COMBINED COATINGS AGAINST MECHANICAL WEAR AND CORROSION LOW CARBON STEEL

BROŽEK Vlastimil[1], POKORNÝ Petr[2], KOLÍSKO Jiří[2], VOKÁČ Miroslav[2],
MASTNÝ Libor[3], STOULIL Jan[3]

[1]*Institute of Plasma Physics CAS v.v.i. Prague, Czech Republic, EU,*
brozek@ipp.cas.cz
[2]*Klokner Institute Prague, Czech Republic, EU, petr.pokorny@cvut.cz*
[3]*University of Chemistry and Technology Prague, Czech Republic, EU, libor.mastny@vscht.cz*

Abstract

In this study, special ceramic coatings were prepared on low carbon steel (1.0060 - EN 10027-2) via the plasma spraying technique using a WSP®-H plasma generator with output of up to 40 kg/h of aluminum oxide. Corundum coatings were deposited directly on the surface of steel plungers equipped with an anti-corrosion interlayer of zinc phosphate. Coating adhesion properties were tested using pin-off tests (modified ISO 4624) and reached a maximum value of 26 MPa. Corrosion resistance was evaluated by measurements of impedance spectra in the 100 kHz - 10 mHz range in a water solution of sodium sulfate. The capacity of electric double-layer varied depending on the porosity and thickness of the coating. Low-porosity coatings of >1.5 mm thickness had R_{CT} $1.29 \cdot 10^5$ $\Omega \cdot m^2$. The abrasive resistance of coatings was measured by rotary/machining test with SiC cutting knives, using a downforce of 50 $kg \cdot cm^{-2}$. Abrasion losses decreased with the quality of finish - starting at 0.00266 $g\ cm^{-2}\ min^{-1}$ down to virtually zero losses after polishing the surface below R_a = 0.55 μm.

Keywords: Plasma spraying, steel phosphating, ceramic coatings, corrosion resistance, abrasion

1. INTRODUCTION

Mechanically strong structural components resisting both abrasion and corrosion must be made of high quality materials. The limited selection of special alloys from very hard and corrosion-resistant materials is paralleled by their high price. The simpler and cheaper solution to this problem is to use a combination of a high strength metal base with a hard, abrasion-resistant ceramic or cermet coating. An example of this approach is fluid suspension pumps for high-volume abrasive microparticles used at present in the mining industry or in the disposal of industrial waste. The abrasion resistance requirement also has a significant corrosion resistance requirement so as to prevent the corrosion of the abrasion-resistant hard ceramic coatings. Plasma coating of metallic substrates with ceramic coatings is still the subject of intense research, particularly in connection with the deposition of thermal barrier coatings (TBC) on gas turbine blades and other intensely heat-stressed components, specifically thermal shock [1]. There is less information on the application and results of such combinations in industries that do not involve the risk of large economic and general losses. In cases where ceramic coatings on metallic substrates have multiple functions, especially abrasion and corrosion resistance, it is necessary to choose an approach based on the specific conditions and requirements of individual instances, so that a universal model of such systems cannot yet be developed. One of the possible selection options is the formation of ceramic coatings on anticorrosive layers which are formed by boriding, chromating, or phosphating steels. Corrosion of borided layers has not yet been satisfactorily described, boride layers on steel function independently or serve to increase the adhesion of hot-applied ceramic coatings [2,3,4]. The preparation of ceramic coatings on phosphated steels has already been tested for a number of combinations of unalloyed steels with simple and stoichiometrically more complex phosphates [5,6].

