

Chemical and phase compositions of boride layers grown on steel bases in molten salts

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The influence of utilized boriding method, of the operating conditions and composition of the base (substrate) on the chemical and phase compositions of boride layers formed by the electrolytic and thermochemical boriding of steels in molten salts has been investigated. As substrates, the low-alloy low carbon steel, the manganese steel, and the high-alloy chromium steel have been tested.

The boride layer formed by the electrolytic boriding consists of two phases, FeB and Fe₂B. In the thermochemical boriding, the phase composition of the boride layer depends on the composition of the boriding mixture and operational conditions, and the formation of the FeB phase can be partially or entirely suppressed. It was also found that under certain conditions an additional phase with chemical composition corresponding to the compound Fe₃B is formed.

When the boride layer was grown on a high-alloyed chromium steel it was found that Cr forms a diffusion barrier which slows down the rate of the boride layer formation and increases the content of the FeB phase.

Исследовано влияние применяющегося метода борирования, рабочих условий и состава основания (субстрата) на химический и фазовый состав боридных слоев, образуемых при электролитическом и термохимическом борировании сталей в расплавах солей. В качестве субстратов были испытаны низколегированная углеродная сталь, марганцевая сталь и высоколегированная хромовая сталь.

Боридный слой, образуемый при электролитическом борировании состоит из двух фаз, FeB и Fe₂B. При термохимическом борировании фазовый состав боридного слоя зависит от состава борлирующей смеси и рабочих условий, причем образование фазы FeB может быть частично или полностью подавлено. Было также обнаружено, что в определенных условиях образуется дополнительная фаза с химическим составом, соответствующим соединению Fe₃B.

Если боридный слой наращивался на высоколегированной хромовой стали, было обнаружено, что Cr создает диффузионный барьер, который замедляет скорость образования боридного слоя и ведет к увеличению содержания фазы FeB.

Boriding has been found to be one of the most effective methods for increasing the surface hardness and the abrasive resistance of various metallic materials, namely of steels. From literature data reviewed in monographs [1, 2] it follows that the boriding methods can be divided into two groups, i) electrochemical and ii) thermochemical, differing in the way of saturation of the surface of the steel base by boron. In the electrochemical boriding, boron is deposited on cathodically polarized substrate immersed in molten electrolyte containing a suitable boron compound (*e.g.* $\text{Na}_2\text{B}_4\text{O}_7$, KBF_4 , *etc.*) as electrochemically active component. Thermochemical boriding is carried out in a gaseous, powder or molten boriding mixture containing, beside the component serving as a source of boron (mostly $\text{Na}_2\text{B}_4\text{O}_7$ in the melts), a suitable reducing agent (*e.g.* B_4C , SiC , *etc.*). The investigation of the boriding process has been aimed mainly on the determination of the influence of various factors on the rate of formation and the phase composition of boride layers. From an analysis of data reviewed in the monographs [1, 2] it follows that the mechanism of the boride layer formation is independent of the way of saturation of the surface of the base: the deposited boron diffuses into the substrate and reacts with the base material under formation of borides.

The electrolytic method and the thermochemical procedures were found to be the most effective with respect to the rate of the boriding process. In both cases, temperature and composition of the base material affected significantly the rate of the boride layer formation [1—6]. In the thermochemical boriding also the composition of the melt (choice of reductant) is of a definite importance while in the electrochemical boriding the composition of the electrolyte (the kind of the electrochemically active component) does not affect the rate of the growth of boride layer and is important only with respect to the working temperature (vapour pressure, viscosity, *etc.*).

The possibility of increasing the efficiency of the electrochemical boriding by increasing the cathodic current is limited by certain "critical" value at which the amount of the deposited boron corresponds to the amount of boron diffused into the substrate [5]. The value of this limiting current density depends again on temperature and the composition of the substrate and it decreases with time of electrolysis because the rate of growth of the boride layer slows down with time [5, 6].

The surface boride layers formed in the boriding of steel substrates consist generally of two phases corresponding to the compounds FeB and Fe_2B . The two phases differ largely with regard to the mechanical properties, namely the hardness

and brittleness (the FeB layer is harder and more brittle than the Fe₂B underlayer). The relative content of the individual phases in the boride layer is governed by the same factors which govern the rate of the boride layer formation. Under certain experimental conditions the formation of the boron-rich FeB phase can be entirely suppressed so that only a single-phase Fe₂B layer is formed. As it will be shown later, also the phase Fe₃B can be formed in the boride layer.

