APPLICATION OF X-RAY DIFFRACTION IN DEVELOPMENT OF NEW TYPE OF MOULDS FOR PRODUCTION OF REFRACTORY AND HIGHLY ABRASIVE OBJECTS

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Ceramic materials can be used due to their high hardness and chemical stability as both the wear and corrosion resistant coatings. Their deposition on moulds for manufacturing of objects from refractory and highly abrasive materials is challenging, because they are traditionally made from hard-to-blast case-hardened tool steels with hardness exceeding 60 HRC. The pressing process imposes further stringent requirements on the coating microstructure; especially in respect to its homogeneity, cohesion and wear resistance. Considering results of laboratory analyses of residual stresses and roughness of blasted surfaces, mould plates from low-carbon C45 steel were sprayed with five different ceramic materials by water stabilized plasma gun. The testing of the moulds with plasma coatings was performed on-site in a factory under standard pressing conditions.

Keywords:
ceramic coatings, plasma spraying, roughness, residual stresses, adhesion, phase composition

1. Introduction

Refractory materials are one of the indispensable essences of the industrial era. No steel works, glass works or even a residential building could exist without them. Their ability to isolate hot air, melted glass or melted iron and at the same time contain them is truly vital. However, their existence comes for a price, most refractory materials are highly abrasive and their manufacturing is a challenge as they cause extreme wear of the contact surfaces during their pressing. The traditional and most common attitude to tackle this issue was to use steels with highest possible hardness, which has been successfully fulfilled by case-hardened tool steels with hardness approaching 65 HRC.

Another option would be to employ a wear protective layer, most conveniently in a form of a coating deposited on mould parts exposed to the pressed mixture. There exists a variety of coatings intended for improvement of wear resistance, so far very good records in this field have HVOF (High Velocity Oxygen Fuel) cermet coatings of tungsten carbide grains in either cobalt or chromium matrix [Wayne 1994] or chromium carbide grains in nickel-chromium matrix [Matthews 2004]. The highest abrasion resistance has been reported for sintered WC-Co with hardness about 2400 HV [Stern 1990] or cold spray WC-Co coating with low porosity with 2050 HV hardness [Kim 2005]. Nevertheless, the cost of sintered mould plates or cold spray coatings renders their usage in the fiercely competitive environment of refractory materials producers practically impossible. The solution which was proposed rises from a similar pattern, but instead of sintered mould plate, cold spray or HVOF coating, much cheaper plasma sprayed ceramic coatings are to be used.

Plasma spraying is capable of complete feedstock powder particles melting and, thus, facilitates creation of ceramic coating via their solidification on the substrate which is a distinctively different mechanism than sintering, cold spray or HVOF. The incurred microstructure of plasma sprayed coating can be characterized by the so called "splats" or solidified particles [Sampath 2004], number of inter- and intra-lamellar cracks, pores and regions of incomplete bonding are usually present as illustrated in Fig. 1. In this research, water stabilized plasma spraying (WSP) [Chraska 1992] was involved. Such plasma jet is distinguished by high jet velocities and by high enthalpy. The temperature of the jet can exceed 25 000 K. The parameters of WSP system result in special performance characteristic in plasma spraying, namely high coating material feed rates, typically tens of kg per hour, or spraying of materials with high melting points.

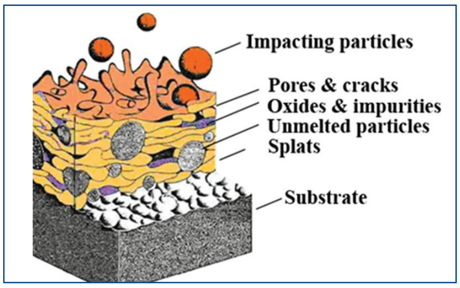

Figure 1. *Typical features of the thermal spray coating microstructure [Herman 1988]*

Residual stresses in the coatings and in the coating/substrate interface significantly affect their performance. Quenching residual stresses are present within the coating as a consequence of rapid solidification of the impacting molten particles on the substrate or previously deposited splats and generally lead to tensile stresses. A mismatch in thermal expansion of the coating and substrate material can give rise to thermal stresses with maxima usually at the coating substrate interface. Transformation residual stresses in the thermal spray coatings originate from an array of possible phase transformations linked with volume changes. In some cases, relaxation of the residual stresses may take place, which is accompanied with evolution of micro and macro cracks, mutual splat sliding or plastic deformation [Bose 2007].