2. EXPERIMENTAL

For the experiments, steel pump plungers of the Hauhinco-type [7] with a cylindrical shape and a diameter of 35 mm and a length of 260 mm were made, and model plungers with a diameter of 60 mm and length 200 mm were made of unalloyed steel of class 11420 according to ČSN 42 0002 (see **Figure 1**). The surface of these substrates was treated with a corundum abrasive with a grain size of 60 µm -125 µm to a value of R_a = 7 µm -10 µm. Subsequently a coating of the corundum AH13Ti was applied using the plasma spraying method, the chemical analysis of which is given in **Table 1**. To prepare this special ceramic coating a WSP®-H plasma generator with a processing power of up to 40 $kg \cdot h^{-1}$ of alumina [8] was used. The corundum coatings were deposited directly on the surface of the steel plungers in the first experimental series and deposited in the second series on the surface of the plungers provided with an anticorrosive layer of zinc phosphate. The conditions for the application of ceramic coatings by the WSP® plasma torch have been described several times [9,10], so the selection of the particular process has been optimized to the current highest quality level. The adhesion of similar ceramic coatings, as well as in the first series, has previously been tested according to the EN ISO 4624 test and can reach maximum values up to 60 MPa [11]. The second series of steel plungers was provided with a phosphate conversion layer prior to plasma spraying. A high-density fine-grained zinc phosphate was chosen (the majority of the coating consists of $Zn_3(PO_4)_2\ 4\ H_2O$). Phosphating was carried out in the Pragofos 1220 commercial bath with the recommended activation pre-wash. The steel was phosphated for 10 minutes in a bath at 60 °C. The reaction was accelerated by adding hydroxylammonium sulfate with a concentration of 1.5 $g \cdot l^{-1}$ [12]. The ceramic-coated steel plungers were then subjected to abrasive wear and corrosion resistance tests.

3. RESULTS AND DISCUSSION

Figure 1 is a picture of the original steel plunger with a corundum coating with a surface roughness of R_a = 13.6 µm, R_q = 17.3 µm, R_z = 97.8 µm and its diamond tooling for the final dimension of the Hauhinco-type pump rod with a surface roughness in the range of R_a = 0.154 - 0.204 µm, R_q = 0.231 - 0.295 µm, R_z = 2.088 - 2.424 µm. Sanding and polishing with a diamond tool was conducted so that the thickness of the ceramic layer on the steel was 1 mm (± 5 %). The thickness of the coatings was measured non-destructively by XRF analysis and in individual cases by a destructive metallographic method (see **Figure 1**). Since the abrasive and corrosion resistant properties of the output product were simultaneously monitored in this experiment, a more detailed characterization of the substances used is provided in **Table 1** to provide a basis for a more accurate interpretation of the results for possible comparison with other materials.

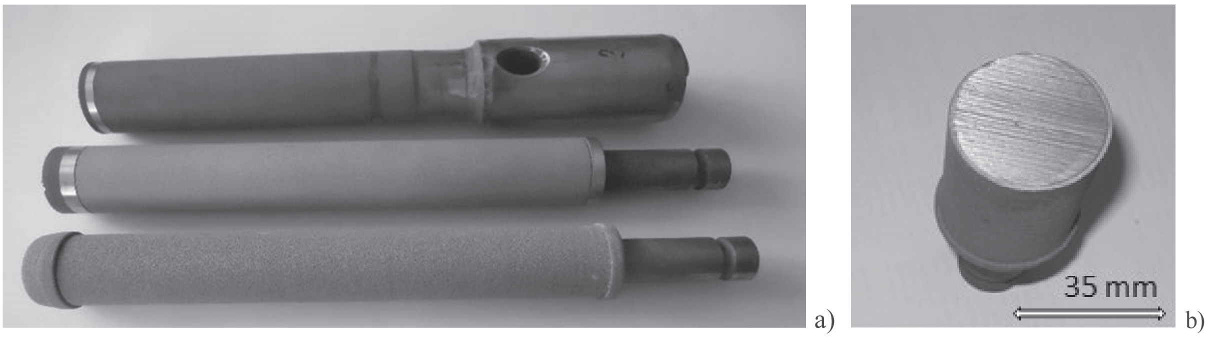
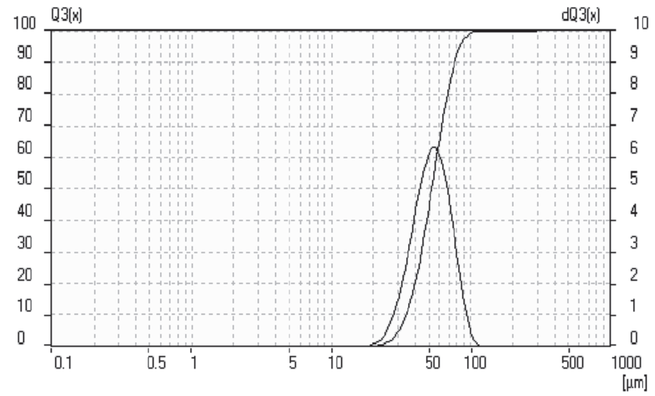
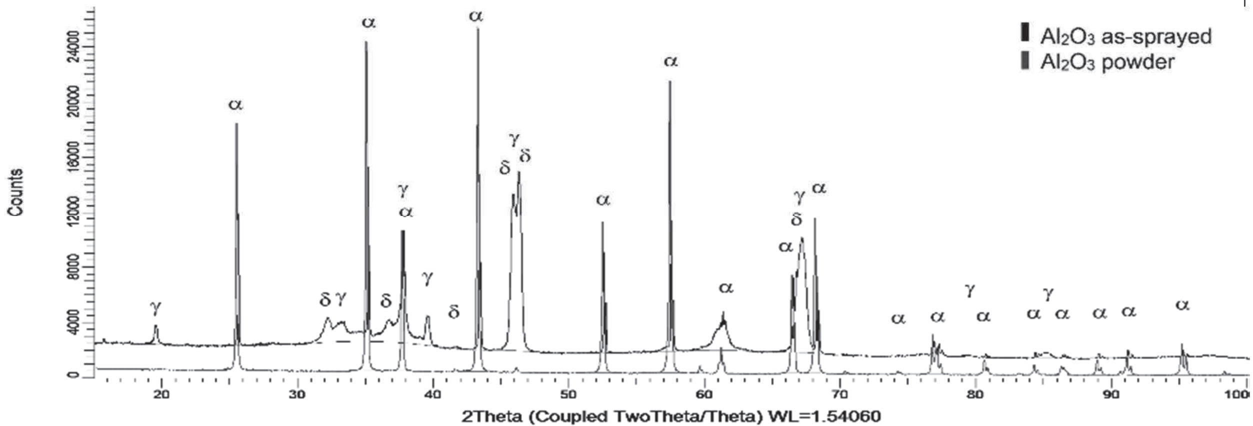


