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ISSN 0543-5846
METABK 55(4) 675-678 (2016)
UDC – UDK 669.14:666.3/7.002.4:620.193=111

CORROSION PROPERTIES OF CHROMIA BASED ECO - FRIENDLY COATINGS ON MILD STEEL

Received – Prispjelo: 2016-01-12
Accepted – Prihvaćeno: 2016-05-10
Original Scientific Paper – Izvorni znanstveni rad

Ceramic nanocrystalline coatings of chromium oxide (III) on steel S235JRH-1.0038 (EN 10025-1) were prepared using the liquid precursor plasma spraying (LPPS) method from ammonia dichromate (VI). Their structure and anti - corrosion properties were compared to the standard chromium oxide (III) coating prepared by thermal spraying. The newly prepared coatings had very high adhesion and minimal porosity. Anticorrosion properties were characterized by the means of the electrochemical impedance spectroscopy (EIS), measuring the charge transfer resistance R_{ct} and capacitance of electrical double layer CPE_{dl} in the 0,5 mol/l NaCl. Coatings of Cr_2O_3 prepared by the LPPS method showed unambiguously improved anti - corrosion properties.

Key words: ceramic, steel coating, corrosion, plasma spraying

INTRODUCTION

Spray - coating of either metals or ceramics on various substrate materials have wide range of variants. One of them is utilization of thermal plasma for deposition of substances with extremely high boiling point. This process – plasma spraying was already used to prepare thick coatings of e.g. tungsten or hafnium carbide, i.e. materials with melting point over 3500 °C [1, 2]. Another variants of thermal coating method utilizing plasma as a heat source are the Suspension plasma spraying [3 - 5] and the Liquid precursor plasma spraying (LPPS) [6, 7]. In liquid-stabilized plasma generators, for example the H - WSP® device, the temperature can go as high as 25 000 K [8] which is enough not only to evaporate the solution, but also to completely drying and subsequently melting of the substance, thus forming ultra - fine droplets of micrometer to nanometer dimension. These droplets can be deposited or condensed on a surface forming product in range of shapes, from nano - powders [9 - 12], up to continuous coating with nanocrystalline structure.

This paper describes preparation of protective anticorrosion and abrasion resistant coatings from chromium oxide on structure steel S235JRH - 1.0038 (EN 10025 - 1), with focus on enhancing the coating adhesion by increasing the compatibility of substrate - coating interface.

EXPERIMENTAL PART

Simple variant of plasma torch head was manufactured (Figure 1) utilizing high temperature of plasma generated by plasmatron WSP® [13]. Aqueous solution of ammonium dichromate (20 °C, saturated – 1,43 mol/l) was fed by dispersion nozzle (1 mm diameter) into the graphite baffle ring (200 mm length, 40 mm inner diameter) which was positioned 100 mm from the outlet nozzle of the plasma jet. As substrate, steel targets made of S235JRH - 1.0038 (EN 10025 - 1) with surface roughness R_a = 6 - 8 μm were used. Spraying distance was 300 mm. Next to the steel target, liquid nanoparticle collector was placed to study their size and morphology (Figure 2). Appearance of produced nanometer ceramic Cr_2O_3 coating is shown in Figure 3. Products were compared to Cr_2O_3 coated samples pro-

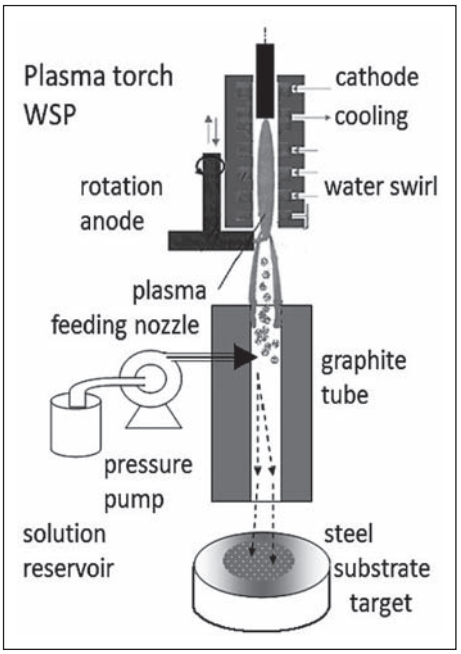

Figure 1 Scheme of plasma torch H-WSP® with graphite reactor for solution plasma spraying