The crucial phenomena closely intertwined with plasma coating quality are adhesion to the substrate and cohesion between splats which take place because of four mechanisms, namely mechanical, chemical, dispersive and diffusive. The most common adhesion mechanism of thermal spray coating adhesion is mechanical anchorage of the splats to the irregularities of the substrate [Balic 2009]. This mechanism is supported by the substrate surface features, especially by the surface roughness by which any type of bond either chemical, dispersive, diffusive or mechanical will be more effective. The substrate surface area may contain features which allow molten material to flow into, fill and solidify. Therefore, the essential parameter for coating adhesion to the substrate is the substrate's roughness.

2. Experimental

Since the lower limit of substrate surface roughness prior to plasma spraying process is Ra = 7 μm and the blasting of the traditionally used tool steels in case-hardened state on-site of the spraying facility resulted only in the roughness lower than Ra = 4 μm, the technologists of the of Czech grade 12 or 14 which have a lower hardness.

2.1 Laboratory analyses

Therefore, the surface residual stresses and roughness of seven squared samples 50 × 50 × 3 mm^3, three from grade 12 and two from grade 14 subjected to various shot-blasting conditions attainable under laboratory conditions were investigated; parameters of laboratory shot-blasting are summarized in Tab.1.

sample	cutting operation	total mass of blasting particles, kg	pressure, MPa
12_AR	as received	---	---
12_4-8	shot-blasted	4	0.8
12_8-8	shot-blasted	8	0.8
12_8–12	shot-blasted	8	1.2
14_AR	as received	---	---
14_8-8	shot-blasted	8	0.8
14_8–12	shot-blasted	8	1.2

Table 1. *Shot-blasting parameters of the laboratory specimens*

The surface roughness was measured by laboratory tester *MITUTOYO SURFTEST 2000*. The arithmetical mean deviation of the roughness profile Ra was evaluated.

The residual stress measurements were performed with a θ-θ *X'Pert PRO* diffractometer in ω-arrangement with CrKα radiation. The line *{211}* of α-Fe phase was measured. Nine different tilts angles (ψ) from 0° to 63° were used. The $\sin^2\psi$ method was applied for determination of macroscopic residual stress [Kraus 2000]. The X-ray elastic constants $\frac{1}{2} s_2 = 5.95 \cdot 10^{-6}$ MPa^{-1}, $-s_1 = 1.325 \cdot 10^{-6}$ MPa^{-1} were used in stress calculations [Hauk 1997]. The single line Voigt function method [Delhez 1982] was applied for corrections of instrumental broadening and determination of crystallite size *D*. In order to analyse the stress gradients beneath the surface of the grade 12 specimens, the layers of material were gradually removed by electrolytic polishing.

2.2 Plasma spraying

Based on the laboratory analyses results, the real moulds were manufactured from the steel grade 12, namely 12 050, otherwise known as *C45* under its international specification. The dimension of the surfaces intended for the ceramic coatings deposition were 200 × 318 mm^2 and 200 × 118 mm^2 for lengthwise and crosswise mould plate, respectively. The surfaces' roughness after grease removal and corundum sand blasting exceeded Ra = 8 µm which was considered satisfactory for the plasma spraying. Five types of ceramic coatings were deposited using water stabilized plasma system WSP® 500 at Institute of Plasma Physics of ASCR. The feedstocks were five commercially available powders as seen in Tab. 2. The process of spraying was preliminary, without the necessary optimization of the process parameters, and was solely aimed at detection of the main modes of wear and load stresses and their effect on the coating and coating/substrate areas.