The determination of the phase composition of a boride layer is closely related to the determination of its chemical composition. Only few papers dealing with this topic have been published thus far. In the analysis of the boride layers in most cases only the concentration of iron and possibly also of some alloying elements has been determined and the concentration of boron has been evaluated indirectly based on the material balance. The recent achievements in the field of the experimental technique, namely concerning the identification ability of the electron microprobe, made a direct determination of the boron concentration in the boride layers possible. This improvement in the experimental technique made it also possible to identify the Fe₃B phase in the boron layer.

The results of a semiquantitative analysis of the boride layers compositions formed by thermochemical boriding of steel substrates in powder mixtures have been reported by *Palombarini et al.* [7] and in the melts by *Shibuya* and *Kimura* [8]. In this work the quantitative composition of boride layers formed by the electrolytic and thermochemical boriding in molten salts has been investigated.

An interesting problem from both technological and theoretical aspects presents the boriding of the alloyed steels. According to the literature data [1, 2, 6], the presence of the alloying elements reduces the rate of the boride layer formation. In this work the influence of manganese and chromium on the phase composition of the boride layer has been determined.

Experimental

For the preparation of molten electrolytes and mixtures for thermochemical boriding the following chemicals were used: Na₂B₄O₇, KBF₄, LiF, KF, NaCl, B₄C, and SiC, all anal. grade.

The experimental set-up has been described in a previous paper [6].

The electrolytic boriding has been carried out at temperatures 750, 850, and 900 °C at a cathodic current density 50 mA cm⁻² which surpassed in all cases the limiting value (*i.e.* a unit boron activity on the surface of the base could be assumed). At 750 °C, an electrolyte based on the LiF—KF eutectic mixture (30 mass % LiF + 70 mass % KF) containing KBF₄ (10 mass %) as the electrochemically active component was utilized while at higher temperatures a mixture of 80 mass % Na₂B₄O₇ and 20 mass % NaCl with a lower vapour pressure has been used.

The thermal boriding has been carried out at 950 °C in the melts (suspensions) containing alternatively 60 mass % Na₂B₄O₇ and 40 mass % B₄C or 65 mass % Na₂B₄O₇ and 35 mass % SiC.

The following types of steels (cylindrical samples $d = 10$ mm, $h = 40$ mm) have been borided:

- i) low carbon, low-alloy steel ČSN 11302 (0.06 % C, 0.17 % Si, 0.30 % Mn),
- ii) manganese steel ČSN 19312 (0.79 % C, 0.40 % Si, 2.00 % Mn, 0.17 % Cr),
- iii) high-alloyed chromium steel ČSN 19436 (1.85 % C, 0.50 % Si, 0.26 % Mn, 11.25 % Cr).

(All concentrations are given in mass %.)

The thickness of the boride layers and that of the individual phases has been determined using the scanning microscope JSM-840 (Jeol). The phase and chemical composition of the boride phases has been determined by the X-ray phase analysis and by means of the electron microprobe Superprobe 733 (Jeol).

The quantitative analysis was carried out under computer control, using slightly modified Jeol programs, with on line evaluation of ZAF corrections [9—11]. In this approach the concentration of an element in the sample is determined as

$$C_A = \frac{I_A}{I_{As}} \cdot F_a \cdot F_z \cdot F_f$$

where I_A is the intensity of the characteristic line in the sample, I_{As} is the intensity in the standard, F_a , F_z , and F_f are the correction factors for absorption, atomic number, and fluorescence, respectively. This relation was used in the quantitative determination of iron, while for boron the integrated intensities of peaks (*i.e.* their areas) were used [12] because of a greater width of the characteristic line.