Figure 1 Plasma spraying of corundum on the 35x180 mm plunger and surface treated ceramic layer on a plunger from steel 11 420 (according to ČSN 42 0002) (a), destructive measurement of the thickness of the ceramic coating on steel (b)

Table 1 Characteristics of the used materials and methods

<table>
<tr><td>XRF analysis PANanalytical AXIOS (Holl)</td><td>Al</td><td>Ca</td><td>Fe</td><td>Na</td><td>Si</td><td>Ti</td><td>Zr</td><td>Mn</td></tr>
<tr><td>Chemical composition of corundum powder (%)</td><td>79.8</td><td>1.8</td><td>1.9</td><td>0.1</td><td>3.7</td><td>7.6</td><td>0.3</td><td>--</td></tr>
<tr><td>Chemical analysis of steel 11 420 (%)</td><td>0.07</td><td>--</td><td>97.5</td><td>0.2</td><td>0.4</td><td>--</td><td>--</td><td>1.4</td></tr>
<tr><td>Statistical means
Arhitmetic mean diameter 51.69 μm
Geometric mean diameter 48.28 μm
Quadratic square diameter 54.66 μm
Harmonic mean diameter 41.39 μm
Average deviation 14.25 μm
Specific surface area 1449.5 cm^2/cm^3</td><td colspan="8"> </td></tr>
<tr><td colspan="9"> </td></tr>
<tr><td colspan="9">XRD starting Al_2O_3 powder and Al_2O_3 as-sprayed
α - trigonal R $\bar{3}$c (cca 20 %); γ - tetragonal Fd $\bar{3}$m δ - orthorhombic P $\bar{4}$m2</td></tr>
<tr><td>Plasma spraying parameters</td><td colspan="8">Arc current 400 A; arc voltage 268 V; power output 107 kW; useable output 68 kW; low rate of the plasma media 0.272 $g \cdot s^{-1}$. Feeding distance FD = 100 mm, spraying distance SD = 300 mm</td></tr>
</table>

The evaluation of the abrasive resistance of the original ceramic surface with initial roughness R_a = 13.6 μm and microhardness of 12.35 GPa (HV 30/100) and the surface after polishing with a diamond tool to a value of R_a = 0.154 μm was done using a simplified method - by monitoring weight loss via rotational wear, see **Figure 2**.

