

## **CORROSION PERFORMANCE AND MECHANICAL STRENGTH OF CONVENTIONAL PRESTRESSING STEEL REINFORCEMENT WITH BORIDE LAYER**

<sup>1</sup>Petr POKORNÝ, <sup>2</sup>Vlastimil BROŽEK, <sup>3</sup>Libor MASTNÝ, <sup>1</sup>Veronika STEINEROVÁ,  
<sup>1</sup>Nikola PRODANOVIC

<sup>1</sup>Klokner Institute – Czech Technical University Prague, Czech Republic, EU, [petr.pokorny@cvut.cz](mailto:petr.pokorny@cvut.cz)

<sup>2</sup>Institute of Plasma Physics of the Czech Academy of Science, Prague, Czech Republic, EU,  
[brozek@jpp.cas.cz](mailto:brozek@jpp.cas.cz)

<sup>3</sup> University of Chemical Technology Prague, Czech Republic, EU, [mastny@vscht.cz](mailto:mastny@vscht.cz)

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### **Abstract**

In this study, the nature of boriding surface treatment mechanism of the steel prestressing strand is evaluated and then the corrosion resistance of the borided steel in hydrochloric acid is assessed (detection of the content of released iron and manganese in the exposure solution). The effect on the bond strength of the treated steel prestressing strand with normal strength concrete is also evaluated (pull-out test). Boriding was carried out in a boron carbide backfill with fluoride activators. This manuscript describes the first informative results on this topic.

**Keywords:** Prestressing steel strand, boriding in backfill; corrosion properties; bond strength in concrete

### **1. INTRODUCTION**

The issue of steel boriding and the intense interest in changing its properties dates back to the 1980s. The vast majority of works, including monographs (e.g. Matuschka [1]), are focused on the investigation of the mechanism of boriding and the influence of iron borides mainly on the mechanical or physical properties of steels [2,3]. The backfill for diffusion boriding process was already developed and commercially produced in 1983 in the then SZKE Benátky n/Jiz. [4]. However, the protection of steel against corrosion by boriding has not yet been systematically investigated. Corrosion damage of prestressing steel reinforcement by chloride anions from the de-icing salts can cause unexpected collapse of concrete structures, especially bridges and footbridges. Typical examples of this are the destruction of the Morandi Bridge in Genoa in 2018, or the Troja footbridge in Prague in 2017. The failure of bridges and other transport structures caused mainly by the action of chloride anions with high NaCl or CaCl<sub>2</sub> content is very common worldwide (influence of de-icing salts and seawater) [5]. Metal boriding in backfill is the result of a combination of chemical transport reactions and physical diffusion in the solid state. The resulting outer layer can be a suitable method of local corrosion protection of the surface of the prestressing reinforcement against the degradation effect of chloride anions. Since steels are alloyed with several elements simultaneously, a combinatorial series of opposing reactions arises, which in practice must be solved by optimization methods [6]. The mechanism of boriding of patented steel strand of prestressing reinforcement has not been investigated in detail before. In the diffusion boriding of steel, Fe<sub>2</sub>B and FeB compounds are formed in the surface layer. The reactive diffusion of boron proceeds similarly to the diffusion of carbon or nitrogen in iron by an interstitial mechanism, with the gradual formation of a solid boron solution in  $\alpha$ -Fe, followed by the formation of a tetragonal Fe<sub>2</sub>B hemiboride with a lower melting point, and with a long diffusion time, FeB boride with an orthorhombic structure is formed. The mechanism of boron transfer to the steel from the boriding powder, which is most often boron carbide, amorphous boron or ferrobore. Opinions differ on the mechanism of boriding through the liquid phase, which is the B<sub>2</sub>O<sub>3</sub> micro-fluids or activators [7,8], especially for information on a successful attempt to boride the inner walls of small diameter

capillary tubes backfilled only from the outside. The boride layer on the inner surface of the capillaries could only be formed by transport from the gas phase [9]. Therefore, a mechanism of boriding through the gas phase is more likely. Gas-phase analysis over annealed technical boron carbide B<sub>4</sub>C (or B<sub>12</sub>C<sub>3</sub>) containing < 3 % B<sub>2</sub>O<sub>3</sub> showed the formation of B<sub>2</sub>O<sub>2</sub> suboxide. However, the formation of carbon mono-oxide by GLC analysis has not been demonstrated, therefore the equation for the formation of the suboxide cannot be agreed (see equation (1))



