

BOND STRENGTH OF PLASMA SPRAYED CERAMIC COATINGS ON THE PHOSPHATED STEELS

Received – Priljeno: 2014-06-24
Accepted – Prihvaćeno: 2014-10-20
Preliminary Note – Prethodno priopćenje

In the presented work, results of adhesion measurements for different systems of steel sheet-phosphate interlayer-ceramic coating are described. The interlayers were produced by zinc phosphating; alumina, olivine and zirconia-silica-alumina (e.g. eucor) coatings were deposited by water stabilized plasma torch WSP®. However, successful application of the WSP technique depends on the choice of correct deposition parameters preserving the hydrated phosphates from thermal destruction by the molten ceramic particles. For the adhesion measurement ISO 4624 standardized test was used. Corrosion resistivity was measured by polarisation resistance and free corrosion potential in 3 % NaCl solution.

Key words: phosphating, plasma spraying, ceramic coatings, corrosion, bond strength

INTRODUCTION

Phosphating is nowadays the highest standard of surface treatment prior to painting in automotive industry. The emergent layer of crystalline phosphates is due to suitable level of porosity highly absorptive not only with respect to paint, but also to oils, waxes and lubricants, which can be thus reliable interlocked into the surface [1,2]. The adhesion improvement of paints deposited in environment with high moisture is manifold when compared with unphosphated surface [3]. Phosphating of metals is mostly performed with the aim to increase corrosion resistance [2], because it stabilizes organic paints, increases their durability and substantially reduces the likelihood of corrosion occurrence under the paint [4]. Phosphate layer serves also as durable and reliable insulation when applied on the surface of transformer steel sheets [5]. Nevertheless, phosphating is most frequently used for adhesion improvement of various materials to ferrous substrates when the common grit blasting is not sufficient or exposition to aggressive corrosion environments is expected. This surface treatment leads to significant prolongation of working life regardless to elevated levels of moisture and in the case of coating's failure the phosphate layer limits the progress of corrosion.

There exist several phosphate layers that are used in technical praxis according to their properties, but all of them enhance adhesion to the substrate when applied and chosen properly. Layers from Zn, Fe, Zn-Ca or Zn-Mn phosphates have not only different crystalline structure, density, hardness, cleavage, but also thermal

stability and fraction of crystalline water, which plays a vital role during choice of the suitable phosphate for plasma sprayed ceramics [6]. However, phosphating does not offer much wear protection and therefore layered structure can be created by e.g. deposition of thin layers or thermal coatings can be sprayed on the already phosphated surface. Combination of phosphating by CVD or PVD by magnetron sputtering is not routinely done, probably because of dimensional limits of both methods. On the other hand, plasma coatings are commonly sprayed on comparatively large surfaces. These coatings have characteristic microstructure where presence of pores is no exception ranging from around 5 % in alumina or zirconia coatings to less than 1 % in the case of eucor plasma coatings. Phosphating of the substrate prior to plasma spraying of material whose coatings have higher porosity can thus lead to an important feature, i.e. corrosion protection of steel substrate that would otherwise corrode and degrade when aggressive substances penetrate through open porosity.

The aim of this study is enhance the adhesion and corrosion properties of plasma sprayed ceramic coatings on carbon steel utilizing phosphate layers as protective bondcoats. The ultimate goal is to verify the potential of Zn phosphate conversion coating in adhesion of the plasma sprayed ceramics while not knowing the behavior of crystal hydrates during first contact with ceramics particles in the molten state impinging on the phosphate surface.