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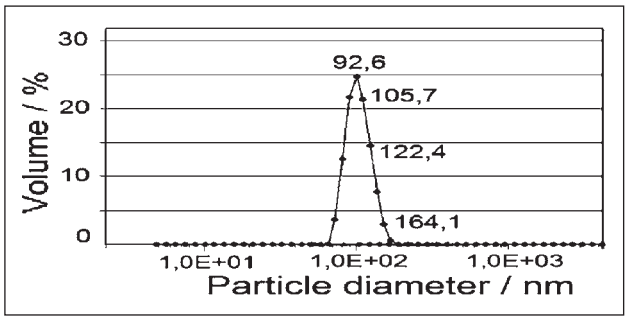

Figure 2 Size of the nanoparticles Cr_2O_3 deposited on the steel surface

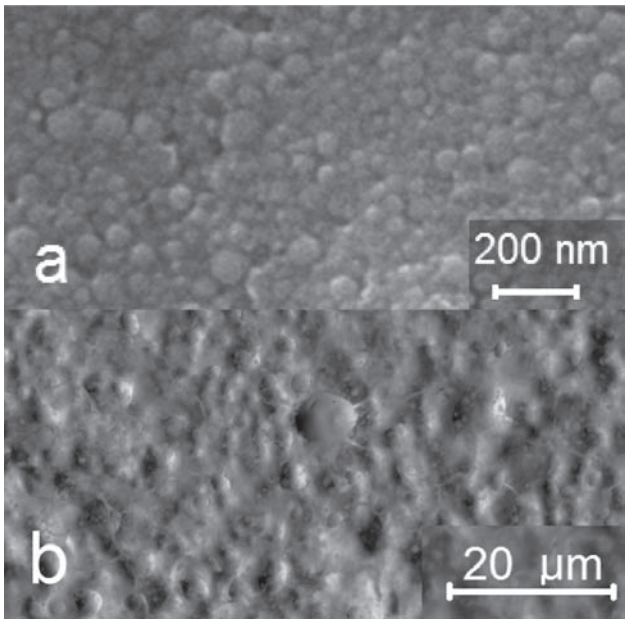

Figure 3 Morphology of the coating surface Cr_2O_3 prepared by LPPS method (a) and Cr_2O_3 as - sprayed from powder precursors (b)

duced by thermal spraying of chromium oxide powder of 30 - 63 µm grain size, according to [11]. Morphology of these coatings is depicted on Figure 3 b.

Metallographic parameters of coatings were evaluated by scanning electron microscopy. Structure and phase composition was measured via X-ray diffractometry (XRD). Temperature during deposition was monitored by thermocamera Micro - Epsilon TIM 160. Corrosion experiments (EIS) were carried out in common three - electrode setup using the Gamry FAS2 potentiostat with Gamry Framework software. Free corrosion potentials E_{corr} were measured in reference to the standard calomel electrode SCE. The temperature during experiment was 22 ± 1 °C. Parameters of impedance measurement were following: amplitude ± 10 mV/E_{corr}, frequency range 10 kHz – 10 mHz, 5 points per decade. The bonding strength was determined by the pull - off test acording to EN ISO 4624 using Loctite Hysol glue and Comtest OP 1/2 apparatus [14]. The size distribution of Cr_2O_3 nanoparticles was measured by dynamic light scattering (photon correlation spectroscopy) via the Zetasizer Nano ZS Malvern with He - Ne laser. Samples were analysed using X-ray fluorescence (XRF) on the spectrometer Panalytical AXIOS.

RESULTS AND DISCUSSION

The dichromate was decomposed by the plasma causing reduction of Cr^{VI} to Cr^{III} – coating was dark to black instead of green typical for Cr^{III} coatings. This behavior is not uncommon for chromium (III) products exposed to high temperature. Diffraction data confirm existence of hexagonal oxide Cr_2O_3 (PDF 01 – 078 - 5433) of symmetry group R - 3c (167), described by reaction:

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4\,H_2O \qquad (1)$$

The crystallinity of the product was determined based on the Scherrer's reaction; the calculated average value was 80 nm, suggesting nanometer structure of the coating. This value is in good correlation with granulometric characterization of nanoparticles measured by photon correlation spectroscopy, see Figure 2. Microscope images of the surface (Figure 3 a) confirm the values.

Properties of deposited microparticles and nanoparticles are determined by many factors, especially the concentration of precursor solution [15], the shape and size of dispersing nozzle, pressure and velocity of carrier gas and also the density and surface tension of dispersed solution. Surface tension of dichromate solution at 20 °C was measured by the stalagmometric method, the value was $\sigma_{(NH4)2Cr2O7}$ = 78,9 mN/m. Afterwards, the effect of gas pressure and velocity was determined. Changing these allows to adjust the conditions of liquid precursors to the dispersion device (Figure 1) with nozzle diameter of 1 mm and graphite deflector diameter of 50 mm. Optimal values were 2 bars and 100 ml/min, and maximum deposition rate at these settings for saturated solution (1,43 mol/l; 27 wt. %) was 1,58 kg Cr_2O_3/h.

