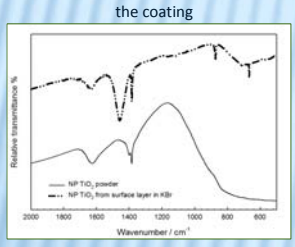
The role of photocatalytic activity of TiO2 nanoparticles in corrosion protection trough fotogenerated cathodic protection has also been investigated .



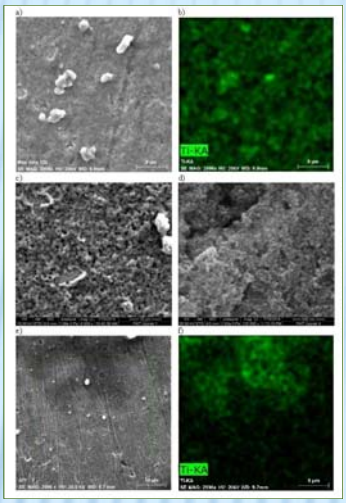
XRD analysis of TiO_2 nanoparticles used for coating preparation



FTIR analysis of the TiO_2 nanoparticles and the coating

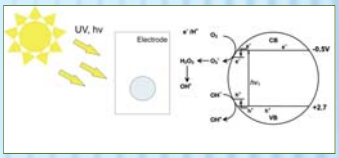


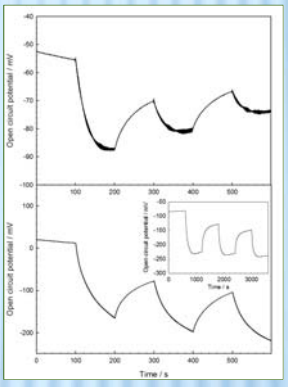
SEM-EDS analysis of the TiO_2 nanocoating applied to the electrode surface

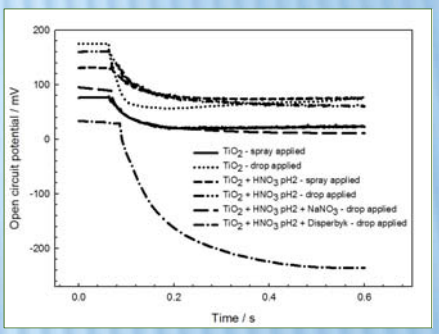


XRD analysis is showed that the tested sample of nanoparticles is composed entirely of the TiO_2 anatase phase. Testing morphology and structure of protective coatings based on TiO_2 showed that nanoparticles are firmly interconnected and form a network of porous structure on the surface of the stainless steel. The homogeneity of coverage depends on the method of application.

Photo-induced OCP variations of 304 SS electrode covered by the nanostructured TiO_2 thin film



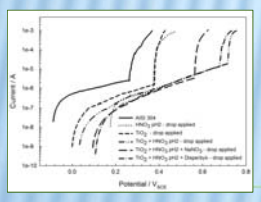


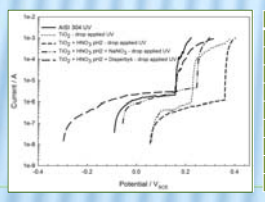


SYSTEM	E_{ocp} / mV	E_{ocpUV} / mV	ΔE / mV
TiO_2 - spray applied	76	23	53
TiO_2 - drop applied	175	77	98
$TiO_2 + HNO_3$ pH2 - spray applied	131	75	56
$TiO_2 + HNO_3$ pH2 - drop applied	160	61	99
$TiO_2 + HNO_3$ pH2 + $NaNO_3$ - drop applied	95	11	84
$TiO_2 + HNO_3$ pH2 + Disperbyk - drop applied	33	-235	268

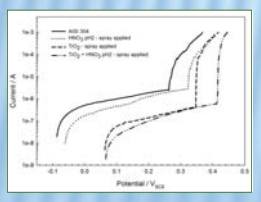
There is a sudden potential drop when the UV lamp is turned on due to the generation of photoelectrons in TiO_2 nanoparticles. Coating behaves as a n-type semiconductor because couples of photoelectrons and positive holes are generated in the coating. Photogenerated electrons are transferred to the metal thereby making its electrode potential lower than its open circuit potential and the effect photogenerated cathodic protection is achieved.

