IMPROVING BOND STRENGTH BETWEEN CARBON STEEL AND PLASMA SPRAYED CERAMIC COATINGS THROUGH A PHOSPHATING PROCESS.

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Abstract
Phosphating is currently the highest standard of surface treatment before painting in the vehicle industry. Excluded phosphate crystal layer is due to its high porosity absorbing not only paints but also oil and lubricants that can reliably maintain the surface. Improved bond strength in the case of coatings exposed in the humid atmospheres in comparison with multiple non-coated surface. Focus of this work is an effort to improve the bond strength between the different plasma-sprayed coatings materials and carbon steel using different phosphate coatings. Because most of the eliminated phosphate crystallizes with four crystal waters the samples was covered by zinc-calcium phosphate, which crystallizes with only two waters [scholzite: Zn$_2$Ca(PO$_4$)$_2$ . 2H$_2$O] and coated from bath of „three-cations” phosphate due to the large thickness of the coating and compaction [phosphophyllite: Zn$_2$Fe(PO$_4$)$_2$ . 4 H$_2$O]. They decided test for measuring the quality of bond strength between coating and steel substrate set by pull-off test according to EN 4624 for using pull-off test device COMTEST OP ½, where the glued joint standard provide recommended special adhesive glue call Loctite Hysol 3425. The test included measurement of the minimum tensile strength between the adhesive roller and the test plasma-sprayed surface, which causes separation of the specimens and the fracture characteristics. Fracture surface evaluated using the electron microscope TESCAN VEGA to fully experience the EDS analysis.

Key words: surface treatments; phosphating coatings; bond strength; plasma spraying; ceramic coatings;

1. INTRODUCTION
Phosphating the surface of common carbon steel is currently the highest standard of surface preparation before painting metal in the vehicle industry. Excluded phosphate crystal coating is porous and therefore highly absorbing not only paints, but also oils, waxes and lubricants [1,2]. If in addition to high corrosion resistance is also necessary to improve the wear resistance of surface layers is possible in special case to make their surfaces thin and hard ceramic coating. Known procedures, for example creating a coating of titanium nitride by CVD methods or magnetron sputtering, but it is limited to small areas and small size samples, mainly because it is carried out under reduced pressure in a closed apparatus. Plasma deposition method, a method such as APS (Atmospheric Plasma Spraying) allows to coat substrates of almost any size, with the surface of several tens dm$^2$. Plasma coating of ceramic materials is high-temperature process and one of its drawbacks is the formation of coatings with porosity up to 5%, depending on the meeting point compounds deposited. Focused on this work is an effort to improve the bond strength between the different plasma-sprayed ceramic materials and the surface of carbon steel use different phosphate coatings as interlayers. The aim of the work described is to verify the ability of phosphate coatings improve adhesion of plasma-deposited ceramic coatings simultaneously applied to present the sub-corrosion of ceramics coatings, because of its increased porosity.
2. EXPERIMENTAL

To carry out the experiment, samples were selected entirely standard carbon steel (according to ČSN 10327 [DX51D]). These samples of composition (0.12 %C, 0.50 %Si, 0.60% Mn, 0.10 %P, 0.045% S and 0.30 % Ti) do not guarantee any increased resistance under normal atmospheric corrosion and do not affect excretion and the duality of phosphate coating. Furthermore, its size (100 x 100 mm) fully comply with technology of plasma spraying as well as its thickness (t = 2 mm) fully meet the standard for objective assessment of adhesion of coating system of pull-out test. Individual samples were standard receive a full prior to phosphating. First was the mechanical surface pretreatment (grinding P120 and P1200) and then chemical surface pretreatment, degreasing (Pragolod 57 N) standard pickling and activation (3 % HCl solution) and eventually non-standard activated (Proofs 1427 or Proofs 1927). The individual steps were inserted pretreatment through rinsing (water spray and immersion utility distilled water). Finally, the individual samples of phosphating in commercial preparations (Pragofos 1220, Pragofos 1600, Pragofos 1900, Pragofos 2060, Pragofos 2400), all surface pretreatment and phosphating own place in accordance with technical data sheets of individual products. The obtained coatings were characterized by X-ray diffraction analysis, mineralogical analysis, spectral analysis, EDS was measured and their surface roughness by the instrument Mittotuyouthe SP X5.