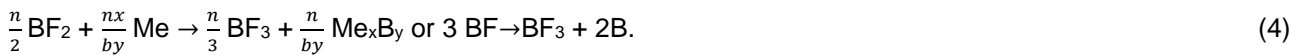
which is mentioned in the current literature [10]. The formation of CO is not thermodynamically possible even according to reaction (2)



leaving unanswered the question of the formation of the volatile suboxide that gives the boron to the borided component according to reaction (3)



The boron dioxide B<sub>2</sub>O<sub>3</sub> returns to the boriding process cycle and the active boron diffuses into the steel surface. The composition of the gas phase can be further modified by the addition of activators (BF<sub>4</sub><sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>) which generate gaseous subhalogenides, e.g. BF<sub>2</sub>, allowing analogous boron transport (see (4)):



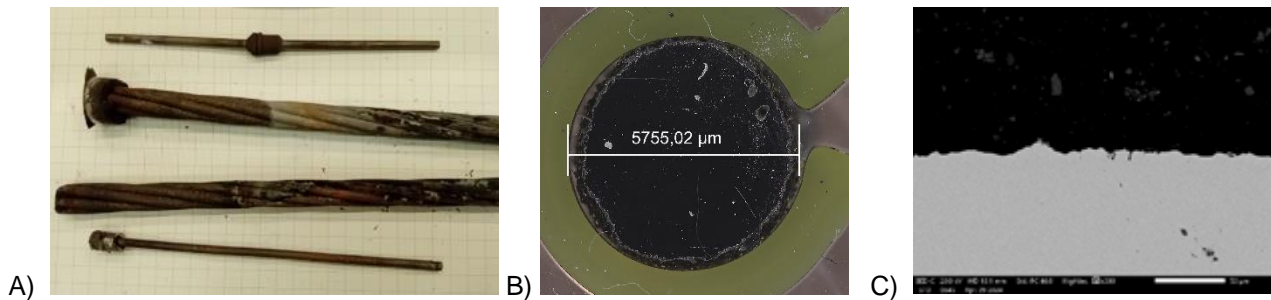
Carbon and other alloying elements in steel play an important role in boride formation, which have a retarding effect on the growth rate of the boride layer in the order Mo>Zr>V>Ti>Nb>W>Cr>C>Al>Si>Ni. In the work of Dufek & Neufuss (1994) [6], the diffusion rate and the thickness of the boride layer were measured for steels of grades 11 and 14 as a function of temperature and time and the value of the diffusion coefficient  $D = 1.89 \times 10^{-14} e^{(1013/T)}$  was determined, for steel ČSN 19552 the value of  $D = 0.42 \cdot 10^{-13} \text{ m}^2\text{s}^{-1}$ . The retarding effect of Cr and Mo has been demonstrated in the case of steel 19541, where Cr and Mo are the main figures. Similar data were arrived at by Sen U. et al. [11] or Orihel et al. [12] in their kinetic study for the boriding process of high-chromium Royalloy steel. When boriding is carried out on an industrial scale, the financial cost of the boriding agents is also taken into account, which, in addition to the main component B<sub>4</sub>C, also include cheap activators - mainly fluorides, which are most often NaF or KF. In this study has been tested the effect of fluoride on the reduction of the boriding temperature by the addition of ScF<sub>3</sub>, which is used in the case we describe primarily as a model to facilitate easier analysis. The scandium does not occur in normal impurities and impurities of alloy steels or boriding materials. However, there is little detailed information on the boriding of special patented steels (heat treated to bainite nature) of prestressing reinforcement in the available literature.

## 2. EXPERIMENTAL RESULTS AND DISCUSSION

Two specimens of prestressing reinforcement were borided: a nominal wire with a diameter of 5 mm and a strain (7 wires  $\phi$  15.7 mm), ( **Figure 1**). The composition of the steel of the prestressing reinforcement supplied by NEDRI WERK HAMM Nederland is shown below. Its chemical composition from the supplier's report is slightly different from the results of the XRF analysis, see **Table 1**.

