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BORONIZED STEELS WITH CORUNDUM-BADDELEYITE COATINGS

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The paper describes preparation and properties of anti-corrosion and anti-abrasive coatings from corundum-baddeleyite ceramics deposited on surface of low-carbon boronized steel S235JRH-1.0038 (EN 10025-1) by plasma spraying method. Adhesive interlayers Fe_2B reaches bond strength of up to 20 MPa in the pull-off tests, the ZrO_2 - Al_2O_3 - SiO_2 coatings have a value of fracture adhesion of 4 - 6 MPa. Hardness of these ceramic coatings on steel is as high as 1 800 HV^{100} and its polarization resistance is 1 600 Ω/cm^2 to 4 000 Ω/cm^2.

Key words: boronized steel, corundum-baddeleyite coatings, anti-corrosion properties, plasma spraying

INTRODUCTION

Technology of diffusion boron coating has been known for several decades [1], however the knowledge about techniques for boron coating from gas phase [2, 3], electrolytic boron coating from melts [4], powder boron coating or from boron paste [4, 5] is still expanding. Another technology is the APSDA – atmospheric plasma spraying with diffusion annealing [6]. Each of the approaches has its positives and negatives such as toxicity of used gases or unfavorable ratio between boronizing medium and the coated component. Apart from enhancing surface hardness and thus also abrasive properties, some of the techniques can also contribute to the corrosion resistance. Benefits of these applications can be further increased by formation of ceramic coatings with higher hardness, heat and corrosion resistance and lower surface porosity. In such case, the iron borides on steel primarily create interlayers with suitable coefficient of thermal expansion compatible with the ceramic coatings which are then applied by the thermal spraying method.

If it is necessary to increase not only the abrasive resistance but also the adhesion of ceramic coatings at elevated temperatures or during cyclic thermal loading, boron coating acts as firm base on the iron, moreover provides transition pseudo-ceramic layer with favorable dilatation coefficient somewhere between steel and ceramics. Thusly characterized boron interlayers can then be calculated with graded dilatation coefficient of $\alpha = 12 \cdot 10^{-6}$/K up to $7{,}85 \cdot 10^{-6}$/K.

EXPERIMENTAL

Steel desks S235JRH-1.0038 [7] were sand blasted by corundum abrasive F 240, achieving surface roughness of $R_a \approx 6$ µm – 8 µm. Samples were then boron coated by burying them in B_4C or LaB_6 powder without activators at temperatures 900 – 1 100 °C for 1 - 8 h (gradient of 10 °C/min), with the aim to achieve formation of Fe_2B, rather than FeB which is more fragile and its structure is not well adherent for modified zirconia ceramics. Figure 1 shows the anchoring depth of iron borons prepared by diffusion boronizing in B_4C powder according to diffusion boronizing conditions. Figures 2

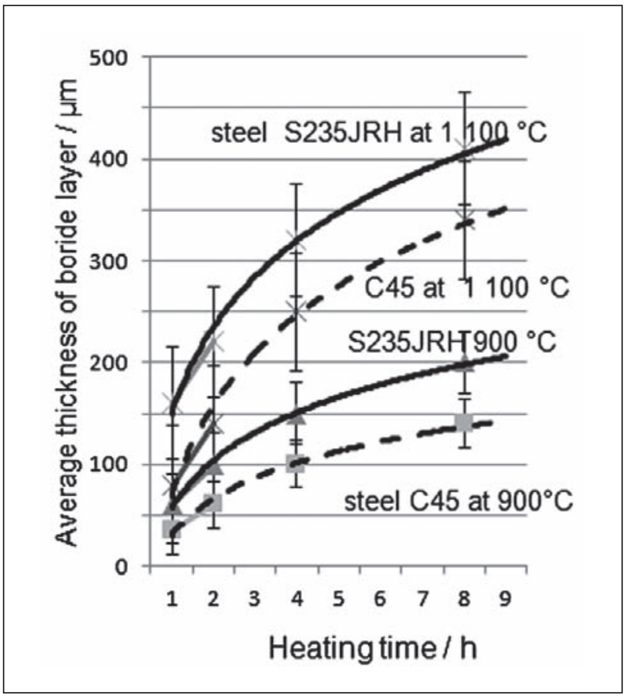

Figure 1 Fe_2B thickness dependence on temperature and time of boronized in B_4C powder for steel classes S235JRH and C45