Were verified by the different type phosphating technology, zinc phosphating (Fig.1), zinc-calcium phosphating (Fig.2), manganese phosphating (Fig.3), and finally called „three-cations“ phosphating (Fig. 4). The experiments were excluded iron phosphate coatings, resulting in compliance with the chemical formula (1), showed no improvement since the adhesion properties of the ceramic coating (the coating is very thin and amorphous (thickness < 1 μm) [3]

\[
4 \text{Fe} + 4 \text{NaH}_2\text{PO}_4 +2\text{O}_2 = \text{Fe}_3(\text{PO}_4)_2 (s) + \text{FeO} + 2 \text{Na}_2\text{HPO}_4 + 3\text{H}_2\text{O}
\]  

(1)

Coatings of zinc phosphate Zn$_3$(PO$_4$)$_2$, prepared in accordance with equation (2), had a perfect crystal structure by XRD analysis, however, was a mixture of structure orthorhombic hopeite (cca 70%) and monoclinic phosphophyllite FeZn$_2$(PO$_4$)$_2$ (cca 30%), see Fig.1. Surface roughness was $R_a = 1.55$. A summary of the reaction of crystal coating of zinc-calcium phosphate can be described by the equation 3.

\[
3 \text{Zn}^{2+} + 2 \text{H}_2\text{PO}_4^- = \text{Zn}_3(\text{PO}_4)_2 (s) + 4 \text{H}^+
\]

(2)

\[
\text{Ca}^{2+} + 2 \text{Zn}^{2+} + 2 \text{H}_2\text{PO}_4^- = \text{CaZn}_2(\text{PO}_4)_2 (s) + 4 \text{H}^+
\]

(3)

Coatings technology acquired zinc-calcium phosphate treatment (see Fig.2 and equation 3) were typical “egg-shaped” shape characteristic orthorhombic scholzite CaZn$_2$(PO$_4$)$_2$·2 H$_2$O. Formations of phosphate layers are always very fine, even without previous activation of the surface. Coatings have a surface weight of 1 – 4.5 g/m$^2$. Coating technologies resulting manganese phosphating (Fig.3.) consist hurealite Mn$_5$H$_6$(PO$_4$)$_4$, 4 H$_2$O, which may have complicated chemical composition, because it occurs at diadochian behavior and manganese is in the summation formula for phosphating steel partially replaced by iron, literature rather show summary session with both metals (Mn, Fe)$_5$ H$_2$(PO$_4$)$_4$ · 4 H$_2$O. In our case, according to EDS analysis, the ratio of Mn/Fe = 3/2. All hurealites crystallizes in monoclinic system and consist of columnar crystals acicular with high surface roughness, Ra, in our case 1.75. This roughness is suitable for plasma spraying, as in the standard plasma injections is necessary to pretreated the surface of substrates, at lest such value of Ra. Coatings have created a weight of 7.5 – 12 g/m$^2$. Comprehensive response to precipitation manganese phosphate coatings show equation 4 [2,4].

\[
5 \text{Mn}^{2+} + 4 \text{H}_2\text{PO}_4^- = \text{Mn}_5\text{H}_6(\text{PO}_4)_4 (s) + 6 \text{H}^+
\]

(4)
Counts of thermal mainly Plasma deposition generator or chemical creates from various sources is plasma high temperature deposition using a generator WSP®. Fig.5 illustrates. Typical surface morphology of corundum coating is shown in Fig.6. Plasma deposition methods have a large number of possible variants. Given that the plasma coatings is mainly the issue of interface between the substrate and coating as two very different materials (metal-ceramic, ceramic A and B ceramic), especially with different melting points and the coefficient of linear thermal expansion, plays an important role in the ability to create the interlayers [5] to improve the adhesion of heterogeneous surface contact primarily by changing the surface roughness $R_a$ and the mean coefficient.
of expansion of the new interface. In the event that we follow in this work, is also expected to improve corrosion resistance and subsurface layers.

Fig.5  Scheme of plasma deposition of powdered alumina precursors

Fig.6  Surface of plasma sprayed aluminium oxide coating (morphology is typical for all investigated samples)