Results and discussion

The boride layer formed electrochemically on the low-alloyed steel ČSN 11302 is shown in Fig. 1. It may be seen that the boride layer consists of two phases. The quantitative electron probe microanalysis and the X-ray diffraction analyses revealed that the composition of the dark-gray layer corresponds to the compound FeB and of the medium-gray layer to the compound Fe₂B, the light-gray area being the base (the black spots were assumed to be holes formed at polishing of the hard and brittle boride layers). Fig. 1 shows also the root-like character of the boride layer which was commented elsewhere [1—8]. It may be seen that the length of the individual “roots” (denoted also as “teeth”) differs considerably. Fig. 2 shows the microphotograph of the same layer obtained on a metallographic microscope after etching in the ethanol solution of picric acid. The latter method obviously gives a picture of an apparently more compact boride layer with a thickness corresponding to the longest “roots” detected by the electron microprobe. This is obviously

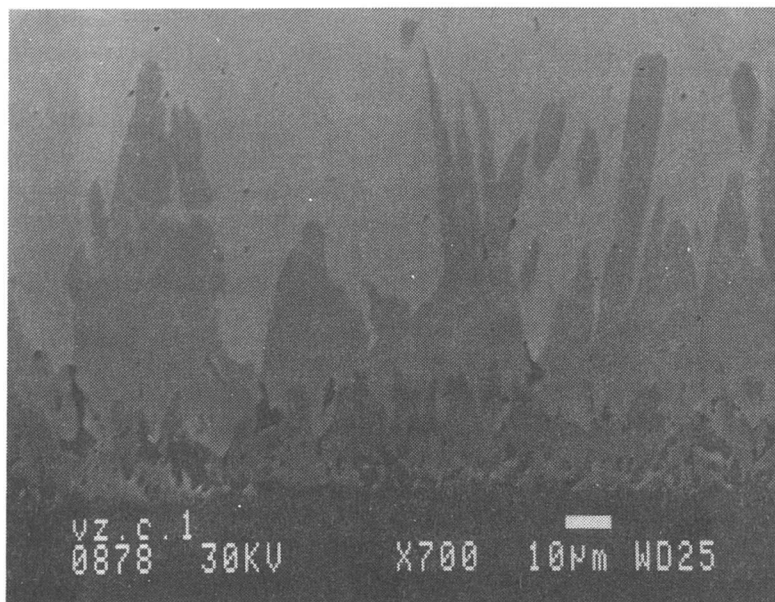


Fig. 1. Composition of the boride layer on the electrochemically borided steel ČSN 11302. Electrolyte $\text{Na}_2\text{B}_4\text{O}_7\text{—NaCl}$, temperature 900 °C, time 2 h.

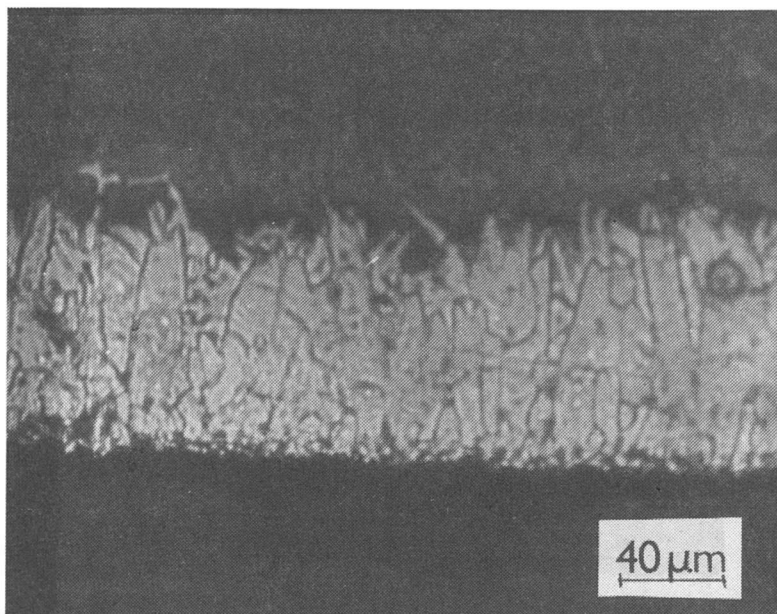


Fig. 2. Microphotograph of the boride layer shown in Fig. 1.