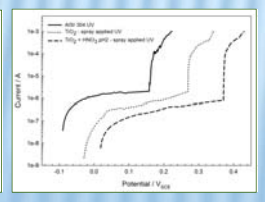
Polarization curves and electrochemical parameters for nanostructured TiO_2 coatings on 304 SS electrode in 3,5 % NaCl solution





SYSTEM	E_{ocp}/mV	E_p/mV	$E_p - E_{ocp}$/mV	I_p/μA
AISI 304	-86	257	343	0.814
HNO_3 pH2 - drop applied	176	374	198	0.541
HNO_3 pH2 - spray applied	-61	323	384	0.426
TiO_2 - drop applied	0	371	371	0.206
TiO_2 - spray applied	63	344	281	0.155
$TiO_2 + HNO_3$ pH2 - drop applied	34	718	684	0.134
$TiO_2 + HNO_3$ pH2 - spray applied	66	412	346	0.123
$TiO_2 + HNO_3$ pH2 + $NaNO_3$ - drop applied	95	556	462	0.149
$TiO_2 + HNO_3$ pH2 + Disperbyk - drop applied	107	677	570	0.196

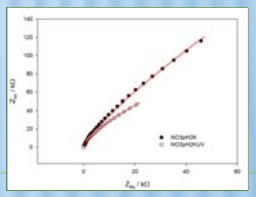


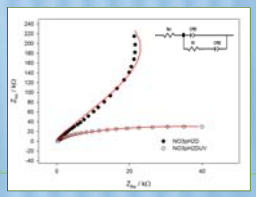


SYSTEM	E_{ocp}/mV	E_p/mV	$E_p - E_{ocp}$/mV	I_p/μA
AISI 304 UV	-90	157	247	1.784
TiO_2 - drop applied UV	63	224	161	0.841
TiO_2 - spray applied UV	-29	270	299	0.433
$TiO_2 + HNO_3$ pH2 - drop applied UV	53	360	307	0.537
$TiO_2 + HNO_3$ pH2 - spray applied UV	19	371	390	0.262
$TiO_2 + HNO_3$ pH2 + $NaNO_3$ - drop applied UV	-55	246	301	1.799
$TiO_2 + HNO_3$ pH2 + Disperbyk - drop applied UV	-296	161	457	0.791

To determine effectiveness of the protective coatings on stainless steel towards the suppression of pitting corrosion, polarization measurements were performed. More positive pitting potential potential, lower current in the passive range and widening of the passive range are indicators of better passive state and increased resistance to pitting corrosion of stainless steel.

EIS plots and electrochemical parameters of nanostructured TiO_2 coatings in 3,5 % NaCl solution at OCP





SYSTEM	Rel / Ω	CPE1 / μS s^n	n1	R1 / kΩ	CPE2 / μS s^n	n2	R2 / kΩ
NO COATING							
304	8.92	85.27	0.89	257.18	--	--	--
304UV	7.24	56.13	0.89	465.80	--	--	--
SPRAY APPLIED							
TiO_2	9.21	65.54	0.88	41.03	37.36	1.00	-712.45
TiO_2UV	8.74	180.77	0.99	23.28	65.79	0.90	-1190.30
HNO_3pH2	10.90	110.71	0.86	63.73	86.63	1.00	-2888.50
HNO_3TiO_2	10.38	57.31	0.86	74.74	46.10	1.00	-534.81
HNO_3TiO_2UV	8.935	102.30	0.89	33.37	42.78	0.96	-965.81
DROP APPLIED							
TiO_2	16.11	201.15	0.86	39.81	71.38	0.95	-1039.90
TiO_2UV	8.36	133.50	0.95	26.43	140.33	0.91	334.68
HNO_3pH2	8.96	159.86	0.91	47.62	132.98	1.00	-2574.80
HNO_3TiO_2	9.63	221.46	0.92	57.64	127.04	0.93	-1216.30
HNO_3TiO_2UV	9.29	63.83	0.95	132.63	42.89	0.87	2275.70
NO_3pH2K	9.67	66.95	0.94	42.79	17.33	0.56	∞
NO_3pH2KUV	7.82	126.80	0.94	10.85	21.74	0.40	-∞
HNO_3pH2D	8.81	45.82	0.93	318.78	18.45	0.34	-58.80
HNO_3pH2DUV	7.75	115.09	0.91	70.25	--	--	--

Electrode/electrolyte interface may be described by an equivalent electrical circuit containing a specific combination of resistances and capacitances. Greater resistance at the interface is an indicator of a better passive state. The appearance of negative impedance at low frequencies on coated samples indicates that the oxidation current decreases with increase of the polarization potential probably due to formation of the more protective oxide layer.

Goal of this study was to investigate the protective effect of nano-structure coatings of TiO_2 nanopaticles with the aim of protection of AISI 304 stainless steel against corrosion.

All the electrochemical tests have shown that the protective characteristics of the oxide layer and the resistance to pitting corrosion improve by application of coatings to the unprotected surface of stainless steel. Additionally, negative shift of the electrode potential under UV illumination light confirms the existence of photogenerated cathodic protection.