Surface profile (Figure 4) and measured surface roughness value suggest that surface irregularities on the substrate surface are of same dimension as the coating splats. Deformed surface with lower fluidity cause formation of closed pores between coating and steel, effectively decreasing effective surface and adhesion quality.

Technological reasons given by feeder type and process of powder entering the plasma stream dictate to use

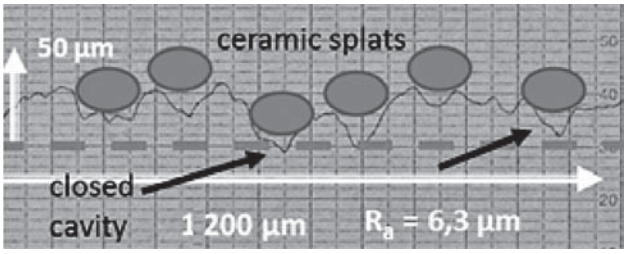

Figure 4 Scheme of liquid ceramic splats deposition on the roughened surface of the substrate

powders of narrow granulometric range for both plasma and thermal spraying. In the case of WSP® generator, the feeder TecFlow 7102 was used – optimal powder grain size for this device is 30 to 63 μm. In such case the melted grains of biggers size, high surface tension and high melting point are very likely to not fully fill finer pits before their solidification to splats, effectively reducing the adhesion. To achieve complete coverage of steel substrate surface, it is necessary to use the finest powder possible, e.g. from suspension or solution. Analysis of microscope images of steel-coating cross-section after 20 second deposition (Figure 5) showed that the coating thickness was about 2 μm even in the deepest pits. This facilitates perfect adhesion of the coating and coverage of spike - like areas which would otherwise cause formation of closed pores. These pores can act as initiation sites for corrosion under coating.

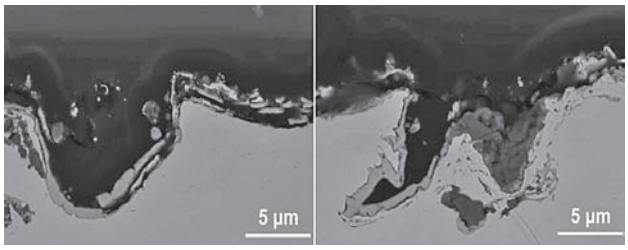

Figure 5 Cr_2O_3 coating on steel produced by thermal decomposition of ammonium chromate

Typical structure of plasma-deposited Cr_2O_3 ceramic coating from powder precursor on steel is shown in Figure 6**.**

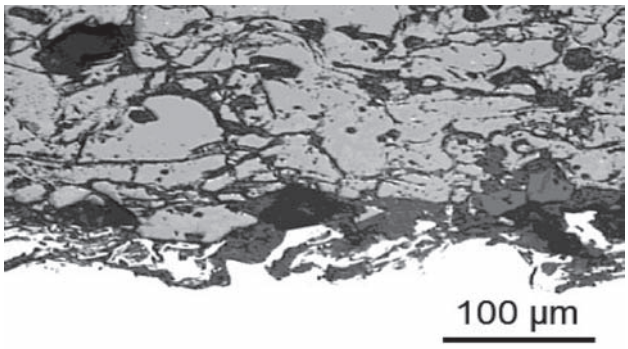

Figure 6 Cr_2O_3 coating on steel produced by thermal plasma spraying

Thermocamera recording revealed that substrate is heated only to slightly below 200 °C during plasma spraying. This is in good agreement with results from the thermogravimetric analysis (TG), the dichromate decomposition according to eq. (1) takes place at 170 °C. All toxic Cr (VI) is thusly transformed to Cr (III). Also, the residual stress on the metal - ceramic interface is conveniently minimized.

Adhesion of chromium oxide coating on steel was evaluated accordingly to EN ISO 4624. The ratio between adhesion and cohesion fracture was determined based on X-ray fluorescence surface analysis of individual elements on substrate and pull - off cylinder (area of 3,14 cm^2).

Primary layers of chromia coating on steel with different thickness were consider a shielding element for X-ray fluorescence (XRF) beam and surface concentration of Fe and Cr was measured.