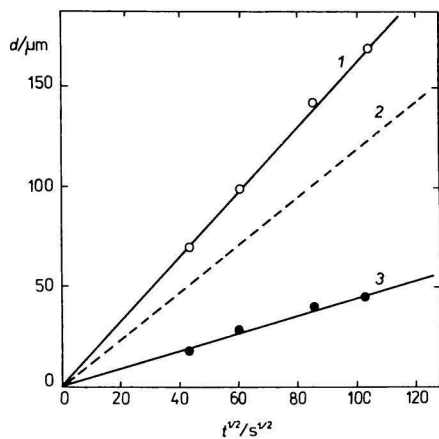


Fig. 3. Dependence of the thickness of the boride layer and of the FeB and Fe_2B phases on the square root of the time of electrolysis at $900\text{ }^\circ C$.

1. Boride layer; 2. Fe_2B (calculated);
3. FeB .

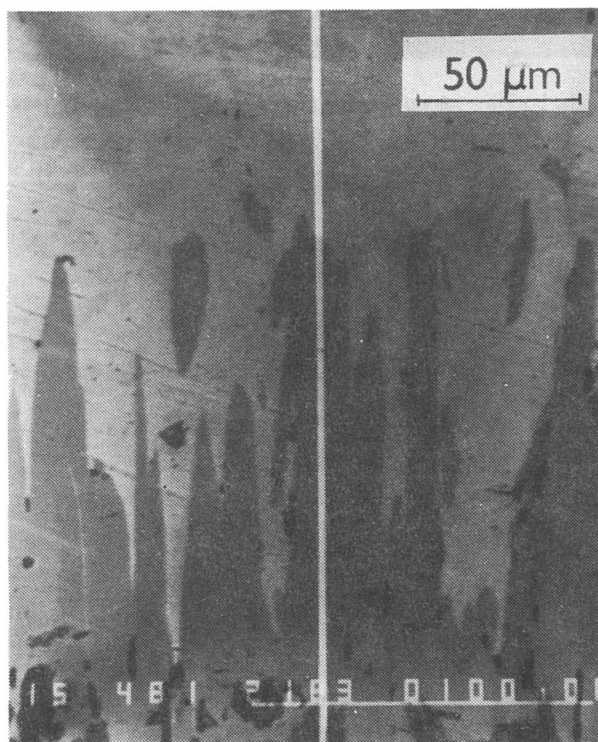


Fig. 4. Composition of the boride layer on the thermally borided steel ČSN 11302. Boriding mixture $Na_2B_4O_7-B_4C$, temperature $950\text{ }^\circ C$, time 4 h.

due to a lower resolving power of the metallographic microscope which after etching does not allow to differentiate the boride "roots" laying in different vertical planes.

The dependence of the rate of the boride layer formation on the time of electrolysis was found to have a parabolic character, which supports the hypothesis of the boriding process being governed by the diffusion of boron into the substrate [1, 6]. This has been confirmed also in boriding of the steel ČSN 11302 [6]. The dependences of the total thickness of the boride layer as well as of the thicknesses of the FeB and Fe₂B phases, as determined in the present work, are shown in Fig. 3. All these dependences are linear and go through zero at the zero time. This indicates the simultaneous formation of the FeB and Fe₂B compounds without a preferential formation of any boride phase.

In the thermochemical boriding, the literature data [1, 6] on the influence of the composition of the boriding medium on the composition of the boride layers have been confirmed. Fig. 4 shows the composition of the boride layer formed in molten Na₂B₄O₇ with B₄C as reductant on the steel ČSN 11302. It may be seen that the boride layer consists mostly (90 %) of the Fe₂B phase and the formation of the FeB phase is so suppressed that it does not form a compact layer. The line concentration profiles of boron and iron on the cross-section of the sample (indicated by a white line in Fig. 4) are shown in Fig. 5. The lower boron activity on the surface of the