coating	feedstock
AH	alumina powder consisting of 96 wt. % corundum + 3 wt.% TiO_2 + iron oxides
EU	commercially available powder known as EUCOR (ZrO_2 + quartz + corundum)
ZR	zircon sand, i.e. $ZrSiO_4$
AST	corundum + quartz + TiO_2
CST	Cr_2O_3 + SiO_2 + TiO_2

Table 2. *Type of feedstock used for individual coatings*

In order to determine phase composition, all five coatings were subjects of phase analyses by X-ray diffraction. X-ray tube with copper anode was installed in the *PANalytical X'Pert PRO* multi-purpose diffractometer. Parameters of the diffraction measurements with CuKα radiation were as follows, 2θ range from 10° to 85°, step size 0.05 °2θ, counting time 80 s, beta filter made from nickel thin sheet placed in front of fast *RTMS* (real time multiple strip) detector. The samples were measured in standard Bragg-Brentano geometry and their surfaces were positioned by laser triangulation distance determination with 5µm precision.

2.3 Factory testing

Mould plates with ceramic coatings were assembled into five moulds in a Moravian producer of refractory products and used in real production of cuboid shaped silica bricks from ganister mixture. Each mould was disassembled after thirty bricks were pressed and the coating surfaces were visually examined. Consequently, the mould plates were cut into five pieces by water jet in order to obtain experimental samples which would fit into chamber of scanning electron microscopy (SEM) and sample holder in X-ray powder diffractometer.

3. Results and their Discussion

3.1 Analyses of laboratory samples

Tab. 3 contains results of surface residual stress measurements (σ_L, s_T) performed in two mutually perpendicular directions, the parameter *FWHM* of *{211}* α-Fe diffraction line, and the arithmetical mean deviation of the roughness profile Ra. The inaccuracy or experimental error is approx. 0.05 °2θ for *FWHM* and less than 15 MPa in case of stress values in Tab. 2

sample	σ_L, MPa	s_T, MPa	<FWHM>, deg	*D*, nm	*Ra*, µm
12_AR	–31	–37	1.41	248	
12_4-8	–338	–347	2.51	48	2.65
12_8-8	–270	–286	2.64	43	3.84
12_8–12	–175	–186	2.78	36	4.33
14_AR	33	–52	1.79	109	
14_8-8	–441	–420	2.94	27	2.42
14_8–12	–404	–391	3.09	24	2.60

Table 3. *Values of surface macroscopic residual stresses σ_L, s_T and FWHM of {211} α-Fe diffraction line, crystallite sizes D and roughness parameter Ra determined on laboratory surfaces*

The back-reflection X-ray diffraction patterns corresponding to diffraction of the spectral doublet $CrK\alpha_1\alpha_2$ on crystallographic planes *{211}* α-Fe (see Fig. 2) of surface crystallites show isotropic fine-grained polycrystalline structure with plastic deformation, i.e. the diffraction line is broad, continuous, and has homogeneous intensity around its perimeter. The shot-blasting lead to higher roughness of the *C45* surfaces and, hence, these specimens were the subjects of further examination.

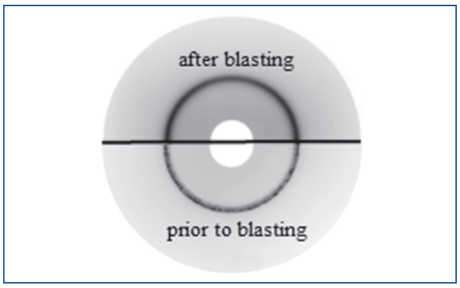

Figure 2. *Comparison of back-reflection X-ray diffraction patterns from athe surfaces of the 12_4-8 (upper) and 12_AR (lower) samples*