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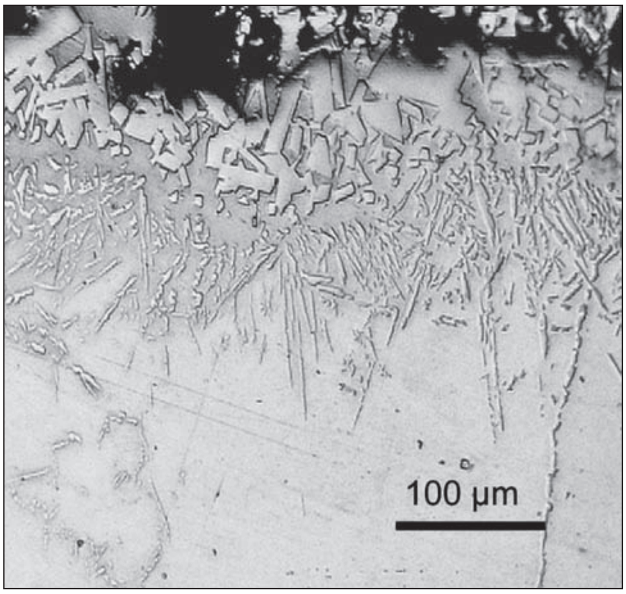

Figure 2 Cross-section of steel S235JRH 1.0038 boronized in B_4C powder; 2 h at 1 000 °C

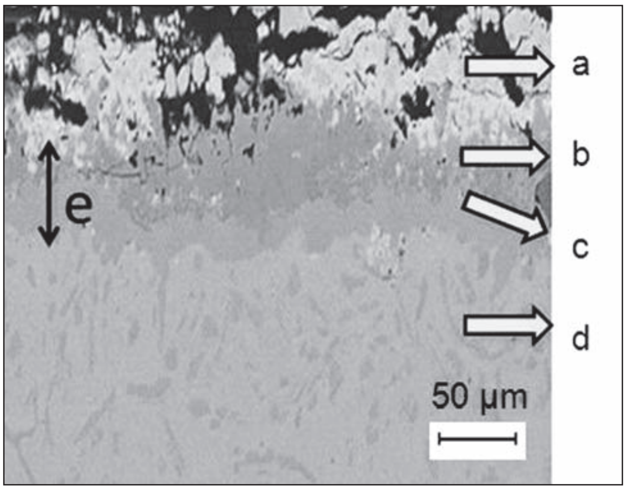

Figure 3 Cross-section of steel S235JRH 1.0038 boronized in LaB_6 powder, 2 h at 1 000 °C

a - mechanically unsteady layer of boron coating medium which needs to be removed (sand blasting, grinding) before plasma spray coating by ceramic
b - firm ceramic layer of LaB_6
c - boron layer composed of La-Fe-B_x
d - base steel S235JRH-1.0038- EN 10025-1
e - maximum anchoring depth of boron layer

and 3 show cross-cut morphology across the interlayers formed after 2 h in B_4C and LaB_6 mixture at 1 000 °C. Boron coated steel substrate was then plasma-spray coated by corundum-baddeleyite ceramics using plasma generator WSP®H-500 [8]. Details of the coating process are described in IPP CAS Prague materials [9,10].

After documenting structural and morphological parameters of these prepared boron-ceramic coatings, their adhesion to the steel matrix and also adhesion between interlayers was measured via the pull-off method on Comtest OP 1/2 device and Loctite 3425 A&B Hysol adhesive mixture. The products were analyzed by the XRD method on PANanalytical X´PERT PRO diffractometer. Surface roughness was measured using the Mitutoyo roughness tester SJ 210. Roughness value is the average of 10 measurements on 10 mm range. Structure of the layers was documented by scanning electron microscope EVO MA 15 (Carl Zeiss SMT). Bond strength was measured according to EN ISO 4624 2003 standard. For more precise determination of ratio between adhesion and cohesion, the concentration of elements was measured on both separated surfaces by the means of XRD analysis on PANanalytical-Axios FAST. The counterpart cylinder was made of titanium: thusly, the iron concentration was directly proportional to the amount of separated iron borides. Concentration of open pores in the coating was determined by water permeability measurement with starting pressure of 1000 mm H_2O.

RESULTS AND DISCUSSION

One of the goals of this experiment was to assess the role of boron coating medium on formation of desired Fe_2B layer, respectively on increasing the Fe_2B/FeB ratio. From the cross cuts, the average depth of FeB and Fe_2B formation and microhardness (HV) in relation to the distance from the surface was evaluated. The average depth of pin-like boron anchoring is depicted in Figure 1. For comparison, the plot also shows data measured on other materials. The hardness of the coating on S235JRH-1.0038 steel increased in the direction towards the surface layer and peaked around the boron pins (1 600 - 1 700 HV^{100}). Boron coating by the LaB_6 created a iron boron interlayer of completely different character, with maximum hardness up to 1 845 HV^{100}. The thickness of the boron coating was circa 40 µm – composed of mixture of Fe_2B, LaB_4 and surplus LaB_6; the thickness was estimated based on hardness measurement – the values below 1 000 HV^{100} indicate presence of base material (Figure 3). The results were then compared to the EDS data of boron distribution.

