BORONIZED STAINLESS STEELS WITH ZIRCONIA COATINGS

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Abstract

The abstract is describing results of characteristics studies of ceramic coatings made from corundum-baddeleyite ceramics, on deposit, boronized corrosion-proof steel AISI 303. Boronizing of steel surface is a technology known for tenths of years. In addition to higher surface strength leading to abrasion resistance some versions of boronisation may contribute also to corrosion-proof protection of the steel. Benefits of these applications can be multiplied by formation of ceramic coatings with higher strength, fire resistance and lower surface porosity. Borides in such a case form on the steel interlayers with suitable coefficient of linear thermal expansion to ceramic coatings which are applied by the method of thermal spraying or plasma spraying. Conditions of boronizing by the method of reactive fusion of boron from boron carbide and lanthanum hexaboride are described so the formation of Fe_2B is preferred to FeB, which is more fragile and the structure of which does not comply with conditions for perfect adhesion of modified zirconium ceramics. Perfect adhesion connection of needle-like anchored interlayers of Fe_2B in corrosion-proof steel AISI 303 prepared by reactive diffusion of boronizing media without activating agents under temperature 1000 °C and with exposure 2 - 4 hours is proving during pin-off tests values of the bond strength 20 MPa - 25 MPa. Ceramic coatings made from Eucor Al_2O_3-ZrO_2 formed on these interlayers have bond strength value 9 MPa - 13 MPa. Thermic cycling in the interval 100°C - 600 °C confirmed good bond strength of coatings with the base steel. The static cycling under higher temperatures (600-1000 °C) proved already higher number of failures of bond strength and mechanical destructions of coatings.

Keywords: Boronised steel, plasma spraying, ceramic coatings, bond strength; zirconia coatings

1. INTRODUCTION

Use of engineering materials on the steel basis in new fields of applications is still rather limited by operational temperatures to which are permanently exposes these materials. Development of heat-resistant steels for steam or combustion turbines or functional parts of other power machines has temperature limitation due to their chemical composition. Further pushing forward of temperature limit of steel usability for structural purposes can be obtained by formation of protective heat-resistant coatings, which are among possibilities of passive protection of functional surfaces of parts, thus providing them with required features in wide spectrum. For example thermal barrier coatings (TBC) must have low value of thermal conductivity, relatively high coefficient of thermal expansion, chemically inert characteristics, mechanical stability to thermal fatigue and good resistance to tear and wear.

Among successful technologies of preparation of surface protection of materials functioning in the environment with extremely high temperatures or in the presence of corrosion or oxidizing media, belong plasma deposition processes [1]. Plasma deposition is allowing formation of functionally graded materials (FGM) on the substrate surface, however the main issue at point is the strength (bond strength) of the joint of plasma formed coatings on the counterpart, i.e. steel material. Among general characteristics of coatings belong mainly their chemical composition, their porosity, strength and roughness. Selective feature which must be checked for each combination separately is mainly the bond strength, markedly depending on the specific couple of interfaces coating - counterpart [2].

With regards to order difference of coefficients of linear thermal expansion of metals and ceramics the problematic issue of bond strength of ceramics with the metal with subsequent application under higher temperatures can be solved by several methods. One of them is formation of one or several transition interlayers with gradually reduced dilatation coefficients α_1, α_2 (x 10^{-6} K^{-1}), which is technologically and of course economically rather demanding. The cheapest method of increased adhesion of coatings to the counterpart steel is therefore roughening of the counterpart, for example by brushing or abrasive agent blasting.

Roughening of the surface of steel materials and subsequent plasma deposition of ceramic coating yet still leads to formation of many failures in the structure of both the coating and mainly of the joint interlayer. Formation of more suitable, for example chemical joint between ceramic coating and steel materials is possible with iron compounds with suitable dilatation coefficient. As such compounds can be considered ironborides or iron hemiborides - FeB and Fe_2B. Specific method of needle-like anchoring of mainly the phase Fe_2B on the steel surface (see **Fig. 1** and **Fig. 2**), given by reactive-diffusive mechanism of its formation, is providing perfect connection with the base and at the same time provides premise for selection of suitable ceramic spraying, which does not degrade by cyclic temperature changes due to different coefficient of linear thermal expansion. [3,4].