Plasma spraying

Plasma spraying belongs to the group of the so called thermal spraying when usually, but not necessarily, a powder material is injected into a plasma jet. The powder is heated by plasma and subsequently impinges onto

P. Pokorny, L. Mastny, V. Sykora, Institute of Chemical Technology Prague, Czech Republic
Z. Pala, V. Brozek, Institute of Plasma Physics ASCR v.v.i. Prague, Czech Republic

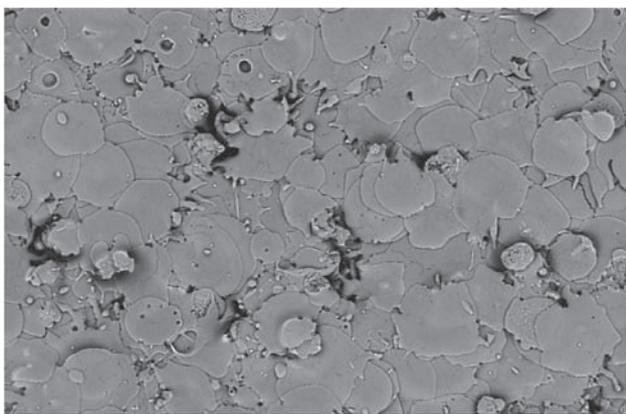


Figure 1 Surface of plasma sprayed alumina coating, magnification 300 x

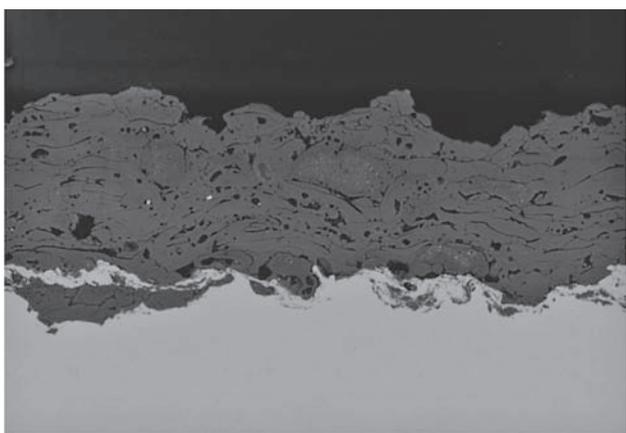


Figure 2 Cross-section of alumina coating on steel substrate, magnification 500 x

a substrate in a form of molten particles. Since the substrate is much colder, the molten droplets solidify upon impact and form the so called splats which can have morphologically complex shapes given by the nature of chemical and physical interactions. Because of rapid cooling, metastable, amorphous or generally less usual phases originate during this process. An example of characteristic morphology on the surface and in the cross-section of alumina plasma sprayed coating by water stabilized plasma gun WSP® which consists mainly of delta and gamma alumina is seen in Figures 1 and 2.

The WSP® has high enthalpy and can process up to 40 kg/h of corundum powder at the power of 150 kW.

EXPERIMENTAL

The preparation and characterization of the analysed samples was carried out following these steps:

- Sheets from DX51D mild steel for cold forming with $100 \times 100 \times 3 \text{ mm}^3$ dimensions were degreased and hand ground onto surface roughness $R_a = 4,7 \mu\text{m} \pm 0,7 \mu\text{m}$.
- Phosphate layer was created according to commercial recommendation *Pragofos 1222* with NaNO_2 as activator. The average area weight of Zn phosphate was 15 g/m^2 .
- The obtained phosphate layers were analysed by X-ray diffraction (XRD) performed on X'Pert PRO

MPD diffractometer with 1D detector and $\text{CuK}\alpha$ radiation. Energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) were employed as well.

- Thermal stability of phosphate layers was assessed by differential thermal analysis and thermogravimetry in the range from $20 \text{ }^\circ\text{C}$ to $400 \text{ }^\circ\text{C}$ and heat rate of $10 \text{ }^\circ\text{C}/\text{min}$ on the air.
- Taylor-Hobson Surtronic 3P analyser was used for surface roughness measurements and adhesion was analysed according to EN ISO 4624 using Loctite Hysol glue and Comtest OP1/2 apparatus.
- Plasma coatings of alumina, olivine/peridot and alumina-zirconia-silica ceramics with commercial name Eucor were deposited by WSP.
- Corrosion resistance of the steel sheet-phosphate layer-ceramic coating was investigated by free corrosion potential approach. Resistance of the barrier layer, i.e. phosphates plus ceramic coating, was further analysed by measurements of polarisation resistance in 3 % NaCl, polarization curves were obtained as well and the impedance spectroscopy was employed as well.

