Physico-mechanical properties of Ti-containing chromium-free conversion coatings on zinc coated steel

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This work aims at physico-mechanical properties of the Ti-containing chromium-free conversion coatings on zinc coated steel. The wear resistance of the whole conversion coating/zinc coating system depends on the deposition time of these coatings. As the duration of the deposition of conversion coatings containing titanium increases, the wear resistance of the samples decreases. The reason for this deterioration in wear resistance is likely worse adhesion of these coatings obtained at longer deposition times. The best adhesion to the zinc substrate posses coatings deposited for 20 s.

Keywords and phrases: zinc coating, corrosion resistance, conversion coating, adhesion, wear resistance.

Introduction

Conversion coatings are commonly used to protect zinc electrogalvanized steel against corrosion. Conversion coatings are obtained mainly in the chromating processes, often known colloquially as 'passivation' or 'chromating'. Chromating is carried out in baths based on compounds of Cr (III) [1–4], but still traditional baths containing harmful chromates(VI) are in use [2–4]. Despite the toxicity of chromate baths they makes it possible to obtain coatings with excellent corrosion resistance at a low operation costs. The toxicity and carcinogenicity of hexavalent chromium compounds and the increasingly stringent standards necessitate the use of more environmentally friendly technologies without the compounds of Cr(VI) or completely free of chromium. For many years in the scientific literature there are reports about the chromium-free alternative baths based on molybdates [5, 6], titanium compounds [7, 8], zirconium compounds [9] and rare earth metals [10]. But only few of them have found application in industry [11].

The paper describes the physical and mechanical properties of Ti-containing chromium-free conversion coatings on zinc coated steel, as the properties relevant to the actual conditions of usage. Therefore adhesion of the conversion coatings to the zinc substrate was tested and the wear resistance of the whole coatings system in dry friction was measured.

Experimental

Zinc electrogalvanized carbon steel discs were used as a metal substrate. Zinc electroplating was conducted in a weak acid chloride bath with brightening additions (electroplating parameters: j_k = 1.5 A dm^{-2}, T = 25°C, pH 4.6, coating thickness h = 7 μm). Ti-containing conversion coatings were deposited from the solution consisted of (mmol dm^{-3}): $TiCl_3$ — 3.9, H_2SiF_6 — 17, H_2O_2 — 53, oxalic acid — 7.9 at pH 2.5 and T = 50°C. Deposition time was set in the range from 20 to 300 s and the corresponding symbols of the samples are respectively Ti20 — Ti300. The properties of Ti samples was compared with that of the chromated samples (sample CC). Chromating process was conducted in a bath having the following composition (g dm^{-3}): $Na_2Cr_2O_7$ — 200; H_2SO_4 — 6 at T = 25 °C, t = 30 s.

The morphology of the conversion coatings was examined by means of an electron scanning microscope (TESCAN VEGA II SBH). Prior to examination, the samples were sputter-coated with a thin layer of gold.

Adhesion of the conversion coatings to the zinc substrate was measured using a CSEM Micro-Combi--Tester equipped with a Rockwell diamond C with a tip

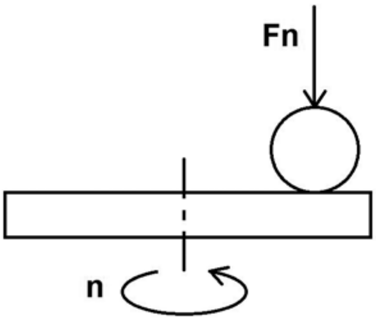

Fig. 1. Test combination for dry-friction test on a ball-on--plane tribotester.

radius of 200 μm. The scratch track length was set to 5 mm. Maximum load P_{max} was 20 N. The load was changed linearly and it ranged from 0.01 N to P_{max}. The indenter movement rate was set at 5 mm min^{-1}.

Friction tests were carried out on a ball-on-plane type tribotester in a rotational motion (Fig. 1) in accordance with ISO 20808:2004, ASTM G 99-05 using polished ϕ 6 mm ball made of Si_3N_4 under: normal load F_n = 0.5 N, rotational speed n = 60 rpm^{-1}, number of cycles N = 5000 and friction track radius R = 5 mm. Three samples of each type were tested. Results analysis was conducted in accordance with PN-EN 1071-3.