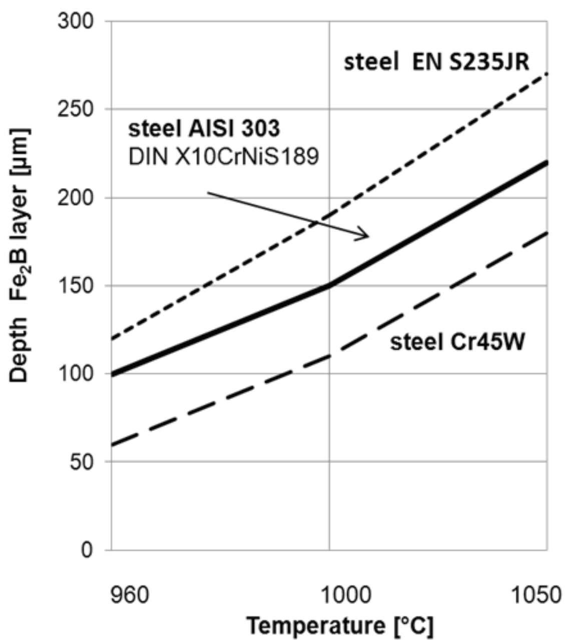


Fig. 1 The thickness of the boride layer after 4 h diffusion boronizing

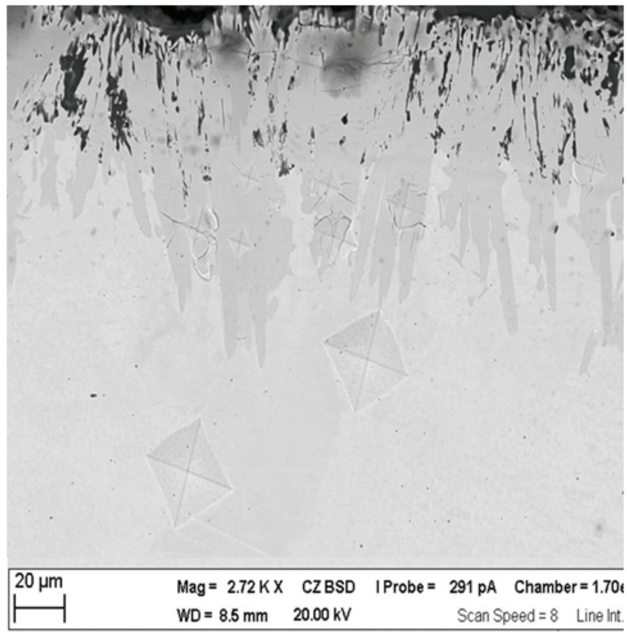


Fig. 2 Morphology of Fe_2B and FeB phases in cross-section surface on the steel AISI 303

If we compare metallographic section of vertical cut of boronized layer with general record of roughened surface with use of profilometer (for example Mitutyo or Hommel roughness tester), we can see obvious equality of needle-line anchoring of iron hemiboride with the roughness profile. Differences are only in cross direction dimensions. Boronizing can anchor the iron hemiboride coating up to the depth of about 250 µm, which cannot be reached by any other roughening method. Roughening to the value around $R_a \approx 10$ µm can be reached only on the primarily formed boride layer on which is deposited another coating. In such characterised boride interlayer can be calculated the graduated dilatation coefficient from the value $\alpha = 12.0 \cdot 10^{-6}$ K^{-1} to the value 7.85 10^{-6} K^{-1}.

2. MATERIALS AND METHODS

Steel plates AISI 303 were blasted with corundum abrasive F 240 to reach the surface roughness $R_a \approx 6$ µm - 8 µm. They were subsequently boronized in individual fills B_4C, LaB_6 and elementary boron, without activating agents, under temperatures of 1000 °C for the time of 2 hour and 4 hours. Temperature rising and cooling was regulated with the speed 10 $°C{\cdot}min^{-1}$. One of the targets of this experiments was to assess how the boronizing medium participates on formation of the desired layer Fe_2B or on higher ratio of Fe_2B/FeB. After the boronized substrates were coated with corundum-baddeleyite ceramics by the plasma spraying method by plasma generator WSP®H-500 [5].

After examination of parameters formed by boride-ceramic coatings we measured their adhesion to the steel counterpart and also their mutual adhesion. Initial materials and products were analysed by XRD method on the diffractometer PANanalytical X´PERT PRO. Surface roughness was measured by the Mitutyo roughness tester SJ 210. Metallographic shots were taken by the scanning electron microscope EVO MA 15 (Carl Zeiss SMT). Bond strength was according to the standard EN ISO 4624 2003, the counterpart was made from titanium. Content of elements in the area of bond strength failure was determined by the areal XRF analysis on the device PANanalytical-Axios FAST.