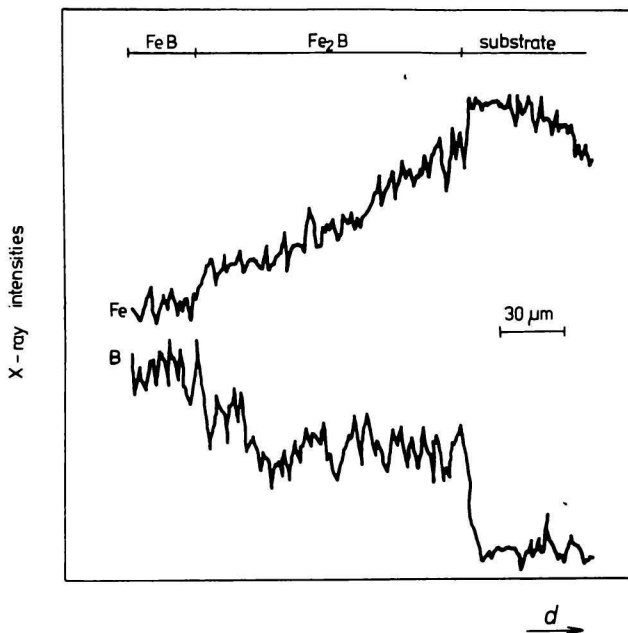


Fig. 5. Concentration profiles of boron and iron in the sample shown in Fig. 4.

base results in a reduced rate of formation of the boride layer (the rate of the electrolytic boriding is by a factor of 1.5 higher than the boriding in the $\text{Na}_2\text{B}_4\text{O}_7\text{—B}_4\text{C}$ mixture).

In the thermochemical boriding in a mixture of $\text{Na}_2\text{B}_4\text{O}_7$ with SiC as reductant which is less active than the mixture $\text{Na}_2\text{B}_4\text{O}_7\text{—B}_4\text{C}$ [6], the formation of the phase FeB is entirely suppressed and only the phase Fe_2B is formed (Fig. 6). This figure however is important as it also demonstrates the presence of another boride phase

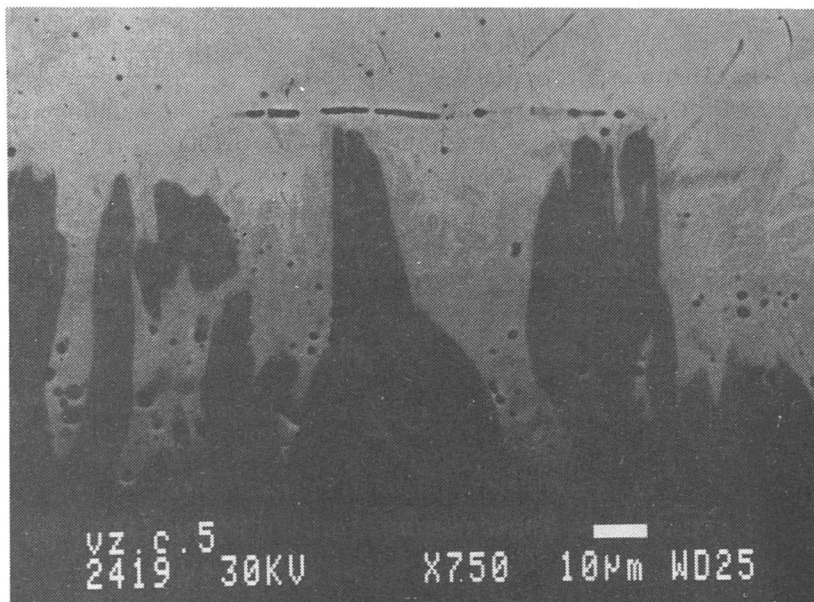


Fig. 6. Composition of the boride layer on the thermally borided steel ČSN 11302. Boriding mixture $\text{Na}_2\text{B}_4\text{O}_7\text{—SiC}$, temperature 950 °C, time 3 h.

beside Fe_2B (the medium-gray areas between the “roots” of the phase Fe_2B). The existence of two phases is confirmed also by the line concentration profiles of boron and iron determined on the cross-section of the sample (Fig. 7). From a quantitative analysis it follows that the boron concentration in this phase is about 6 mass %, which corresponds to the compound Fe_3B which has not been identified in the boride layers thus far. The presence of this compound has been confirmed also by the X-ray phase analysis. After abraising the Fe_2B surface layer, diffraction lines corresponding to the 3 strongest d -lines of the compound Fe_3B [13] have been identified.