Morphology of Ti-containing conversion coatings on zinc

The SEM micrographics of the surface are shown in Fig. 2. The surface of zinc coated steel (Zn) sample is finely crystalline, but with some small granules on the surface (Fig. 2a). The conversion coating obtained after 20 s of the immersion (Ti20) is not smooth and looks like porous (Fig. 2b) and as the treatment time is extended to 5 min (Ti300) it becomes uniform, but with visible micro-cracks (Fig. 2c). The micro-cracks are probably the result of the buildup of internal stress as the layer thickness increases and the coating is dried.

Adhesion and wear resistance of the coatings and coatings system

Figure 3 depicts the tracks after 'scratch test' for Ti20 and Ti300 samples under characteristic loads L_{C1} (cohesive critical load). For Ti20 sample load L_{C1} ranged from 3.6 to 3.8 N while for Ti300 it ranged from 2.3 to 3.1 N. The fracture of the coatings on Ti20 — Ti300

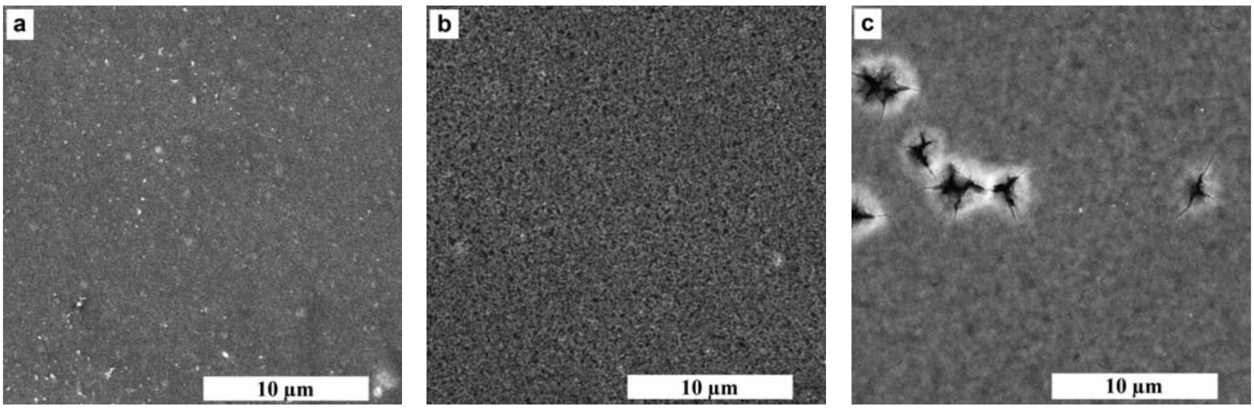

Fig. 2. Morphology of zinc coated steel (a), Ti20 (b) and Ti300 (c) sample.

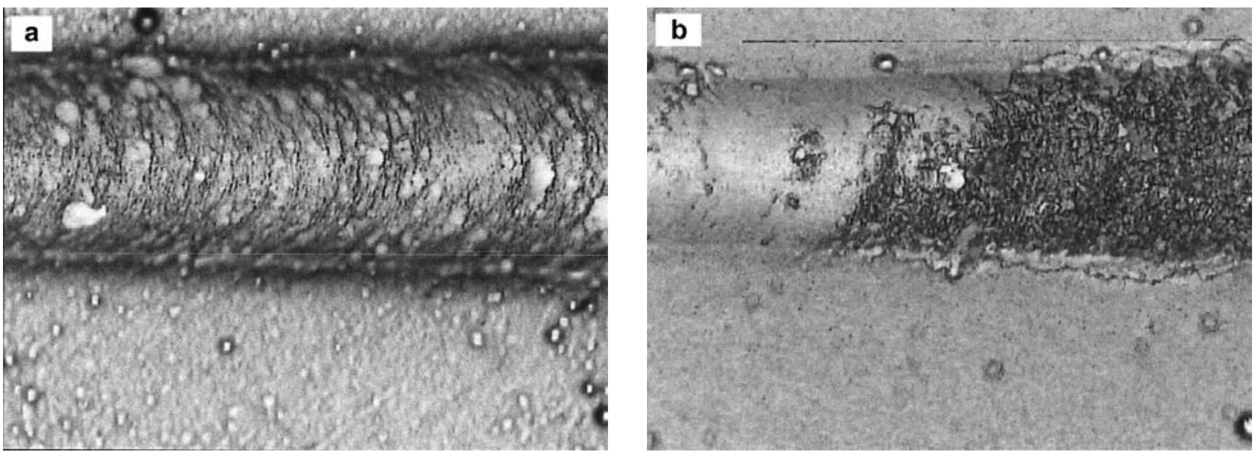

Fig. 3. Images of scratch tracks under characteristic load L_{C1} for sample Ti20 (a) and Ti300 (b) at magnification 200x.

