Accelerated test for the evaluation of corrosion resistance of nitrided layers

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Abstract

Research has been carried out for years to find accelerated corrosion tests which would differentiate between the corrosion resistance of particular materials in a way most similar to the natural operating conditions. The NSS test (5% NaCl, 35°C, 24h) is the most often used. In the opinion of many authors, it does not represent, however, the conditions of atmospheric corrosion.
During the research the usability of the Prohesion tests, considered by many as more similar to the natural conditions (0.05% NaCl + 0.35% $(NH_4)_2SO_4$), has been checked in two versions – cyclic and continuous. The results presented in this paper explicitly confirm the usability of the continuous test for the evaluation of the corrosion resistance of nitrided layers generated on steel 40HM.

1 Introduction

In recent years more and more scientific centres and equipment manufacturers for corrosion research, offer better and better tests to estimate the corrosion resistance of various materials. The NSS test (5% NaCl, 35°C, pH 6-7, continuous cycles) is the most widespread one, used for checking the corrosion resistance of metals and their alloys, galvanic coatings and painting coatings [1,2]. Recently, according to the demands of Qualicoat [3] the test ASS (5% NaCl, 35°C, pH3.3 regulated with acetic acid, continuous cycles) is used to check the coatings of powder paints on an aluminium bed. This test is used also to check galvanic coatings Cu-Ni-Cr. To check coatings Cu-Ni-Cr and Ni-Cr the CASS test (5% NaCl, 35°C, with addition of $CuCl_2$ and acetic acid, pH 3.3, continuous cycles) is also applied.

More frequently three-cycle tests are used: (wet – dry – wet): the AAR test (artificial acid rain) [6] and the CCT test (natural salt mist) are used [7]. The cycles are applied alternately:

(a) the first, two-hour wet cycle where 5% NaCl mist with addition of nitric acid, sulphuric acid and sodium hydroxide, pH 3.5, 35°C is used for the AAR test or 5% NaCl mist for the CCT test, followed by:

(b) two cycles: dry (60°C, 20 – 30% relative humidity RH, 4h) and wet (50°C, 95%RH, 2 h) in both tests.

The Prohesion test (0.05% NaCl + 0.35% $(NH_4)_2SO_4$, with alternate cycles: mist 25°C, 1h / dry 25°C, 1h) [8] is applied mainly to check paint coatings because this test is more similar to the natural environment. Scientific literature presents data about paint coatings and the results of tests in a natural environment. Results show that the corrosive changes which appear during the Prohesion test are closer to the results of tests found in natural conditions than the changes obtained in the NSS test [9, 10, 11, 12,13, 14, 15].

The CCT, AAR and Prohesion tests were used to check corrosion resistance of metals and their alloys, electrolytic coatings and zinc coatings hot-dip [16, 17, 18,19].

The increase in demand for the corrosion resistance of materials in various environments has required that the usability of nitrided layers depend not only on their higher hardness, their good tribological parameters and higher wear resistance but also on their corrosion resistance [20, 21, 22, 23, 24].

In paper [24] on the corrosion characteristics of nitrided layers and their modifications, the results of the evaluation of corrosion resistance in neutral salt mist (NSS test) and the value of corrosion currents obtained from polarisation curves in a 5% NaCl solution are given. The observed character of the corrosion changes (pitting) and the propagation of these changes during the tests explicitly showed (in spite of the possibility of differentiation of the corrosion resistance in particular nitrided layers in the longer period of research), that the corrosion products generated on the surface of a layer obscure the picture of those changes. It made the observation more difficult in the case of thin, porous nitrided layers which by their nature are much less resistant to corrosion. Assuming that the nitrided layers generated on steel are not under such a strong corrosion hazard as in a 5% salt mist, it was decided to check them by applying the Prohesion test. Similar tests were earlier conducted with electrolytic zinc, chromate coatings[15] and the obtained results were close to those from the testing of corrosion stations in environmental conditions.

2 Purpose of research

The verification for the usability of the Prohesion tests in two versions – continuous and interrupted – for the estimate of the corrosion resistance of nitrided layers on steel 40HM (4140), was the purpose of the research. The places of corrosion initiation and the propagation of corrosion were compared with the changes in environmental conditions.

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3 Methodology of research

3.1 Specimens for tests

The specimens for corrosion tests were made from quenched and tempered constructional steel 40HM (4140) and had the dimensions: Ø 30x10 mm. The specimens were ground to R_a=0.3 mm. The specimens were subjected to nitriding treatments which gave the thickness of generated layers between 8 –50 μm, depending on the kind of treatment.

3.2 Kinds of nitriding treatments

Kinds and parameters of treatments are shown in Table 1.

Table 1: Kinds and parameters of nitriding treatments.