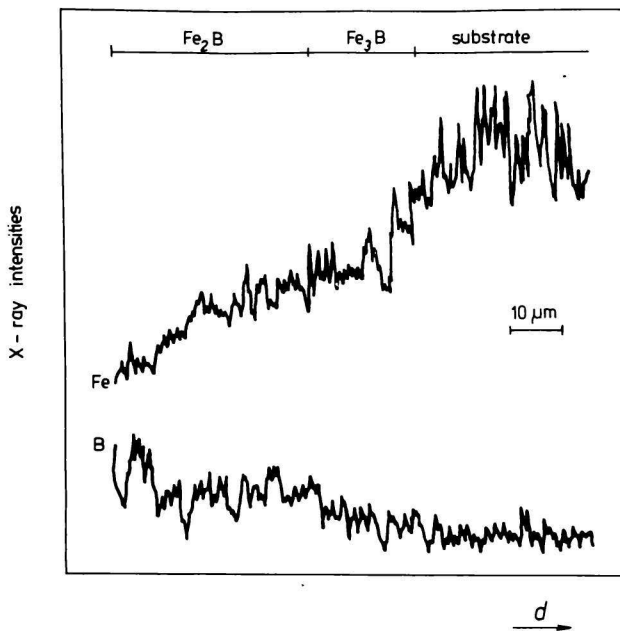


Fig. 7. Concentration profiles of boron and iron in the sample shown in Fig. 6.

In the boriding of the manganese steel ČSN¹19312 it was found that at the concentration of 2 mass % manganese has no significant influence on the rate of the boride layer formation. From a comparison of the compositions of the boride layer on the manganese steel (Fig. 8) and on the low-alloyed steel ČSN 11302 (Fig. 1) it follows that at this concentration manganese does not affect the phase composition either.

Fig. 9 shows the line concentration profiles of boron, iron, and manganese on a cross-section of the electrolytically borided manganese-steel cathode. The course of the Mn concentration profile supports the hypothesis that boron reacts preferentially with manganese, either under formation of FeB and Fe₂B phases with manganese isomorphously replacing iron or formation of the independent B—Mn phases [14—16]. This figure also shows that the concentration of elementary boron, which is deposited at the over-limiting current densities on the surface of the base, decreases rapidly to the value corresponding to the compound FeB. A higher boron content (with respect to the FeB composition) in the surface layer has been confirmed also quantitatively. No Fe—B compounds corresponding to a higher boron content than FeB have been identified and consequently it may be assumed that a solid solution of boron in FeB is formed in this surface layer.

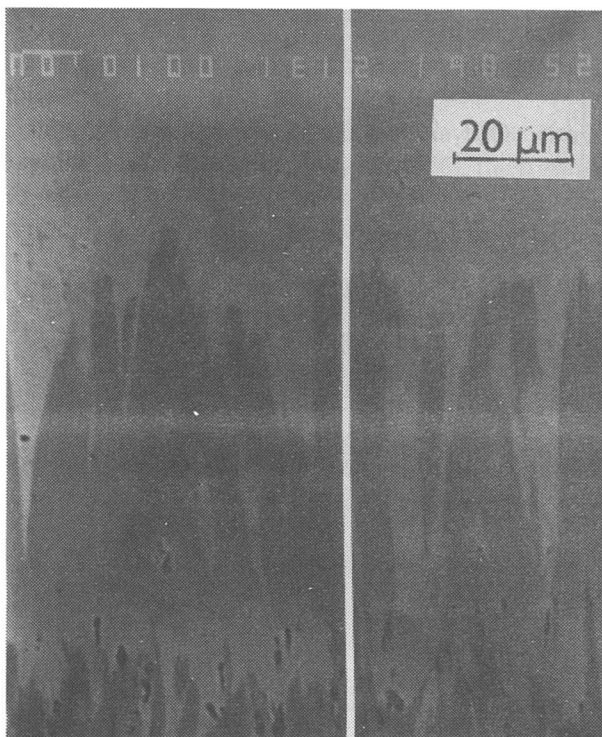


Fig. 8. Composition of the boride layer on the electrochemically borided steel ČSN 19312. Electrolyte LiF—KF—KBF₄, temperature 750 °C, time 20 h.