For thickness of Cr_2O_3 over 30 μm, the substrate Fe concentration was below detection limit of XRF analysis. After the pull - off, significant amounts of Cr^{III} was found at the interface – the adhesion between Fe - Cr_2O_3 is higher than cohesion in the Cr_2O_3 coating. Bond strength value can, in ideal case, reach tensile strength of compact Cr_2O_3, however, bond strength is reduced based on chosen plasma deposition technology. Highest value of bond strength between individual layers of step-by-step deposited Cr_2O_3 was 11,7 MPa for substrate steel roughness of R_a = 6 – 8 μm.

During raster-like deposition on larger surfaces, delayed deposition occurs at previously coated surfaces of lower temperature. In such case, coating delamination can take place at lower stresses. Nevertheless, primary coating layer remains and adhesion bond-strength depends more or less on primary roughness of steel substrate surface.

Abrasion resistance was not directly measured by wear - resistance methods, but described samples were evaluated based on the hardness of polished chromium oxide surface. Hardness of 12,3 GPa is comparable to the time - tested anti - abrasion coatings [12].

For corrosion testing, samples with minimal coating thickness of 0,3 – 0,5 mm were selected. Using the electrochemical impedance spectroscopy (EIS), R_{ct}, i.e. charge transfer resistance and capacitance of electrical double layer (CPE_{dl}) were measured. The solution was 0,5 mol/l NaCl. Standard equivalent circuit (Figure 7) was used. Results are shown in Table 1.

Charge transfer resistance R_{ct} and capacitance of electrical double layer CPE_{dl} data are in good correlation. Comparing the charge transfer resistance values (R_{ct}) with the capacitance (CPEdl) clearly shows better

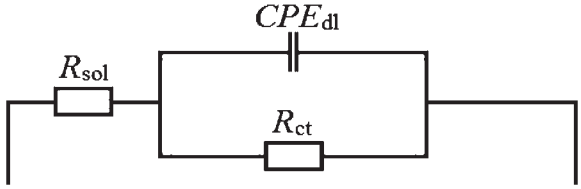

Figure 7 Scheme of equivalent circuit used to evaluate EIS data

Table 1 **Overview of results obtained by EIS method**

type of surface	R_{sol}	R_{ct} / Ω·cm²	CPE_{dl} / S·sᵃ·cm⁻²
Cr_2O_3 prepared by atmospheric plasma spraying (APS)	31	498	$1{,}10 \cdot 10^{-2}$
Cr_2O_3 prepared by liquid precursor plasma spraying (LPPS)	34	1 018	$2{,}70 \cdot 10^{-4}$

coverage of steel substrate by nanometer particles of chromium oxide by LPPS technology. Coating prepared by LPPS method from dichromate according to eq. (1) has higher corrosion resistance in the solution of 0,5 mol/l NaCl. Value of CPE_{dl} also suggest lower overall porosity of the coating.

CONCLUSIONS

Experiments shown that dispersing ammonium dichromate solution in extremely hot thermal plasma stream can, depending on the setup geometry and plasma generator parameters, vaporize the solvent, form spherical nano - sized Cr_2O_3 particles of 20 – 160 nm and heat them to their melting point in as short as 5 – 10 ms. Using the decomposition of isopolyacid salts of chromium, the chromium oxide with the melting point 2 435 °C was successfully deposited on steel substrate (S235JRH - 1.0038 EN 10025 - 1) and formed corrosion-resistant and abrasion-resistant coating of > 2 μm thickness, perfectly covering the pits on sand - blasted steel. Coating thickness can be changed almost arbitrarily by prolonging the time of plasma spraying, since local temperature of the substrate does not exceed 200 °C and evolution of structure defects, caused by residual stresses, is thus limited. Perfect coverage of steel substrates by nano - crystalline chromium oxide is inversely proportional to precursor concentration but also depends on deposition device configuration. The coatings are well - adherent – bond strength is limited only on mechanical properties of chromium oxide ceramics, specifically its tensile strength. Maximum cohesion strength was up to 11,7 MPa.

Corrosion properties of both coatings was evaluated using the EIS method. It has been shown that LPPS Cr_2O_3 coating provides better corrosion protection than conventional chromium oxide coating produced by the APS technology.

Neither coating contained any Cr^{VI} and can be thus be considered as a suitable replacement for common chromate coatings.

Acknowledgment

This paper presents research carried out in the Klokner Institute within the framework of Czech Science Foundation, project 13 - 12676S.

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Note: The responsible translator for the English language is K. Štětková, CTU – Klokner Institute, Prague, Czech Republic