No of process	Kind of treatment	Code of treatment	Parameters of treatment
1	Quenching and tempering	-------	H.840°C/0.5h/endo/oil O.590°C/2h/vacuum
2	Ion nitriding	JON-N	540°C/6h/40%N_2/60%H_2 60 l/h/3.2 mbar
3	Ion cyaniding	JON-NC	540°C/6h/40%N_2/58.5%H_2/1.5% CH_4 60 l/h/3.2mbar
4	Cyaniding and ion oxidation	JON-NCO	Wa_j 540°C/6h/40%N_2/58.5%H_2/1.5% $CH_4$60l/h/3.2mbar U_j 70°C/o.5h/90%Ar/10%air 0.7 mbar
5	Nitriding and ion oxidation	JON-NO	A_j 540°C/6h/40%N_2/60%H_2 60 l/h/3.2mbar U_j 70°C/0.5h/90%Ar/10% air 0.7mbar
6A	Ion nitriding Generation of Ti(NCO) (MOCVD)	JON-N Ti(NCO)	A_j540°C/4h/40%N_2/60%H_2 60l/h/3.2 mbar MOCVD 500°C/1h/N_2+vapours $Ti(OC_3H_7)_4$ 2ml/h $Ti(OC_3H_7)_4$/1.7 mbar
6B	Ion cyaniding Generation of Ti(NCO) (MOCVD)	JON-NC Ti(NCO)	A_j540°C/6h/40%N_2/58.5%H_2/1.5%CH_4 60l/h/3.2 mbar MOCVD 500°C/1h/N_2+vapours $Ti(OC_3H_7)_4$ 2ml/h $Ti(OC_3H_7)_4$/1.7 mbar
7	Fluidised nitriding	A_r	640°C/ 2h/ NH_3+H_2O (300l/h NH_3+0.024l/h H_2O)

Table 1: Kinds and parameters of nitriding treatments (cont).

8	Fluidised nitriding Fluidised oxidation	A_f+U_f	A_f 640°C/2h/NH_3+H_2O (300l/h NH_3 + 0.024l/h H_2O) U_f 550°C/5'/o.27l/h H_2O (bed: aloxite no 120)
9	Fluidised nitriding Fluidised oxidation Impregnation	A_f+U_f + Impr	A_f 640°C/2h/NH_3+H_2O (300l/h NH_3 + 0.024l/h H_2O) U_f 550°C/5'/o.27l/h H_2O (bed: aloxite no 120) Impr 80°C/0.5h/85%lux10+15%BS43
10	Nitrocarburizing (continuous furnace)	AW	AW. 860°C/1h/endo+6.5%NH_3/ Olej PR+2°C (5m^{3}endo + 325l/h NH_3) O.160°C/2h/air
11	Nitrocarburizing (fluosolids furnace without bed)	AW	AW. 860°C/2h/endo+22% NH_3/oil; PR+2°C (1,27m^{3}endo+283l/h NH_3)
12	Regulated gas nitriding	N_{N570}	N_N 570°C/5h/80%NH_3/20%N_2 Np.= 6.3 → 2.35
13	Regulated gas nitriding Impregnation	N_{N530}	N_N530°C/6h/40%NH_3/60%N_2 Np. =15.5→5.7 Impr 80°C/0.5h/85%lux10+15%BS43
14	Regulated gas nitriding Impregnation	N_{N570} + Impr	N_N 570°C/5h/80%NH_3/20%N_2 Np.= 6.3 → 2.35 Impr. 80°C/0.5h/85%lux10+15%BS43
15	Regulated gas nitriding Fluid oxidation Impregnation	N_{N570}+U_f +Impr	N_N570°C/5h/80%NH_3/20%N_2 Np.= 6.3→2.35 U_f 550°C/40'/4l/h H_2O/bed Impr 80°C/0.5h/85%lux10+15%BS43
16	Ion nitriding Impulse	JON-N impulse	540°C/4h/40%N_2/60%H_2/66k Hz 60 l/h/3.2 mbar

H – quenching, O – tempering, N – anitriding, U_j, U_f – ion oxidation, fluidised oxidation, A_j, A_f – ion nitriding, fluidised nitriding.

3.3 Measurements of a layers' thickness and the determination of their phase composition

The measurements of the nitrided layers' thickness and their modifications were carried out by a microscope method at a multiplication of 200x on metallographic specimens etched by Nital. A microscope manufactured by Zwick was used.

The phase composition was determined by means of an X-ray diffractometer DRON-2. The research was carried out at radiation CoK_α.