In the boriding of the high-alloyed chromium steel ČSN 19436 Cr was found to be one of the alloying elements which exert substantial influence on both the rate of formation and the phase composition of the boride layers, apparently due to the slow-down effect on the transport of boron into the substrate. The electrochemically as well as thermochemically formed boride layers are more regular, *i.e.* without distinctive “roots” on the boride layer/substrate interface (Figs. 10 and 11). From comparison of composition of the boride layer on the high-alloyed chromium steel with the composition of this layer formed on the low-alloyed steel ČSN 11302 (Fig. 1) and on the manganese steel (Fig. 8) it follows that the phase composition of the boride layer (the relative content of the FeB and Fe₂B phases) differs substantially due to the retarding effect of chromium on the diffusion of boron into the high-alloyed steel: the ratio of thicknesses of the entire boride layer and of the phase FeB on the steels ČSN 11302 and ČSN 19436 (Fig. 10) is 3.5 and 1.4, respectively.

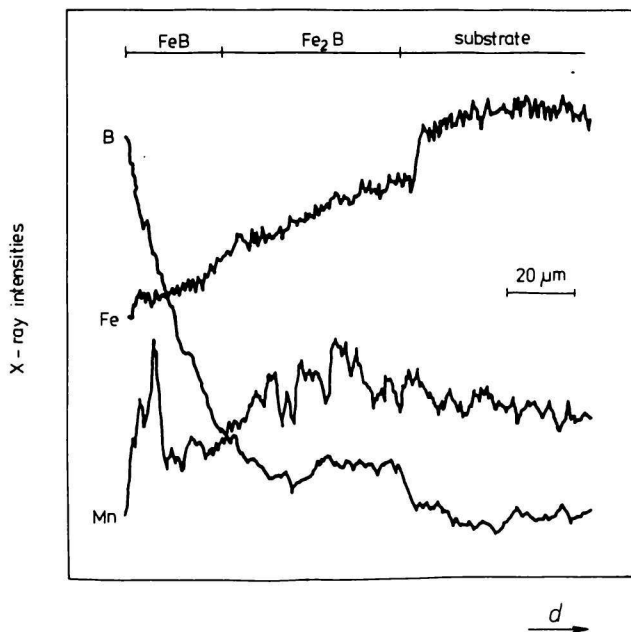


Fig. 9. Concentration profiles of boron, iron, and manganese in the sample shown in Fig. 8.

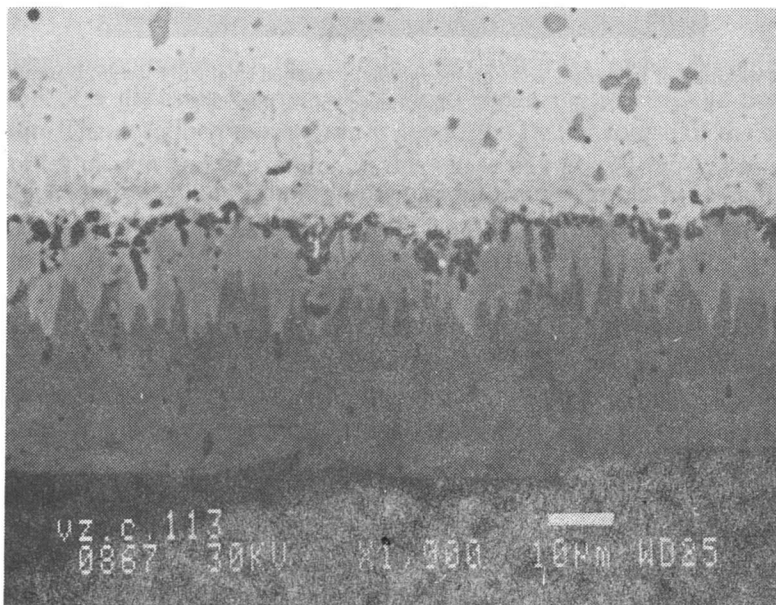


Fig. 10. Composition of the boride layer on the electrochemically borided steel ČSN 19436. Electrolyte Na₂B₄O₇—NaCl, temperature 850 °C, time 5 h.