A bar of sintered SiC type Rocar G or high-speed steel AISI M2 - 1.3343 with a pressure area of 1 cm^2 was used as an abrasive pressing element. Radial velocity of the tested cylindrical sample was 50 rpm, pressure 50 $kg \cdot cm^{-2}$, measuring time 15 min - 20 min, width of abrasive path 10 mm, grinding track 1000 m. The weight loss of the coating is measured from the volume of the abraded annulus, followed by weight conversion using a specific corundum weight of 3.9 $g \cdot cm^{-3}$. In the case of the use of pressure segments from steel with a 1 cm^2 friction area, the unpainted surface of the cylindrical plunger behaved like a rotating grinding tool. There was wear of the steel segment and, at the same time, sealing and smoothing of the surface irregularities of the ceramic plunger coating, which to some extent simulates the conditions of the plunger movement in the cylindrical metal housing of the pump. The process was terminated upon sealing and smoothing of the cylinder surface to a value of R_a of about 0.55 μm, see **Figure 3.** In the case of diamond plunger surfaces polished to

R_a = 0.154 µm - 0.204 µm, only ROCAR G silicon carbide with a friction area of 1 cm^2 was used as the pressure segment. In this case, the ceramic layer was ground to a thickness of 0.04 ± 0.02 mm after 60 minutes at a rotation speed of 50 rpm and a grinding track length of 338 m.

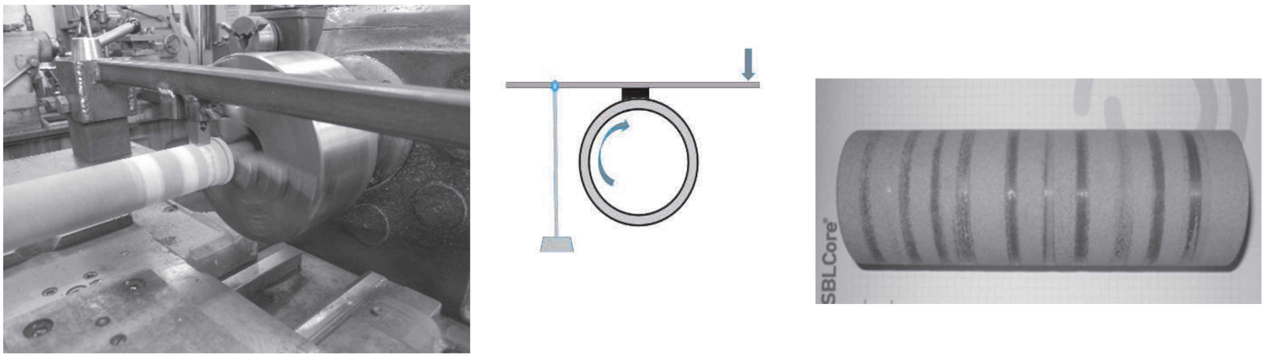


Figure 2 Measuring abrasion resistance to smoothing and sealing the plunger surface with steel abrasion

For corrosion resistance testing, accelerated corrosion tests were carried out in concentrated hydrochloric acid (10% HCl, 2.78 $mol \cdot l^{-1}$), a similar determination of resistance to intergranular corrosion according to ČSN EN ISO 3651-1. It has been shown that corrosive attack of the underlying steel has a strongly localized character, see **Figure 4**. The localized emission of corrosion products is concentrated in defect areas of the hot-applied ceramic coating. Localized forms of corrosion damage induced by the low pH of the environment and the presence of Cl^- ions were then quantified by measuring impedance spectra (EIS) at the locations captured in the photograph **Figure 4**.

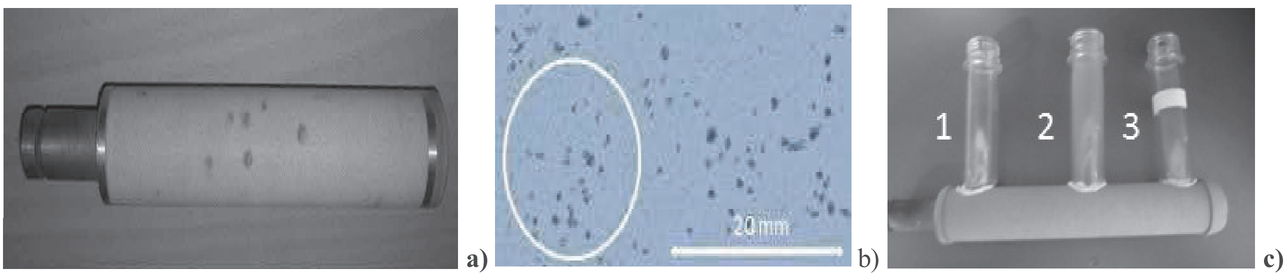


Figure 4 Example of a corrosion of the coated plunger a) after 24 hours in 10% HCl
b) detail of the surface; c) measuring position of impedance spectra (EIS)