RESULTS AND DISCUSSION

Microstructure of the two phase phosphate layer seen in Figure 3 is supplemented by XRD and DTA results in Figure 4 and Figure 5, respectively.

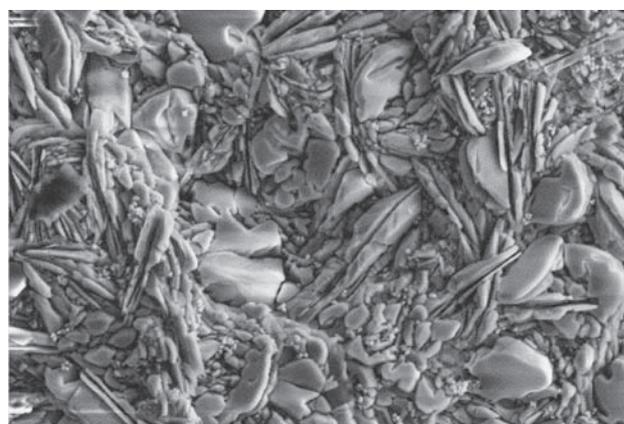


Figure 3 Structure of the two-phase phosphate layer, magnification 500 x

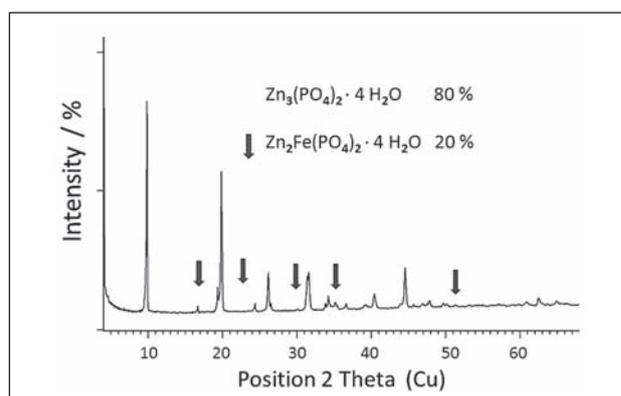


Figure 4 Phase composition of the phosphate layer

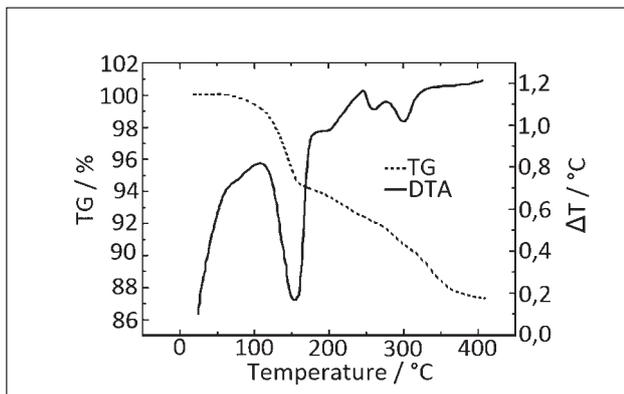


Figure 5 DTA and TG of the phosphate layer scraped away from the steel sheet

DTA results show that the critical temperature is at about 160 °C when two molecules of crystalline water are lost in the surface layer of phosphate.

The primary layer of the monoclinic phosphophyllite $FeZn_2(PO_4)_2 \cdot 4H_2O$ is very thin, nevertheless it facilitates disproportionation reaction, via lowering the pH of phosphating bath, when the primary layer diminishes and the presence of Zn^{2+} leads to the emergence of orthorhombic hopeite $Zn_3(PO_4)_2 \cdot 4H_2O$. Average surface roughness of the phosphated steel sheets was $R_a = 1,69 \mu m \pm 0,2 \mu m$.