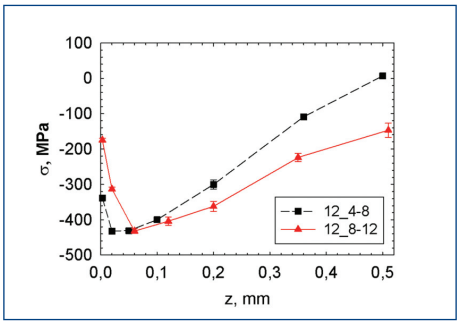

Figure 3. *The depth profiles of macroscopic stresses in surface layers of investigated samples.*

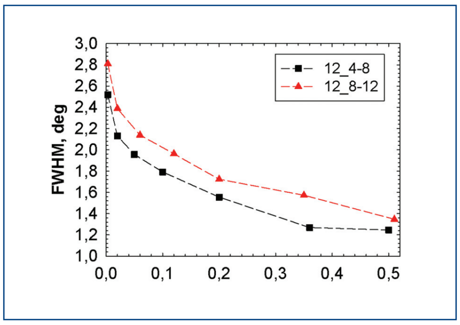

Figure 4. *The distributions of width of {211} α-Fe diffraction line beneath the blasted surfaces*

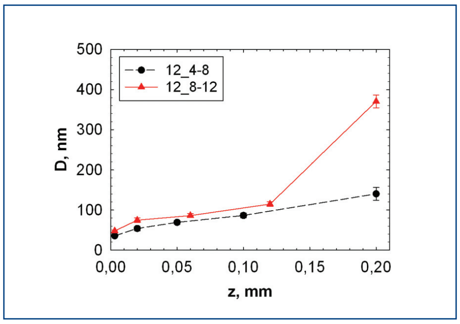

Figure 5. *The depth profiles´ courses of crystallite size D determined from the α-Fe {211} line profiles*

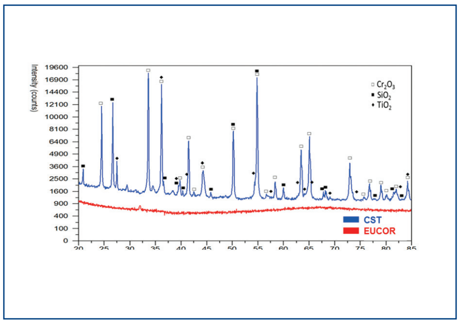

Figure 6. *Results of X-ray diffraction phase analysis of crystalline CST and amorphous EU coatings*

On the surface of all the investigated samples was identified the so called centrally symmetric biaxial state of favourable compressive residual stresses, i. e. $\sigma_L \approx s_T$ (Table 2). In this case, depth investigation was realised only in the longitudinal direction. Depth profiles of monitored values σ and *FWHM* were determined (Figs. 3 and 4). The crystallite size *D* depth profiles (Fig. 5) calculated from the *{211}* α-Fe diffraction lines according to [Kraus 2000] give additional information about the influence of blasting on the real structure of the samples under investigation.

3.2 Phase analyses of WSP coatings

Phase compositions of all five coatings were established prior to their testing in factory and is summarized in Tab. 3. As expected, only the coating *EU* was fully amorphous as seen in its comparison with *CST* coating in Fig. 6.

coating	phase composition
AH	corundum and γ-Al_2O_3
EU	amorphous
ZR	tetragonal and monoclinic ZrO_2
AST	corundum, TiO_2 (rutile & anatase), SiO_2, Al_2TiO_5
CST	Cr_2O_3, SiO_2, rutile

Table 4. *Phase composition of sprayed coatings*

3.3 Investigation of mould plates after factory testing

During the pressing process of cuboid shaped silica bricks from ganister mixture, the particles of the mixture find their way into the space between the mould plates and pressing plunger which causes severe wear of the plates. The pressing stress was set to 50 MPa.

All the surfaces exhibited macroscopic traces of wear after pressing of 30 bricks, however, there are marked differences between *AH, EU, ZR* on one side and *AST, CST* coatings on the other. This was also confirmed by SEM fractografic analyses of the samples cut by water jet. Adhesion of the first group of coatings was good and no delamination of the coating was observed, but cohesion damage and splat crushing was found by the SEM in the area of severe wear as seen in Fig. 8. In comparison, the area where the wear was not so severe, the splat crushing did not took place as seen in Fig. 7. The much harder *AST* and *CST* coatings showed improved cohesion resulting in a rather large extent of coatings' delamination so that visible areas of the substrate were exposed.