3. RESULTS AND DISCUSSION

The X-ray diffraction analysis found out that boronizing in various types of boronizing media brings under equal exposition conditions different final results. The least suitable proved to be boronizing with use of elementary boron, where the predominant formed phase was FeB_{49} (PDF ref.code 00-039-0418), then the less desired fragile phase FeB and then the Fe_2B phase in the ratio of about 55:40:5 (after mechanical removal of residuals of unreacted boron). Boronizing with use of LaB_6 gave rise to formation of surface layer LaB_4, under which was found the predominant phase Fe_2B. Study of this combined layer will be subject to a separate article. Boronizing in the fill B_4C passed off with standard results with preferential formation of the iron hemiboride phase Fe_2B. From metallographic cross-sections were found average depths of formation of iron hemi-boride and iron boride layers and the microhardness HV was measured in relation to the distance from surface. Average depth of needle-like anchoring of borides is shown in the graph on **Fig. 1**. (The graph is for information containing other values obtained during measurement on other materials too). Morphology of ferroborons prepared in the fill B_4C is shown on **Fig. 2**, together with introduction of indents by Vickers indenter. Measurement found the value of strength of corrosion-proof steel 3.29 GPa (329 HV) and E-modul 248 GPa, the hardness was increasing towards the surface layer, in the place of anchored needles the iron hemi-boride Fe_2B reached the maximum value of 16 - 17 GPa.

On such treated surfaces was applied the ceramic coating of corundum-baddeleyite ceramics by plasma spraying (see **Fig. 3** and **Fig. 4**) from commercial material Eucor of company Eutit [6]. Description of plasma deposition with apparatus using water stabilized plasma from the generator WSP® was introduced in many previous publications released by UFP, e.g. [7,8]. In this specific case were applied parameters: current 500 A, voltage 300 V, flow of carrier gas 240 $l{\cdot}h^{-1}$ at 0.30 MPa, feeding distance 32 mm, spraying distance 350 mm, production capacity 10 $kg.h^{-1}$, powder granularity 63 µm -100 µm.

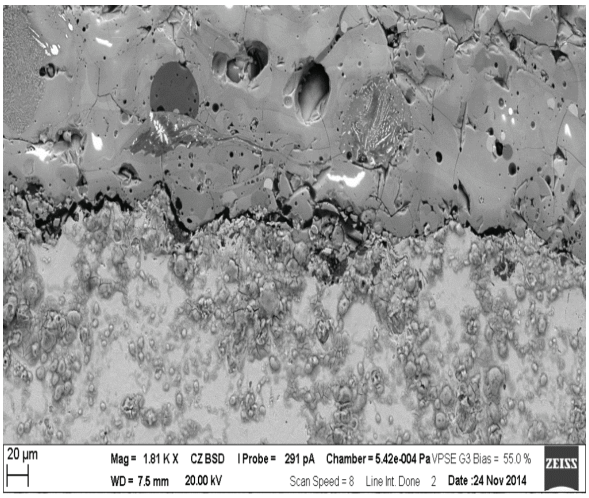


Fig. 3 Ceramic (Eucor) coating on steel AISI 303

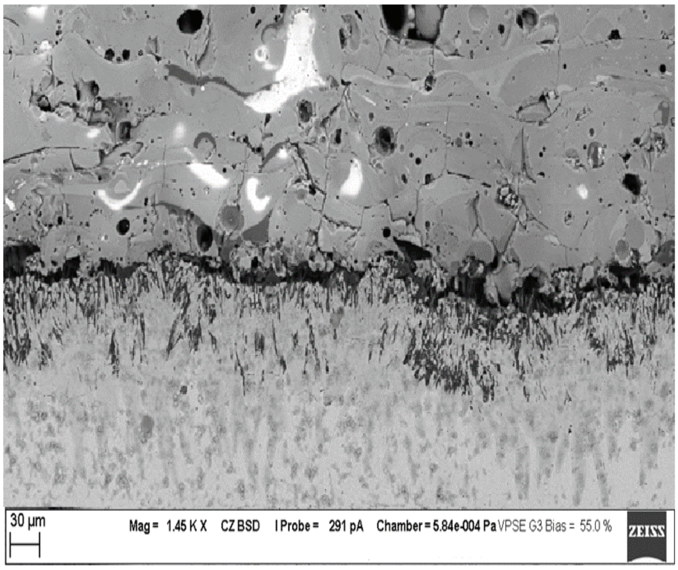


Fig. 4 Ceramic (Eucor) coating on Fe_2B interlayer

Obtained samples were analysed according to the following scheme (**Fig. 5**). Pull-off tests for adhesion were performed according to the standard EN ISO 4624 2003. Pull-off device part of the pull-off test was made from titanium in order to simplify the subsequent analysis of pulled-off ferroborone layers by XRF method by determination of Fe content.