When ceramics coatings are deposited onto phosphate layers, a system or a multilayer of steel-phosphate-WSP coating is created. The very selection of the three materials for spraying was done on purpose as (i) the eucor in the as-sprayed state is fully amorphous and its porosity is lower than 1% [7] while (ii) olivine is a ceramic with comparatively low melting point and (iii) the process of alumina spraying by WSP is the most widely used and understood. Microstructure of selected multilayer steel-phosphate-alumina coatings can be seen in Figure 6.

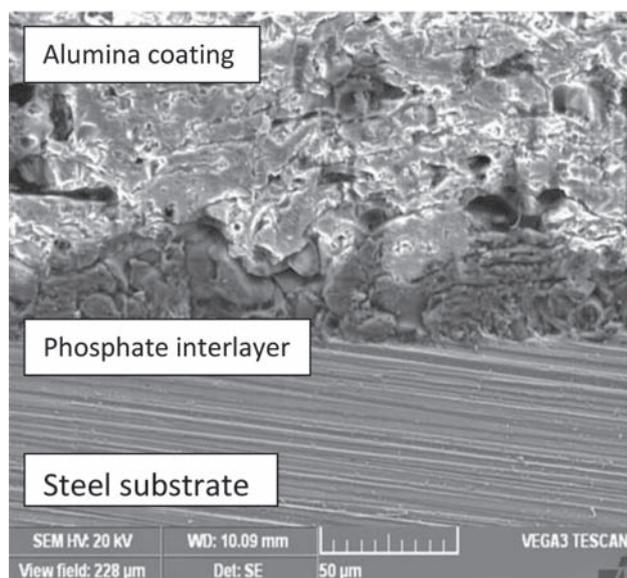


Figure 6 Cross-section in system steel – phosphate - alumina coating

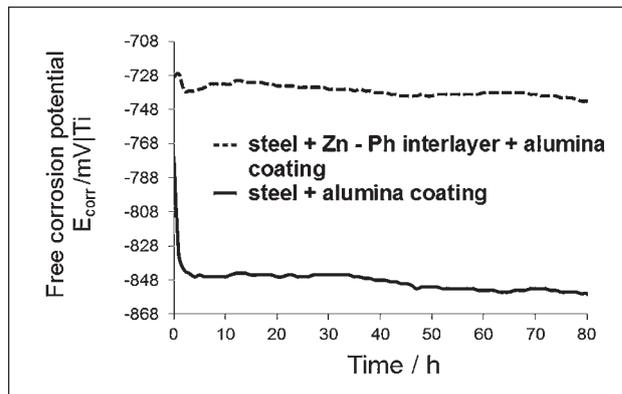


Figure 7 Free corrosion potential of the carbon steel covered by WSP alumina coating

The results of corrosion resistance analyses of the phosphate layer - ceramic coating systems are in Figures 7 and 8. The former figure includes comparison of alumina coating directly on steel and with the interlayer of Zn phosphates. Low negative E_{corr} value means higher corrosion resistance. Moreover, the high polarization resistance of phosphate with alumina coating in Figure 8 corresponds to much higher protection of the steel substrate against corrosion. In order to assess mechanical resistance and stability of the Zn phosphate layer and ceramic coatings, the alumina WSP coatings with thickness $0,3 \text{ mm} \pm 0,1 \text{ mm}$ were selected and the multilayers were subjected to the testing of bond strength.