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3.4 Kinds of accelerated corrosion tests

3.4.1 Test in neutral salt mist (Test NSS)

The tests of the corrosion resistance were carried out in accordance with the Standards ISO 9227:90 and ASTM B-117 [1, 2] with the following conditions: 5% solution NaCl , pH 6.7 – 7.2, temperature 35°C, pluviometric constant 1-1.5 cm^3/h, continuous mist spray in 24 h cycles. Three specimens were used in each variant of the test. Total time of the tests in a salt chamber was 264 h.

3.4.2 Cyclic Prohesion test.

The test was carried out in accordance with [13] the following conditions: solution of 0.05% NaCl + 0.35% $(NH_4)_2 SO_4$, pH 5.0 – 5.4, in cycles:
1 h spraying of the above mist, T = 25°C,
1 h drying of specimens, T = 35°C, in a jet of compressed air in order that within 3/4 h the drops of solution were completely removed from the surface of the specimens. The cycles were repeated several times. The total time for the tests was 264 h.

3.4.3 Continuous Prohesion test

The test was carried out as a continuous (modified by the authors) version of the Prohesion test. The solution of 0.05% NaCl + 0.35% $(NH_4)_2 SO_4$, pH 5.0 – 5.4 was sprayed in continuous, 24-h cycles at temperature T = 35°C.
The total time of testing was 431 h.

4 Results of research

The results of the thickness measurements and the phase composition of the nitrided layers and their modifications, generated on steel 40HM are shown in Table 2.
The results of testing of corrosion resistance are presented as follows:
in Table 3 – for the NSS test,
in Table 4 – for the cyclic Prohesion test,
in Table 5 – for the continuous Prohesion test.

Table 2: Thickness and phase composition of nitrided layers and their modifications generated on steel 40HM.

No of process	2	3	4	5	6A	6B	7	8 (9)	12 (14)	15	16
Process	JON-N	JON-NC	JON-NCO	JON-NO	JON-N TiNCO	JON-CO TiNCO	A_f	$A_f + U_f$	N_{N570}	N_{N570} U_f	JON-N Imps
g_{mp}	12	1.5	11.5	15	14	14	45	50	16.5	17.5	10
g_{sz}	3.5	2.5	4	5	4	3.5	25	25	5	-	3
g_{zw} min	6	5	4	10	7	6	15	15	7.5	-	2.5
g_{tl}	-	-	-	-	-	-	-	-	-	4.5	-
g_{TiNCO}	-	-	-	-	2	4	-	-	-	-	-
Phase	54	23	21	53	42	40	100	100	70	54	37

g_{mp}-thickness of nitrides layer, g_{sz}- thickness of porous zone,
g_{zw}- thickness of compact zone, g_{tl}- thickness of oxides layer,
$g_{Ti(N,C,O)}$- thickness of Ti(N,C,O) layer.

Table 3: Characteristics of corrosion resistance of nitrided layers on steel 40HM; 5% neutral salt mist test NSS (continuous).

Process	Corrosive changes (%) after specified time of testing (h):										
	6	28	48	72	96	120	144	168	192	212	264
2	bz	5pk	5pk	10pk	10pk	20	20	20	20	20	20
3	bz	4pk	4pk	5pk	5pk	15	20	25	35	35	40
4	bz	bz	bz	3pk	20	40	40	60	60	60	60
5	bz	pl	pl	40	45	55	55	60	60	65	70
6A	bz	pk	pk	pk,pl	pk,pl	pk,pl	pk,pl	15	15	15	20
6B	bz	bz	pk,pl	pk,pl	pk,pl	pk,pl	pk,pl	pk,pl	pk,pl	pk,pl	pk,pl
7	pk	pl	30	45	55	60	70	80	80	80	80
8	bz	bz	bz	bz	5pk	5pk	5pk	5pk	5pk	5pk	5pk
9	bz	bz	bz	bz	bz	bz	bz	bz	bz	bz	bz
10	50	100	100	100	100	100	100	100	100	100	100
11	50	90	100	100	100	100	100	100	100	100	100
12	bz	bz	bz	bz	bz	bz	bz	bz	bz	bz	bz
13	bz	bz	bz	pk	pl	20	25	25	30	30	30
14	bz	bz	bz	bz	bz	bz	bz	bz	bz	bz	bz
15	bz	bz	bz	bz	bz	bz	bz	bz	bz	bz	bz
16	bz	25	25	35	40	40	50	50	60	60	60

bz - no changes, pk, pl - single points and spots of corrosion,
% - percent of corroded surface.

Table 4: Characteristics of corrosion resistance of nitrided layers on steel 40HM after cyclic Prohesion test.