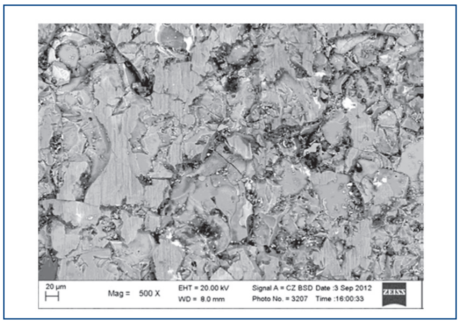

Figure 7. *SEM image of the surface of the EU coating where the severe wear did not take place. The characteristic splat microstructure of the WSP coating is seen*

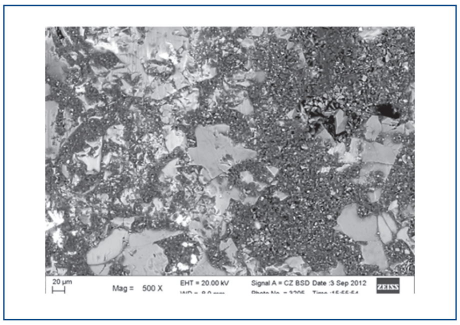

Figure 8. *SEM image of EU coating surface which was exposed to severe wear. Splat crushing, clearly visible as dark grey regions in the image, is a distinctive feature of the area which was in contact with the pressed mixture*

4. Conclusions

From the performed experiments and their ensuing discussion the following conclusions could be derived:

- Blasting with corundum sand of case-hardened tool steels does not bring sufficient roughness of the surface and, hence, does not facilitate their spraying with wear resistant ceramic layer.
- Laboratory tests proved that low-carbon *C45* steel can be used as a substrate for plasma coating.
- Hook-like residual stress depth distributions of both shot-blasted laboratory samples correspond to the stress field which is considered as favourable for service life prolongation and is even recommended in the European standard for pre-treatment of surfaces for thermal spraying [EN 13507 2010].
- The shot-blasting results in decrease of the crystallite size *D* on the surface when compared to the bulk, which is seen in Fig. 5 and to the as received surface state as well, which is visible in Fig. 2.
- Four crystalline and one amorphous thermal spray coating were deposited on the mould plates made from *C45* steel as seen in Tab. 3 and Fig. 5. Nano-crystalline *EU* coating which is distinguished by higher hardness of approximately 1600 HV, roughly double the hardness of amorphous *EU*, and which is possible to deposit using WSP technology [Chraska 2008], was not obtained in this preliminary study. For nano-crystalline *EU* coating, deposition condition will have to be optimized, namely in terms of thermal treatment of the deposited surface during or after deposition.
- Replacement of case-hardened tool steels in moulds for refractory materials pressing by ceramic plasma coating is a challenging task, and for the time being, has not bring the coveted prolongation of service life. The heterogeneous coatings' microstructure at the present state is not suitable for improvement of wear resistance. Hence, the more expensive HVOF coating and modification/post-treatment of deposition conditions for WSP coatings will be tested in the next phase of the project.
- The low-carbon *C45* steel is a suitable substrate for spraying of alumina, eucor and zirconia sand powders. The deposited coatings have good adhesion to the substrate. On the other hand, hard ceramic coatings *AST* and *CST* exhibit not sufficient adhesion to the substrate of *C45* steel and substrate/coating optimization has to be performed.
- Testing of the coatings' wear resistance in real production environment leads to cohesion damage of the coatings which can be eliminated by plasma spraying process optimization which will be carried out in the follow-up of this study.
- Testing of selected preliminary WSP deposits in the conditions of the real production enabled identification of the most severe loading conditions and will facilitate further development of the wear protective coatings tailored/designed for this application.

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