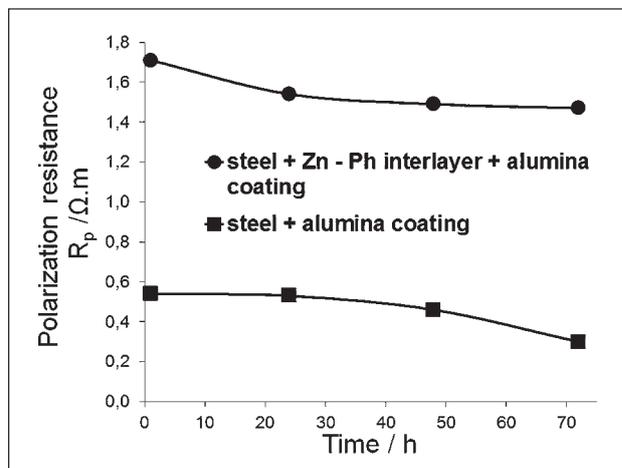


Figure 8 Polarization resistance of the carbon steel with the phosphate interlayer

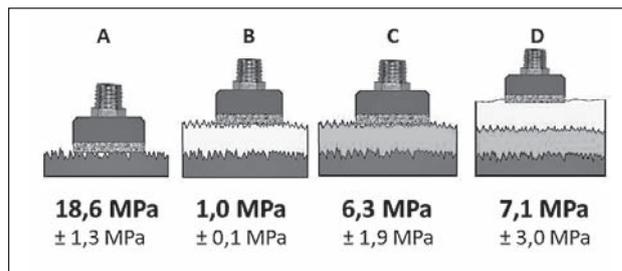


Figure 9 Schematic depiction of bond strength testing; from left to right: steel substrate and glue (A), steel + WSP coating + glue (B), steel + phosphate layer + glue (C), steel + phosphate layer + WSP coating + glue (D)

Several set-ups of bond strength experiments were tested, all of them are schematically depicted in Figure 9. All the experiments took place 3 days after the actual conglutination.

Experiment according to the set-up B showed that there is a adhesion fracture in the coating probably caused by the penetration of the glue. However, the bond strength increased from 1 MPa to around 7 MPa when the alumina coating was combined with phosphate layer. It should be noted that the destruction during the D set-up took place not in the alumina coating, but in the phosphate layer. The same effect was observed in samples with olivine and eucor coatings.

CONCLUSIONS

In this work, phosphated steel sheets were sprayed by ceramic coatings which would lead to increased wear resistance while limiting the possible corrosion of the steel sheet via corrosion media penetration through open porosity of the ceramic coating. It was, indeed, found that the samples that included phosphate layer exhibited lower negative E_{corr} values and higher polarization resistance, both of which means substantially higher corrosion protection.

However, the adhesion and cohesion of the whole system is an issue. The applied phosphate layer contains components with two and four crystalline waters and the loss of two crystalline waters, or partial dehydra-

tion, at around 160 °C as shown by DTA leads to the observed fact that adhesion of the phosphate layer is preserved even though molten particles of ceramic material impinged on its surface. The phosphate layer can, hence, also serve as the so called bond coat increasing adhesion of the ceramic coatings to the steel substrate.

Acknowledgment

This project is financially supported from specific university research (MSMT No 20/2014) and Czech Science Foundation grant No. P108/12/1872.

REFERENCES

- [1] H. Dettner, J. Elze, *Handbuch der galvanotechnik Band III*; Carl Hanser Verlag (ed.), München, 1969.
- [2] W. Rausch, *Die Phosphatierung von Metallen*, Eugen G. Leuze Verlag (ed.), Frankfurt am Main, 1988.
- [3] W. Machu, *Die Phosphatierung*, Verlag Chemie, Berlin, 1950.
- [4] E. L. Ghali, R. Potvin, *Corrosion Sci.* 12 (1972), 583-594.
- [5] P. Tegehall, R. Vannerberg, *Corrosion Sci.* 32 (1991) 635-652.
- [6] P. Pokorný, V. Brožek, L. Mastný, in *METAL 2012 Conference Proceedings, Brno 2012*, Tanger Ltd (ed.) pp. 69-70
- [7] T. Chraska et al., *J. Thermal Spray Technology* 17 (2008) 872-877.

Note: Zdenek Pala (IPP CAS Prague, Czech Republic) is responsible for English language