The impedance spectra were measured in a solution of 0.85 $g \cdot dm^{-3}$ sodium sulfate after 1 hour of stabilizing the conditions. For measurements, 3 sites were selected on the sample surface, see **Figure 4c**. The impedance spectra were measured in a frequency range of 100 kHz - 10 mHz with a recording density of 5 points per grequency decade and an amplitude of 20 mV for porous coating (position 1a, 3a and 3b) and 100 mV for compact coating (position 2a, 1b and 2b). The reference electrode was a saturated silver-silverchloride electrode, and the counter-electrode was a platinum wire with an exposed area of 1.6 cm^2. The coating at the position (2a, 1b and 2b) behaves almost as an ideal capacitor. It has a high impedance, and the phase shift throughout the entire frequency range is -90°. The othere positions (1a, 3a and 3b) already show the behavior of the porous coating where part of the base metal is exposed. The spectra were fitted with equivalent circuits and **Table 2** summarizes the results (index **a** for original spraying, index **b** for the polished surface spraying). The resistance to charge transfer is higher in the middle position. The capacities of the electric double layers were recalculated (relative to the uncoated substrate) at the two extreme positions due to the porosity. Porosity at position 3a is higher than position 1a. These differences are obviously related to the plasma spray technique where the cylindrical substrate in the central portion is heated over a different time period than the edge portion of the substrate.

Table 2 Overview of results obtained by the EIS method

position	1a	2a	3a	1b	2b	3b
R_{CT} ($\Omega \cdot m^2$)	15.70	1.29×10^5	8.46	493	873	65
V_{rel} (%) *	7.00×10^{-5}	--	1.69×10^{-3}	--	--	5.2×10^{-4}
* Relative surface of exposed substrate - Na_2SO_4 contact surface ratio and total area of R_{CT} measurement						

The irregularity of these values, which depend mainly on the thickness of the ceramic coating and the number of macro-structural defects, shows that irregular macrostructural defects, which cannot be avoided during plasma or heat deposition, have a major influence on corrosion resistance. Therefore, in order to avoid corrosion of ceramic coatings, which should fulfill the primary abrasion resistance of the pieces in use in liquid, corrosive, and abrasive environments, the anti-corrosion protection step of the steel substrate was preceded by the usual anti-corrosion treatment, i.e. by phosphating [13]. The total corrosion resistance of the coatings was verified by measuring the open circuit potential (E_{OC}) and the polarization resistance against the activated titanium electrode in a solution of 3 wt.% NaCl. The E_{OC} value for the non-phosphated system dropped from -840 mV/Ti to -860 mV/Ti during the 80 hour interval, whereas the zinc coating maintained an EOC value of -730 ± 10 mV/Ti. Over the same time interval, the polarization resistance (R_p) for unphosphated samples was only 0.54 $\Omega \cdot m^2$, while the polarization resistance of the combined corundum-zinc phosphate coating was maintained at 1.50 $\Omega \cdot m^2$. These values apply to corundum coatings where mercury porosimetry has a porosity value of 5.9 %.

3. CONCLUSIONS

Plasma deposition of metallic, ceramic, or cermet coatings on metallic substrates can be considered technologically feasible [14]. The question, however, is what properties must such combinations of coatings and substrates meet. In the event of demand for high corrosion and abrasion resistance, not only the high hardness and adhesion of the coating, but also its macrostructure must be considered. All ceramic coatings prepared by thermal spraying are in principle porous, with frequent cracks or open porosity. Therefore, the thermal spraying method has been modified or applied to secondary corrosion-resistant coatings on phosphated steel [15]. The relatively low mechanical strength and low hardness of phosphate was thus mechanically covered by a much stronger and harder coating with a combined structure of aluminum oxides (R-3c, Fd-3m, P-4m2) with an average microhardness of 12.35 GPa. Here it must be noted that the maximum observed value of phosphate adhesion to the metal substrate is < 10 MPa, but cracking and tearing occurs in the phosphate layer, with the contact residue of the thin layer of phosphate being bonded to the steel substrate by chemical bonding.