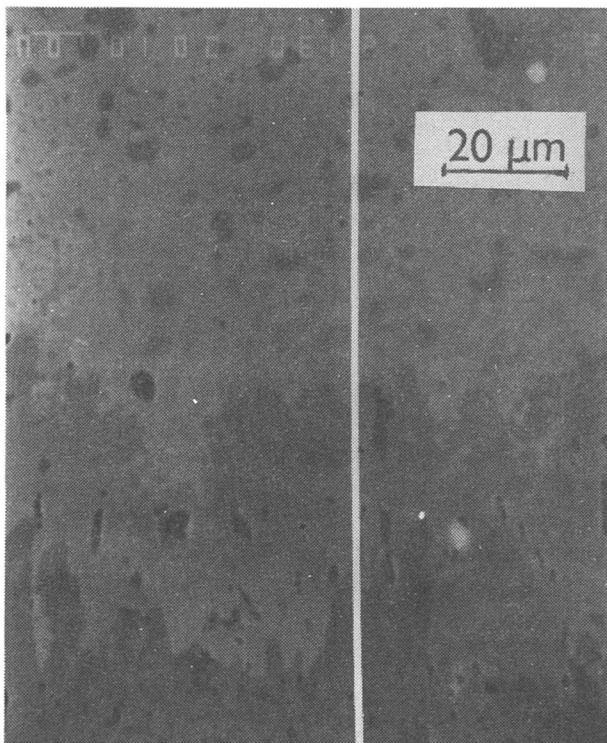


Fig. 11. Composition of the boride layer on the thermally borided steel ČSN 19436. Boriding mixture $\text{Na}_2\text{B}_4\text{O}_7\text{—B}_4\text{C}$, temperature 950°C , time 5 h.

The influence of chromium on the growth of the boride layer may be explained by an analysis of the concentration profile marked by a white line in Fig. 11. The irregular distribution of chromium in the substrate (Cr inclusions can be seen as irregular medium-gray spots in the light-gray substrate in Figs. 10 and 11), makes a quantitative evaluation of the boron—chromium interaction difficult. Based on the courses of the Cr, Fe, and B concentration profiles in Fig. 12 and the literature data, however, some semiquantitative conclusions can be made. The courses of the concentration profiles indicate that in boriding of the high-alloyed chromium steel the diffusing boron, beside reacting with iron, reacts also with chromium either with formation of the binary Cr—B compounds (the existence of several compounds of boron with chromium has been reported by *Andrieux* and *Marion* [17]) or of the ternary compound $\text{Fe}_{1.1}\text{Cr}_{0.9}\text{B}_{0.9}$ [18]. Besides, also the possibility of a partial substitution of iron for boron in the compounds FeB and Fe_2B cannot be ruled out [1]. Only a part of chromium, however, is bound in the boride layer, apparently due to the low rate of the corresponding reaction(s), and the excess

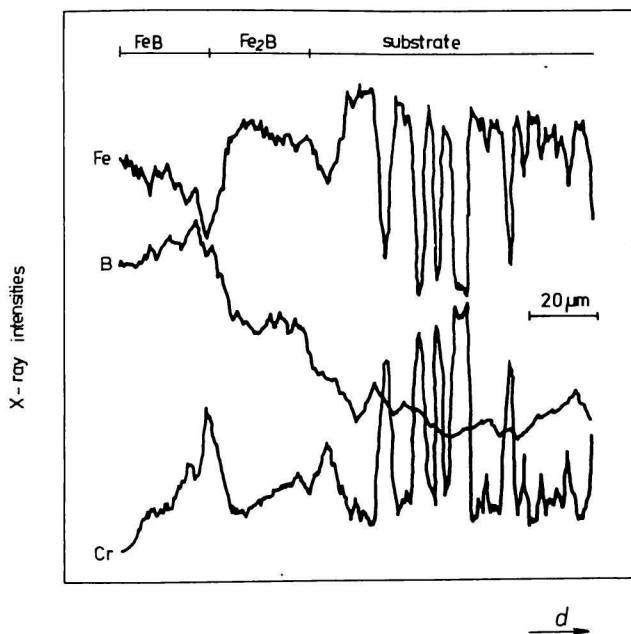


Fig. 12. Concentration profiles of boron, iron, and chromium in the sample shown in Fig. 11.

chromium concentrates on the boride layer/substrate phase boundary under formation of a diffusion barrier which slows down the rate of the boride layer formation. The described mechanism is supported by the course of the concentration profiles of iron and chromium on this phase boundary (Fig. 12) as well as by the existence of a continuous chromium layer contouring the phase boundary (the medium-gray stripe in Figs. 10 and 11). More experimental data will be required, however, to give a quantitative characteristic of the influence of the individual alloying elements on the rate of formation and the phase composition of boride layers on the alloyed steel bases.

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