On thusly prepared boron coating, the corundum-baddeleyite coating was applied by plasma spraying of 0,3 – 0,6 µm thickness (see Figure 4) from commercial material (Eucor) [11]. The structure of the Eucor coating changes substantially by the plasma spraying method. The coating is characteristic for its multi-phase composition, mostly gamma and delta-ZrO_2 with high amount of amorphous phase, caused by SiO_2 contained in the Eucor. Based on the conditions – spraying distance (SD) and feeding distance (FD), the amount of amorphous phase can increase up to 90 % (lower SD) – see the diffractogram in Figure 5.

The hardness of crystalline Eucor coating reaches 1 650 HV^{100}, but is lower for the amorphous coating (1 070 HV^{100}). Permeability of porous Eucor coating depends on its thickness – incrased thickness leads to reduction of its open porosity. Water permeability with initial hydrostatic pressure of 1 000 mm H_2O was mea-

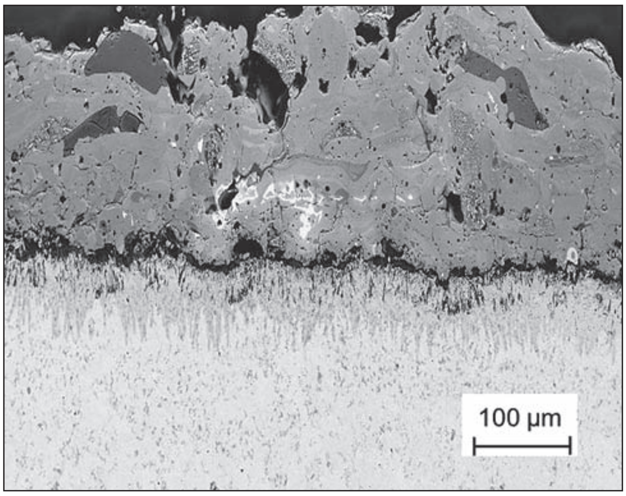

Figure 4 Cross-section of corundum-baddeleyite crystalline coating on the boronized steel S235JRH

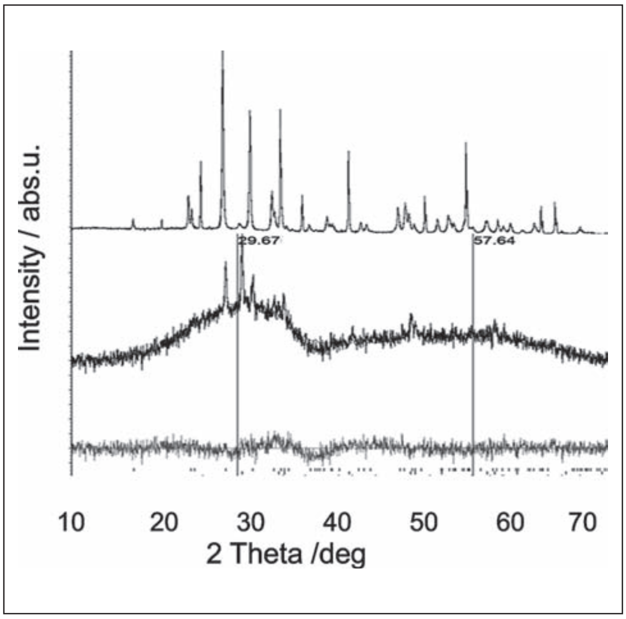

Figure 5 Diffraction pattern of crystalline and amorphous spray-coating of corundum-baddeleyite ceramics

sured on Eucor coating of the same batch of 0,4 mm thickness separated from temporary pad. Penetration of liquid (corrosion medium) through separated coating which can be considered a quasi-filter or ceramic membrane is described by following equation:

$$y = 65{,}29 \ln(x) + 3{,}32 \qquad (1)$$

where y is the amount of liquid (cm^3) passed through the filter/membrane of 1 cm^2 during x days (24 h).

The polarization resistance, measured by the means of EIS impedancy in the case of Eucor coating of 0,4 mm thickness on boron coating of 30 μm was 1 560 Ω/cm^2. Eucor coatings of higher thickness (more than 0,5 mm) were virtually impenetrable by the liquid and thus provide perfect anti-corrosion properties. Polarisation resistance was generally higher than 4 000 Ω/cm^2.

Pull-off tests were realized according to the schematics on Figure 6.