3. RESULTS AND DISCUSSION

To assess the suitability of individual phosphate coatings for subsequent plasma coating is necessary to characterize their dehydration behavior, because the temperature-induced spontaneous dehydration can cause distortion of the crystal structure of phosphate and thus reduce its protective and adhesive properties. In the initial part of the research were excluded individual swabs phosphate coatings subjected to differential thermal analysis (DTA). In a purely empirical testing of coatings at different curing temperatures up to 150 °C at which deposited organic coatings [3] was not observed loss of bond strength between the metal and the coating system. It can therefore predict that dehydration in this temperature plays a key role in the distortion of the phosphate coating. The question remains, however, application of coatings at significantly higher temperatures during plasma coating or dipping, and the actual course of dehydration under the ceramic coating. To the first compare the suitability of each coating method was used DTA whose waveform is shown in Fig 7. The underlying assumption in front of our tests was the view that they are more resistant phosphate coatings which contain less water of crystallization (Pragofos 1600: Zn₃Ca₂(PO₄)₂·2 H₂O, scholzite) and the resilient coating will be harder (Pragofos 1900: "tree-cations" phosphating and Pragofos 2400: manganese phosphating), zinc phosphate coatings have similar dehydration curve (Pragofos 1220 and PZn). Since the process is endothermic dehydration reaction can be attributed to the decrease of temperature curves around 150 °C was dehydrated phosphate coatings. To the Fig.7 phosphate Pragofos 1600 and Pragofos 1220 and non-commercial zinc phosphate PZn observe a similar curve. The apparent dehydration begins to occur at about 120 °C and dehydration becomes temperature maximum at 150 °C, the process ends at about 180 °C. These samples are close not only the temperature at which dehydration begins and ends, but also in the same comparison made ground in the DTA analysis, it is evident that there is a corresponding loss of stoichiometric water. Samples Pragofos 1900 and Pragofos 2400 differ from this behavior. Sample the beginning of Pragofos 1900, dehydration shifted to about 130 °C, but again the end of dehydration ends at 180 °C, but the amount of dehydrated water is significantly smaller. Sample Pragofos 2400 begins to dehydrate at 150 °C and ending up dehydrated at 220 °C (again with the volume of water abstracted sub-stoichiometric). However, with this curve, there's yet another endothermic process at about 310°C. The
question is, what marks this process, if other (residual) dehydration, and phase change in our hurealite crystals, which due to its complexity and the existence of numerous structural forms is possible.

Plasma corundum coating deposition proceeded in a standard procedure described in [6]. In the plasma torch power of 150 kW and the spraying distance parameters) SD = 300 mm and the feeding distance FD = 80 mm and administered amount of Al2O3 40 kg/h have been developed coating thickness from 0.1 to 0.3 mm. Metallographic cross section of a steel washer, and corundum interlayer phosphate coating on Fig.8. Deposition rates and flow of molten material were chosen to avoid overheating and dehydration of the phosphate crystallohydrates. Substrate temperature and total deposition temperature was controlled by the thermal imager Micro-Epsilon TIM 160. The initial alumina layer with a thickness of about 15 mm and thermal conductivity of 25-30 W m⁻¹K⁻¹ it has already acted as a thermal barrier, the increase in other layers of coating a scanning mechanism. The footage imager (Fig.9) shows that the temperature of the substrate at the beginning and end of deposition ranged from 94 °C to 206 °C.

The decisive test for measuring the quality of cohesion between coating and steel substrate has been cited by tearing-off according to ČSN EN 4624 for pull-out device COMTEST OP 1/2, which provides a special...
bonding glue Loctite Hysol the 3425. The test includes measurement of the minimum bond strength between the test roller diameter of 15 mm and plasma-sprayed surface, which causes separation of the specimen and determine the characteristics of the quarry. Fracture surface is evaluated using the electron microscope TESCAN VEGA to fully experience the EDS analysis. Records obtained fracture stress tests will be with regard to a wide range of results limited to coatings that exhibit the greatest resistance to spontaneous dehydration at elevated temperature. According to DTA are coatings "tree-cations" phosphate (Pragofos 1900) and manganese phosphate (Pragofos 2400). Performed stress tests on samples of phosphated steel with a plasma sprayed alumina ceramics were correlated with the values measured for alumina coatings on stainless steel ČSN 17021 (AISI 410), which range from 17-70 MPa [7].

4. CONCLUSION

In this paper we present the first information about the adhesion of ceramic coatings on steel materials class ČSN 10327 bearing the phosphate layer. The systems are not only complicated multiphase formation of phosphate coatings, but also applied to the ceramic aluminum oxide may contain, in addition corundum structure and phase delta-Al2O3. The research program also includes coating of zirconia and mullite which increase surface wear resistance of structural materials and the high corrosion resistance is no doubt. The data collected will be used to refine the selection of appropriate interlayer between the concrete and steel with ceramic coating so that several times the abrasion resistance increased slightly porous ceramic coating has been compromised corrosion resistance of the metal substrate. The best is yet seems phosphate coating ready for application of thermal technologies Pragofos 1900 ("three-cations" phosphating) and coating technologies ready Pragofos 2400 (manganese phosphate coating), while for the phosphate coating is necessary to investigate the phenomenal endothermic behavior at temperatures between 310°C to 350°C, in order to determine the upper temperature limit of application. The values of the ceramic coating adhesion to steel surfaces such treated materials are in the range 10-20 MPa. Cohesive fracture was more pronounced in samples coated manganese phosphate. It was found that corundum coating bond strength with the phosphate interlayer is higher than the bond strength of phosphate coating with the underlying steel material.

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REFERENCES