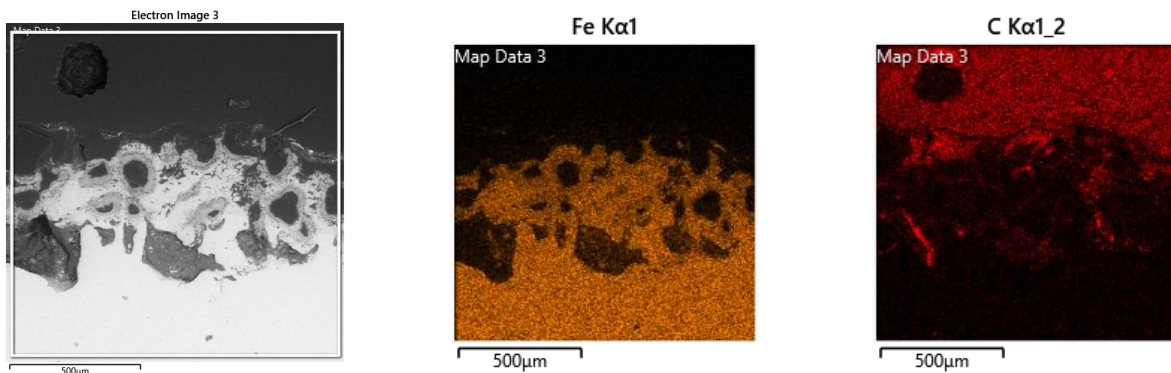
**Table 1** Melt Analysis Spannbetonlitzte prestressing strain steel and by XRF method after casting

	<b>C</b> ( wt.%)	<b>Mn</b> (wt.%)	<b>Si</b> (wt.%)	<b>P</b> (wt.%)	<b>S</b> (wt.%)	<b>N</b> (wt.%)	<b>Cr</b> (wt.%)
940710	0.81	0.70	0.25	0.006	0.009	0.006	unmeasured
937230	0.82	0.72	0.26	0.01	0.007	0.006	---
analysis of XRF	0.70	0.76	0.08	0.04	0.025	unmeasured	0.06



**Figure 1** The view of the borided fine prestressing reinforcement wires (A - overall view; B - diameter of nominal reinforcement wire, C – cross-section of the surface of nominal prestressing reinforcement wire (SEM))

Steel reinforcement samples were heated in powder batches in the following proportions: batch 1: 50% steel, 50% B<sub>4</sub>C; batch 2: 50% steel + 40% B<sub>4</sub>C + 10% KF; batch 3: 50% steel + 40% B<sub>4</sub>C + 10% ScF<sub>3</sub>. Two boriding temperatures were chosen: 800 °C and 1200 °C. Only half of the length of specimen in the boriding backfill was treated at 1200 °C. The upper part of this samples were left untreated to determine the surface condition after corrosion test. The structure of the steel surface after boriding process at 800 °C indicates presence well-adhered Fe<sub>2</sub>B hemiboride (**Figure 2** and **Figure 3**). The diffractogram of the borided surface after partial ultrasonic cleaning of the excess boron carbide is shown in Figure 3.



**Figure 2** The detail of the Fe<sub>2</sub>B porous layer on the surface of NEDRI WERK HAMM steel (SEM cross-section of top steel layer)

Testing of the effect of the boride surface layer on the bond strength of the prestressing reinforcement in the normal strength concrete was carried out by a modified pull-out test. The individual prestressing reinforcement specimens were only 20 cm long due to the specific geometric arrangement of the boriding process. The samples were placed in concrete cubes with a length of 15 cm and anchored at an anchor length of 10 cm. A total of 6 parallel samples were tested. The anchoring was realized by means of a centering insert created by 3D printing. Bond strength testing was carried out by monitoring the displacement of the reinforcement from the concrete (measured from the concrete surface) at a rate of 0.01 mm.min<sup>-1</sup>. Portland cement (CEM I) and

conventional aggregate distribution were chosen to create the concrete cubic specimens. The produced concrete had an average cubic strength of 48.1 MPa. A representation of the average bond stress - slip curve for blank reinforcement and borided reinforcement (at 800°C) by the modified pull-out test is shown in (Figure 4 and Figure 5).