Experiment **A**: Substrate steel AISI 303 (R_a1 = 7.94 µm; R_q= 10.7 µm; R_z = 60.5 µm), Adhesive Loctite 3425 A&B Hysol, pull-off device with titanium counterpart cylinder and screw (R_a2 = 8.27 µm; R_q= 10.8 µm; R_z = 58.5 µm).

Experiment **B**: Substrate steel AISI 303 (R_a1= 7.94 µm) Eucor ceramic coating (R_a3 = 25.4 µm; R_z = 32.3 µm; R_q = 155,1 µm). Adhesive Loctite pull-off device, titanium cylinder (R_a2 = 8.27 µm).

Experiment **C**: Substrate steel AISI 303 (Ra1=7.94 µm) FeB/Fe_2B interlayer (original surface R_a4 = 14.3 µm R_q = 17.8 µm; R_z = 79.9 µm and after blasting R_a5 = 16.6 µm; R_q = 21.0 µm; R_z = 97.2 µm) Adhesive Loctite, pull-off device, titanium counterpart cylinder (R_a2 = 8.27 µm).

Experiment **D**: Substrate steel AISI 303 (R_a1 = 7.94 µm), FeB/Fe_2B interlayer (R_a5 = 16.6 µm), Eucor ceramic coating (R_a6 = 10.6 µm; R_z =13.4 µm; R_q = 65.7 µm), Adhesive Loctite, pull-off device with titanium counterpart cylinder (out of plane) (R_a2 = 8.27 µm).

Experiment **A** verified behaviour of the pull-off device. Pull-off strength of the adhesive Loctite was numerically the highest (26.8 MPa) and the joint of specimen broke into its parts in the middle of the Loctite layer. XRF analysis confirmed that major part of the adhesive (checked by the ratio Ba Ti - compounds of Ba^{II} are the main inorganic components in the adhesive) rested on the counterpart titanium cylinder (out-of-plane) with higher value of surface roughness R_a and the smaller part on the surface of steel substrate with lower value R_a.

Experiment **B** followed the bond strength of ceramic coatings Eucor with steel substrate. Value of the pull-off was 9.8 - 12.7 MPa) and again the destruction appeared in the Eucor mass. The effect resembled very much delamination of the layered ceramics, as the ceramic coating from Eucor was prepared by plasma spraying raster procedure. According to areal XRF analysis more Eucor remained on the counterpart Ti- cylinder (out-of-plane).

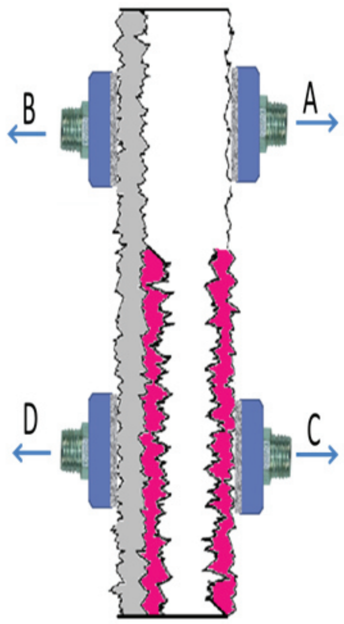


Fig. 5 Scheme of coating adhesion measurement on the boronized steel

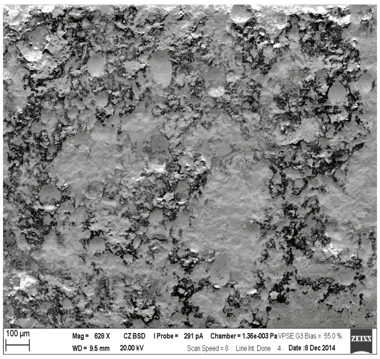


Fig. 6 Surface of counterpart titanium cylinder with Loctite adhesive and Fe_2B fragments

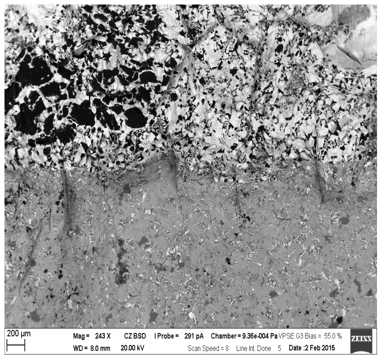


Fig. 7 Eucore coating on FeB/Fe_2B substrate

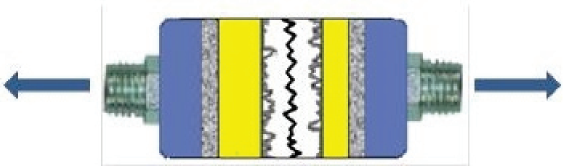
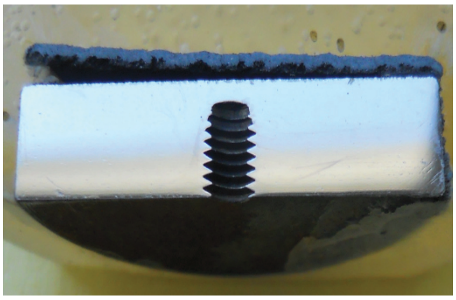