Mechanical wear of such coatings with a silicon carbide abrasive (which in this case was a model example of the hardest abrasive in a normal price range) shows a low, and practically same, degree of wear for both types of coating, i.e. for the coating of aluminum oxides formed directly on the steel substrate or on the interlayer of the hopeite coating Zn-phosphate. Abrasive wear values of rotating parts are important only in specific application conditions. In this case, experiments were terminated after 60 minutes of test operation without any significant change in wear or attack of the structural substrate.

The corrosion resistance is clearly dependent on the porosity of the ceramic coatings whose surface irregularity was clearly demonstrated by impedance tests (EIS). Corrosion-protected phosphate layer based on hopeite has a long-term mostly stable open circuit potential and a higher polarization resistance than for samples without a phosphate interlayer. Since there is no serial production of such plungers or similar metal products, the data obtained were not statistically significant. The variability of the wear and tear of the combined materials and the extension of their service life by special surface coatings is very great.

ACKNOWLEDGEMENTS

This research has been supported by Czech Science Foundation, project No P105/12/G059.

REFERENCES

[1] Valarezo, A., Dwivedi, G., Sampath, S., Mušálek R., Matějíček. J. Elastic and anelastic behavior of TBCs sprayed at high-deposition rates. *Journal of Thermal Spray Technology* 24, 2015, pp.160-167.

[2] Fichtl, V. Boronizing and its practical applications, M*aterials in engineering*, 1981, Vol. 2, pp. 276-286

[3] Pokorny, P., Tej, P., Szelag, P. Chromate conversion coatings and their current application. *Metalurgija* , 2016, vol. 55, pp 263-256.

[4] Sankara Narayanan, T.S.N. Surface pretreatment by phosphate conversion coatings - a review, *Rev. Adv. Mater. Sci.* 2005, vol. 9, pp. 130-177.

[5] Rausch W., Die Phosphatierung von Metallen 2nd ed. Eugen G. Leuze Verlag; Frankfurt am Main 1998

[6] Pokorny, P., Mastny, L., Sykora, V., Pala, Z., Brozek, V. Bond strength of plasma sprayed ceramic coatings on the phosphated steels, Metalurgija 54, 2015, pp. 411-414

[7] Hauhinco. Water treatment solution for Longwall Mining system. In *Magazine World Coal*, March 2017 Issue.

[8] Chráska, P., Hrabovský, M. Water-stabilized Plasma Guns and their Applications. In *Proc. of Inter.Thermal Spray Conf. ITSC'92*, Orlando, Fl., June 1992: ASM International, p. 81.

[9] Neufuss, K., Chráska, P., Kolman, B., Trávníček, Z., Sampath, S. Properties of Plasma Sprayed Free-Standing Ceramic Parts, *J.Thermal Spray Technology* 1997, vol.6, no. 4, pp. 434-438.

[10] Ilavský, J., Berndt, C. C., Herman, H., Chráska, P., Dubský, J. Alumina-Base Plasma Sprayed Materials, Part II: Phase Transformations in Aluminas. *J. Thermal Spray Technology* 1997, vol.6, pp. 439-444.

[11] Mušálek, R., Vilémová, M., Matějíček, J., Pejchal, V. Multiple-approach evaluation of WSP coatings adhesion/cohesion strength. In *Thermal Spray 2012*: *Proc. International Thermal Spray Conference and Exposition*. Materials Park Ohio 2012, pp. 746-751.

[12] Safety Data Sheet Pragofos 1220, Pragochema Praha Ltd.

[13] Kiss, K., Coll-Palagos, M. Cyclic voltammetric and scanning electron microscopic evaluation of the corrosion resistance of Zn-phosphated steel. *Corrosion* 43, 1, 1987, pp. 8-14.

[14] Mušálek R., Glanc A., Medřický J., Pala Z., Chumak O., Janata M., Chráska T. Repeatability study of plasma sputter deposition using WSP technology - Studie opakovatelnosti depozice plazmových nástřiků pomocí technologie WSP. In *Zborník prednášok Vrstvy a povlaky 2013*. Trenčín LISS a.s, 2013 - (ed. Šošovičková, J.), pp. 109-114.

[15] Pokorny, P., Szelag, P., Novak, M., Mastny, L., Brozek, V. Thermal stability of phosphate coatings on steel. *Metalurgija* 54, 2015, pp.489-492.