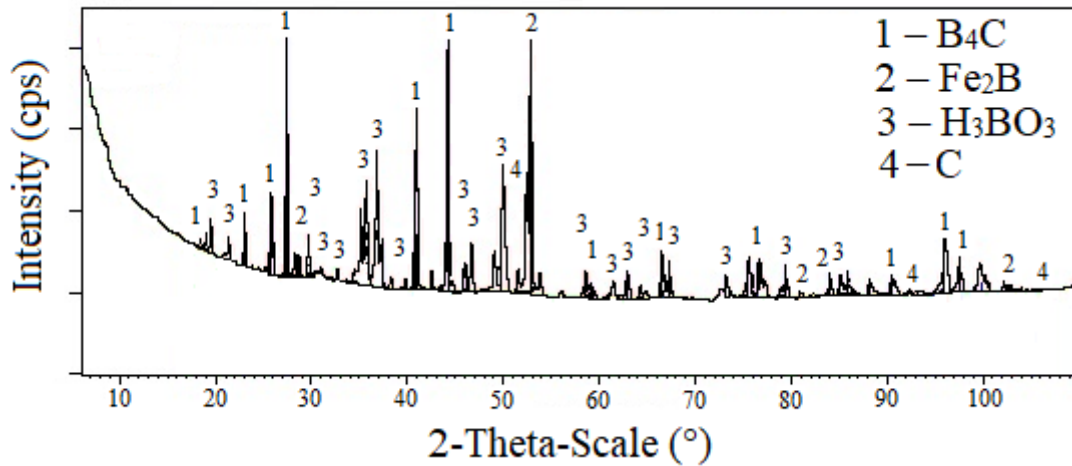


Figure 3 Diffractogram of the borided surface after partial removal of excess B<sub>4</sub>C

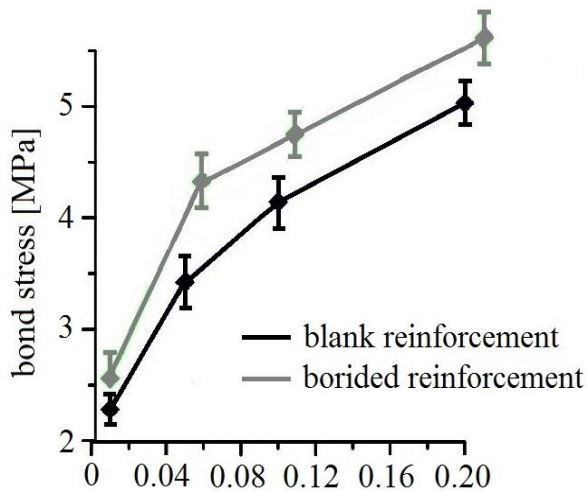


Figure 4 The average values (pull-out test) bond stress - slip curve for blank reinforcement and borided reinforcement (at 800°C)

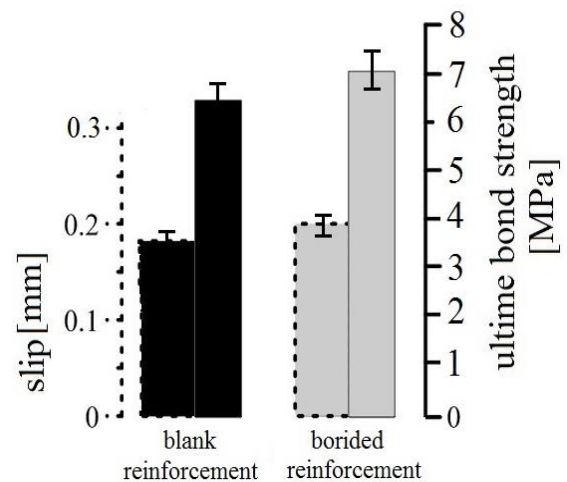
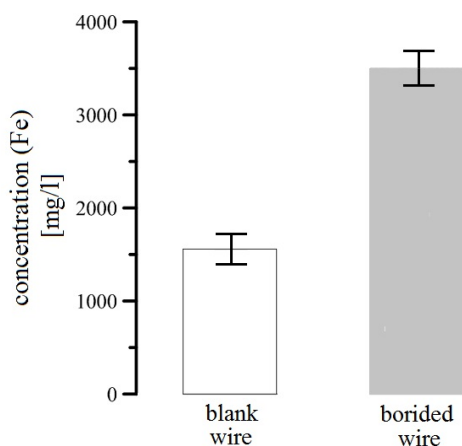
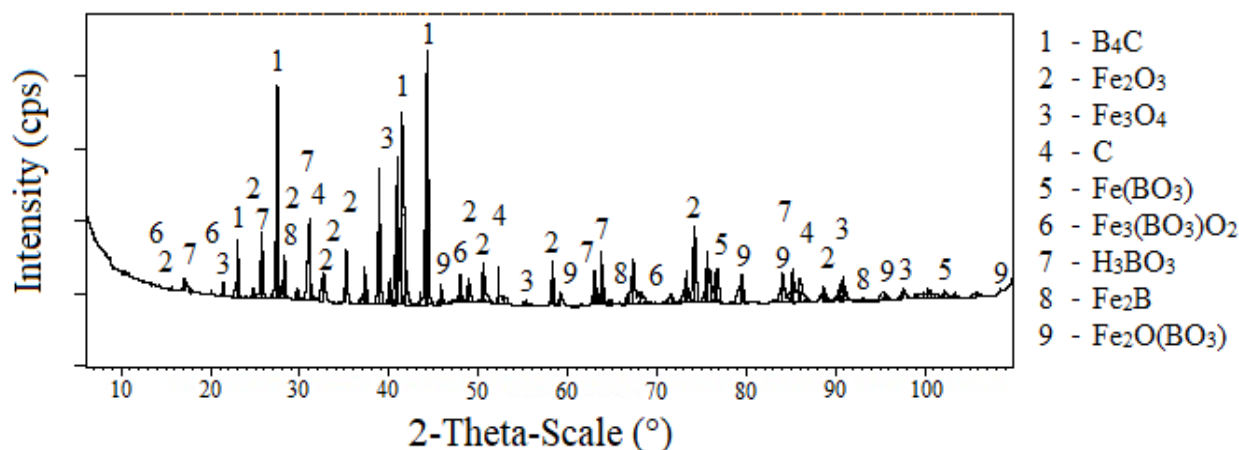