Fig. 8 Scheme of pull-of test: Ti-cylinder-Loctite adhesive-Eucor-FeB-Eucor-Loctite-Ti-cylinder

It follows from the above, that strength of the eucor-steel joint is higher than tensile strength of eucor ceramics. Relation between this strength and impact on its value by primary roughness in the joint /on the interface/ has not been in this case measured quantitatively but proved logic and followed also from our similar measurements performed for example on phosphate systems [9].

Experiment **C** was monitoring the bond strength of boride surface layer with the steel counterpart. On the surface of titanium-counterpart cylinder were identified by XRF method and microscopically (**Fig. 6**) particles of FeB/Fe_2B, caused by the pull-off from the fragile boride surface. Bottom part of anchored needle-like formations of the phase Fe_2B remained intact. This chemical-diffusion joint is maximum from the aspect of the bond strength. Breaking or fracturing of the upper part of boride layer in the contact joint with the adhesive Loctite is caused by the nature of boride layer formed in the initial phase of the boronizing in the fill. This opinion was verified by another experiment, when primary, partially cracked and porous boride layer of the thickness ≈ 150 µm was first metallographically ablated by about 10 µm and subsequently blasted for the roughness R_a = 9.34 µm. The pull-off test then confirmed higher bond strength of the joint FeB_x-Ti counterpart cylinder up to the value 8.9 MPa. Another experiment for this phase was performed by preparation of the flat target from ferroborone FeB with surface roughness R_a = 10.9 µm; R_q =13.5 µm; R_z = 66.9 µm by the SPS method. This target was in SPS device from both sides provided with surface Eucor layers, sintered under the temperature 1400 °C and the pressure was 60 MPa (see **Fig. 7**). The assembly as shown on the **Fig. 8** (schema) was subjected to a loading test. The boride target was pulled apart about in the middle (bond strength about 3.46 MPa), in the Ti-counterpart cylinder remained residuals of FeB connected with intact Eucor and adhesive. This confirmed that adhesion or chemical bonding of ferroborone with Eucor is stronger than the mechanical tensile strength (out-of-plane) of fragile phases of ferroborones on the surface of boronized steel. Experiment **D** was monitoring strength of connection between ceramic eucor coating and layer of boride on the steel surface. From obtained values of bond strength followed the information that adhesion in the couple Eucor-Fe_2B is higher (7.8 MPa - 8.9 MPa) than tensile strength of ferroborone. Destruction caused by the tensile stress appeared again in the boride layer.



Steel substrates with boride interlayer and external coating from corundum-baddeleyite ceramic were subjected to cyclic heating in the interval 20 °C - 600 °C with temperature gradient of heating 100 $°C.min^{-1}$ and free cooling 30 min. There were no noticeable changes. During thermic cycling under higher temperatures (600 °C - 1000 °C) was already damaged the bond strength and mechanical destruction of coatings appeared. Picture on **Fig. 9** demonstrates high gradient of tensile residual stress in the coating.

Fig. 9 Destruction of ceramic coating during cycling under 1000 °C

4. CONCLUSION

Formation of transition layer of Fe_2B on the surface of steel substrates AISI 300 is an advantageous technological operation prior to application of hot or plasma spraying. It is possible to reach remarkably higher bond strength of coatings, in particular for cases of further cyclic thermal loading. The interlayer Fe_2B was applied with the coating from corundum-baddeleyite ceramics, the plasma spray of which is characterised by double-phase composition, mostly from alpha-Al_2O_3 and monoclinic modification of ZrO_2 and high quotient (to 90 %) of amorphous component. Such coating is reliably resistant to cyclic thermal loading up to the temperature of 600 °C. Under higher temperatures occured another important diffusion of boride in the steel connected with stoichiometric loss of iron hemiboride Fe_2B on the contact interlayer. Residual tensile stress in the ceramic coating would then cause destruction on the interface with boride layer.

ACKNOWLEDGEMENTS

This research has been supported by Czech Science Foundation, project GA ČR No 104 / 15-22670S (Experimental and numerical analysis of bond behaviour between steel reinforcement and Ultra High Performance Concrete (UHPC)).

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