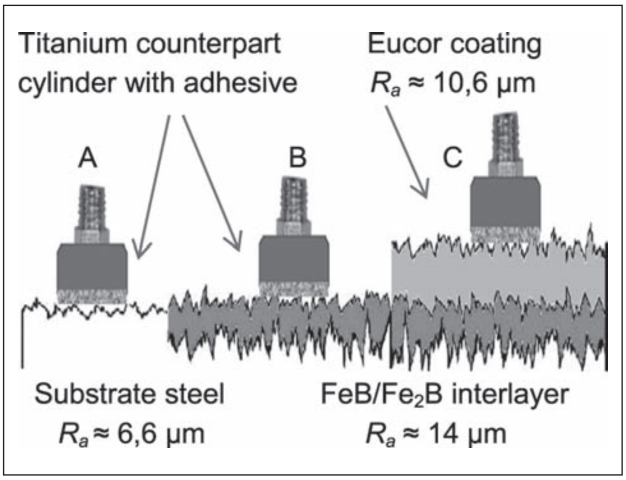

Figure 6 Scheme of bond strength measurement on the interface of individual layers.

A: steel ↔ adhesive Loctite,
B : steel ↔ Fe$_2$B
C : Fe$_2$B ↔ Eucor

A-type experiments verified the properties of the pull-off device. Substrate steels S235JRH-1.0038 with the average surface roughness of R_a = 6,59 μm; adhesive Loctite 3425 A&B Hysol; pull-off device with titanium counterpart cylinder with R_a = 8,27 μm. Pull-off strenght between Loctite glue and steel reached maximum of 26,8 MPa and the separation occurred in the middle of the adhesive layer.

B-type experiments studied the bond strenght between boronized surface layer with the steel surface. Substrate steels with FeB/Fe$_2$B interlayer with initial value of surface roughness of boronized layer $R_a \approx 14$ μm. Pull-off strenght of the bond was 7,8 MPa, the separation occurred in the ferroboron layer. On the surface of the titanium counterpart cylinder, the FeB and Fe$_2$B particles were detected via XRD and SEM microscope – these particles came off the brittle boronized surface during separation. The bottom part of the pin-like particles of Fe$_2$B phase remained undamaged.

The top part of the boron layer in contact with unreacted boronizing medium contained higher volumetric amount of FeB phase which is brittle and is does not bond with the steel matrix. It is necessary for the subsequent deposition of ceramic coatings to remove cca a half of the layer thickness by grinding or preferably sand blasting which also allows for roughness regulation, necessary for plasma spraying. For further experiments, this primary, partially cracked and porous boronized layers of ≈ 100 μm thickness, was removed by grinding (about 10 μm) and sand-blasted (R_a = 16,5 μm). Pull-off experiment then confirmed higher strenght of the FeB$_x$-Ti counterpart cylinder bond up to ≈ 20 MPa. Similarly, maximum value of bond strenght on ground layer of LaB$_6$ - LaB$_4$ - Fe$_2$B increased up to 10,2 MPa.

C-type experiments focused on bond strenght between ceramic Eucor layer and the boride layer on the steel surface. Substrate steels S235JRH-1.0038, FeB/

Fe_2B interlayer (R_a = 16,5 μm), Eucor ceramic coating (R_a = 10,6 μm). Pull-off bond strength of 3,9 MPa to 6,1 MPa, the separation occurred on the iron boride layer-Eucor interface. The new surface on the Ti counterpart cylinder again contained some amount of Fe from the FeB particles, according to the XRD analysis. The bond strength data suggest that the adhesion between Eucor-Fe_2B is higher than tensile strength of iron boride. The destruction caused by tensile stress occurred again on the outer interface of the boronized interlayer. Similar effect was observed on the phosphate interlayers with ceramic coating [12]. In the case of Eucor layer deposited on interlayer prepared by LaB_6, the separation occurred more frequently in the Eucor layer (some form of coating delamination), maximum value of bond strenght between Eucor and boronized layer was 8,5 MPa.

CONCLUSIONS

Formation of Fe_2B interlayer on the S235JRH-1.0038 steel surface is viable technological operation for subsequent application of hot-dip or plasma coatings. This chemical-diffusion link provides continuous change of both hardness and coefficient of thermal expansion. Cracking or rather separation of top of the boronized layer in the area of contact with ceramic layer or adhesive layer, measured according to the standard [13] is caused by character of this layer formed in the initial stages of boronizing in powder. Mechanical removal of this damaged layer can achieve enhancement of layer adhesion, namely in cases of cyclic thermal exposure. The Fe_2B interlayer was further coated with the corundum-baddeleyite layer (Eucor) – this layer, prepared by plasma spraying method, is characteristic for its multiphase composition with high concentration of amorphous phase caused by presence of SiO_2. Amount of amorphous phase depends on the technological conditions of plasma deposition. Such coating reliably withstands cyclic thermal exposure up to 600 °C. Higher thickness of the coating reduces the concentration of open pores, reduces the amount of corrosive medium to the steel and the polarization resistance reaches up to 1 650 Ω/cm^2.

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Note: The responsible translator for the English language is K. Štětková, CTU – Klokner Institute, Prague, Czech Republic