Figure 5 The summary evaluation of the bond strength in concrete results for blank reinforcement and borided reinforcement (800°C)

Comparative corrosion testing was carried out on nominal separated wire samples of the prestressing reinforcement strain in 1 M hydrochloric acid. Samples of the solution were taken at time intervals and the iron and manganese content (Mn - 0.74% found) were analysed by AAS atomic absorption spectrometry. 6 samples were monitored for a maximum period of 60 minutes, the results are summarised in (Figure 6).



**Figure 6** Results of the determination of the iron content in the HCl exposure solution for the blank wire samples and the borided wire samples treated at 800 °C



**Figure 7** The surface layer diffractogram of a mixture of unreacted B<sub>4</sub>C and the products of the reaction of B<sub>4</sub>C with iron oxides

Not only from the results exhibit in the bar chart, but also by visual observation was found that the surface of the borided steel dissolves faster in hydrochloric acid than the surface of the reference sample. The surface of the borided steel may exhibit a lower hydrogen overvoltage. Based on this results a control X-ray diffraction of the adhered layer on the surface of the samples immediately after boriding at 800°C and also at 1200°C was carried out. The results of both analyses are virtually identical, hence the X-ray diffraction results of the sample borided at 1200°C is shown in (**Figure 7**). The used X-ray analysis device is capable of making measurements to a depth of about 100 µm. After mechanical removing of a part of the layer, further X-ray diffraction analysis was carried out, which penetrated to the actual boride layer on the steel, since the diffractograms could already identify reflections corresponding to Fe<sub>2</sub>B hemiboride.

## CONCLUSION

The following essential conclusions can be summarized based on the experiments carried out with boriding surface of the conventional prestressing steel reinforcement. The boriding surface of prestressing steel in backfill clearly leads to increased surface hardness and roughness. This increase is related to abrasion resistance and bond strength in concrete also (normal strength concrete). It has been verified that the influence of the cations in fluoride compounds does not seem to significantly affect the boriding process (particularly regarding to the reduction in process time and/or exposition temperature). These conclusions have been confirmed by application of KF and ScF<sub>3</sub> in boriding surface of prestressing steel (the depth of boron diffusion was evaluated). The kinetics of corrosion process of borided steel in hydrochlorid acid is significantly influenced by presence of Fe<sub>3</sub>(BO<sub>3</sub>)O<sub>2</sub> and/or Fe<sub>2</sub>O(BO<sub>3</sub>), formed by the reaction of excess boron carbide with the products of thermal oxidation of iron (Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>). The ionic bonding nature of the compounds of boron, iron and oxygen forms porous surface layer, with low stability in acidic condition (at pH < 3). The kinetics of electrochemical corrosion degradation can be significantly affected by this fact, therefore the corrosion stability of borided steel prestressing reinforcement in HCl cannot be clearly assessed. The results obtained in this work are informative and require further continued research. In particular, it is necessary to verify the corrosion stability in simulated concrete pore solutions with chloride ions by electrochemical testing and bond strength in concrete by means of a normatively defined pull-out test.

## ACKNOWLEDGEMENTS

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