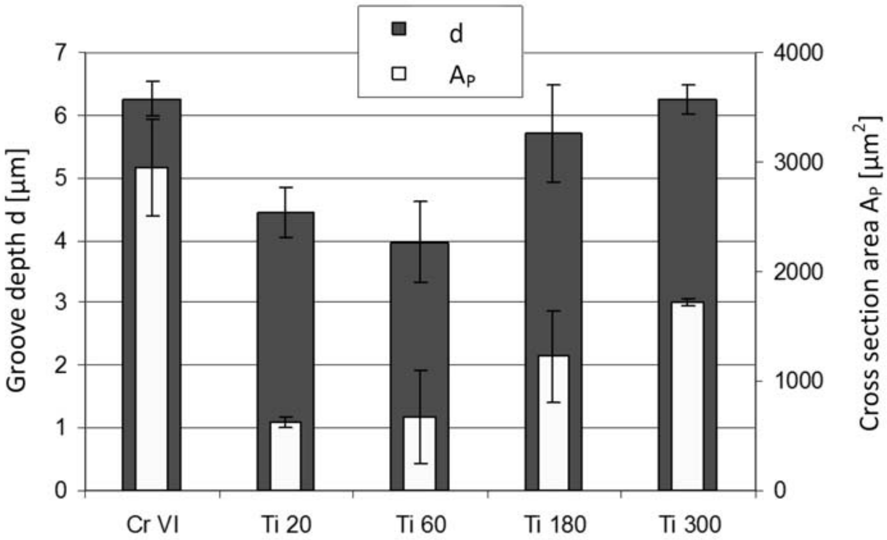

Fig. 4. The penetration depths d and cross section areas of the grooves for tested samples after dry friction with Si_3N_4 at F_n = 0.5 N; n = 60 obr min^{-1}; N = 5000 cycles, R = 5 mm.

samples was similar for all coatings. At the earlier stage, under load L_{C1} cohesive critical fracture of the coatings in front of the indenter were observed. These fractures are the results of plastic deformation of the substrate and high tensile stresses in the conversion coating (Fig. 2a). In the course of Ti300 sample the amount of fractures under L_{C1} markedly increased and the conversion coating was completely destroyed. Cracks in the scratch track was also accompanied by cracks in its sides along with small areas of coating exfoliation (Fig. 3b).

The wear resistance for each of the samples was calculated on the basis of cross-sectional profile of the groove formed after friction with the Si_3N_4 ball. Penetration depths and cross section areas of the grooves after friction are shown in Fig. 4. Based on the measured values the volumetric wear (W_V) was calculated as a quantitative measure of wear resistance of the material. Among the tested materials sample Ti20 showed the highest wear resistance. For Ti20 the volumetric wear ranged from 239,0 10^{-6} to 274,3 10^{-6} mm^3 N^{-1}m^{-1}. Compared to the chromated sample its wear resistance was more than four times higher. Also, during tribological tests for Ti180 and Ti300 samples some exfoliations were present at the edge of the ball track (Fig. 5). These defects may indicate a worse adhesion of coatings deposited at longer immersion times.

Discussion and conclusions

Geometric parameters of scratch tracks, microscopic analysis, as well as acoustic emission, appearing in the case of brittle fracture of the coatings are an interesting source of information about the nature of the fracture process of the coatings. Scratch test is a very good method to determine the adhesion of the coatings to the substrate on the basis of measured critical load L_C.

In the course of tribological tests it was observed that the outer conversion coatings affected the wear resistance of the whole conversion coating/zinc coating system. Sample Ti20 showed the highest wear resistance, i.e. over four times higher than that of sample CC. However, as deposition time increases, the wear resistance decreases.

In the course of the 'scratch tests' it was observed that the cracking of the coatings on samples Ti300 and CC was markedly more intense than for the other samples. Once the load L_{C1} was exceeded, the coatings would undergo practically total destruction (Fig. 3b). The results of the scratch tests carried out on the coatings suggest that the cause of a decrease in wear resistance is poorer adhesion. Such deterioration of adhesion is related to the cracking of coatings during friction.

Fig. 5. Image of the cracks for sample Ti180 after tribological test at magnification 200x.

Acknowledgements

This work was supported by a fellowship co-financed by the European Union within the European Social Fund and a Grant from the Ministry of Science and Higher Education of Poland (Grant N N209 022039).

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