Pro cess	Corrosive changes (%) after specified time of testing (h):										
	6	28	48	72	96	120	144	168	192	212	264
2	bz	bz	bz	30	30	40	60	70	90	100	100
3	bz	10	20	40	60	75	90	100	100	100	100
4	bz	5	5	10	40	60	80	90	100	100	100
5	bz	bz	bz	10	50	70	80	90	100	100	100
6A	bz	bz	bz	20	40	50	80	90	100	100	100
6B	bz	bz	bz	10	30	40	60	100	100	100	100
7	bz	pk	20	30	60	75	90	100	100	100	100
8	bz	bz	bz	10	30	30	30	50	60	95	100
9	bz	bz	bz	10	20	20	40	50	70	90	100
10	90	100	100	100	100	100	100	100	100	100	100
11	20	50	100	100	100	100	100	100	100	100	100
12	bz	bz	10	20	30	40	45	50	80	90	100
13	bz	bz	bz	bz	bz	bz	50	50	80	100	100
14	bz	bz	bz	bz	bz	pk	pk	40	50	60	90
15	bz	bz	bz	bz	bz	bz	bz	bz	bz	10	20
16	10	60	60	60	60	80	80	85	90	90	90

Table 5: Characteristics of corrosion resistance of nitrided layers on steel 40HM after continuous Prohesion test.

Pro cess	Corrosive changes (%) after specified time of testing (h):										
	6	28	48	72	96	120	144	168	226	315	431
2	bz	10pk	30pk	30pk	30pk	60pk	90pk	40	80	100	100
3	bz	20pk	20pk	20pk	20pk	20pk	30pk	40	50	80	80
4	bz	bz	bz	bz	bz	bz	bz	bz	20	80	80
5	bz	30	30	40	60	60	60	60	60	60	60
6A	bz	bz	40pk	40pk	50pk	50pk	50pk	60	70	90	90
6B	bz	5pk	5	5	5	10	10	10	10	10	10
7	bz	bz	1	3	5	10	20	30	30	30	40
8	bz	bz	bz	bz	bz	bz	bz	1pk	4pk	1	10
9	bz	bz	bz	bz	bz	bz	bz	bz	bz	bz	1
10	30	80	100	100	100	100	100	100	100	100	100
11	10	50	60	100	100	100	100	100	100	100	100
12	bz	bz	bz	10	20	20	20	20	30	30	30
13	bz	bz	bz	10	10	10	40	40	40	40	40
14	bz	bz	bz	bz	bz	bz	10	10	10	20	20
15	bz	bz	bz	bz	bz	bz	bz	bz	bz	4pk	4pk
16	bz	bz	bz	bz	bz	bz	20	30	60	90	90

bz – no changes, pk – single points of corrosion, % - percent of corroded surface

5 Analysis of the research results

The presented results of the research try to answer the question: In which way and in what medium should the corrosion resistance of nitrided layers be evaluated?
All the accelerated corrosion tests used do not fully represent the conditions in which products with nitrided layers are used. They permit, however, the rapid estimate of the corrosive resistance than it could be obtained under real operating conditions. The obtained results for the corrosion resistance after the NSS test (continuous), the cyclic Prohesion and the continuous Prohesion test clearly indicate the differentiation of these tests' aggressiveness to the nitrided layers.
In result of the aggressiveness of the NSS test and the cyclic Prohesion the products of corrosion generated during these tests in a significant way limited the actual observation of the corrosion progress. This fact is clearly seen on the thin layers (8 – 12 μm). During the continuous Prohesion test the changes which take place on the surface take a more mild course. The observation of the corrosion and the estimate of the sites of corrosion initiation are easier to define. The corrosive changes shown in Table 5 show the much lower aggressiveness of the continuous Prohesion test and confirm the possibility of the distinct differentiation of corrosion resistance of the nitrided layers and their modifications. This fact was confirmed by the measurements of corrosion resistance performed by the electrochemical methods [25, 26]. The obtained values of passivation currents in solution used in the Prohesion test are much lower than those obtained in the 5% NaCl solution. The polarisation curves have the same character and testify to the similar way of corrosive changes in both solutions. The quantitative analysis of the corrosive changes on the surface, based on computer analyse of the picture, also confirms this.

6 Conclusions

The research permitted us to conclude that:

a) The Prohesion test in a continuous version is more usable to differentiate the corrosion resistance of the nitrided layers than in its cyclic version (dry – wet).
b) The Prohesion test more closely represents the corrosive changes which occur on the surface of a specimen during testing in a corrosion medium,
c) The corrosive changes observed on the surface of specimens during this test are similar to the changes in the environmental conditions,
d) The dry cycle in the cyclic Prohesion test causes the rapid acceleration of the corrosion speed and an increase in the aggressiveness of the test itself in such a way that this version of the Prohesion test is much more aggressive towards the nitrided layers generated on steel 40HM than in the normalised NSS test.

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