

# Diffusional Growth Kinetics of Boride Layers at the 13% Cr Steel Interface with Amorphous Boron

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**Abstract.** Two borides FeB and Fe<sub>2</sub>B were found to form as separate layers at the interface between a 13% Cr steel and boron at 850-950 °C and reaction times up to 12 h. The chromium distribution within the boride layers is rather irregular. Its average content is 8 at.% in the FeB layer and 9 at.% in the Fe<sub>2</sub>B layer. Both layers are characterized by a pronounced texture. The strongest reflections are {002} and {020} for the orthorhombic FeB phase and {002} for the tetragonal Fe<sub>2</sub>B phase. Diffusional growth kinetics of boride layers are close to parabolic and can alternatively be described by a system of two non-linear differential equations, producing a good fit to the experimental data.

## Introduction

Boriding is one of the widespread thermochemical surface treatments used to improve service characteristics of metals, alloys and steels [1-3]. Iron borides Fe<sub>2</sub>B and FeB are known to exist in the Fe-B binary system [4-7]. Hence, with iron, its alloys and steels, either one-phase or two-phase coatings can be obtained, depending on boriding media employed and temperature-time conditions of a boriding procedure.

Note that even if three or more compounds exist in the metal-boron binary system, in most cases only two of them are formed as separate layers at the interface between reacting phases [8]. This contradicts diffusional considerations [9] predicting the simultaneous formation and subsequent parabolic growth of the layers of all compounds of any binary system, whatever their number, but agrees with a physicochemical viewpoint [10], according to which only one or two layers can occur and grow simultaneously under conditions of diffusion control, with other compound layers being skipped for kinetic and not thermodynamic reasons.

Boriding at 950 °C for 6 h in a mixture of 30% SiC and 70% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> produce a coating of a thickness of 15 μm on the surface of the 30X13 (0.30% C and 13% Cr) steel material [11], similar to that material employed in this investigation. With a mixture of 30-35% B<sub>4</sub>C and 70-65% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> melt (electrolysis), appropriate thickness values are 40 μm and 55 μm, respectively. Mixtures of amorphous boron and KBF<sub>4</sub> appear to be more effective boriding agents due to the formation of a gas phase at elevated temperatures [1, 8, 11]. In this work, the results of investigation of the interaction of a commercial 13% Cr steel (40X13) and boron in a mixture of amorphous boron powder and 5% KBF<sub>4</sub> at 850-950 °C are presented, with the main emphasis on establishing the boride layer-growth kinetics that received comparatively little attention.

## Experimental procedure

**Materials and specimens.** The materials used included a commercial 40X13 steel rod (16 mm diameter), amorphous boron and analytical-grade KBF<sub>4</sub>. The content of main components of the steel was 85.2% Fe, 13.6% Cr, 0.38% C, 0.30% Mn, 0.30% Si and 0.20% Ni. Initially, the boron powder contained 98.3% B, 0.04% C, 1.6% O and insignificant amounts of Si, Cu, Mg (< 0.01%

each) and Fe (< 0.001%). Before the boriding experiments, the powder was first heated slowly in vacuum up to 1450 °C and then calcined at this temperature for 2 h in an atmosphere of argon at a pressure of  $2.5 \times 10^4$  Pa to remove volatile oxides.  $\text{KBF}_4$  was preliminary dried in steps at 95, 110, 130 and 170 °C (24 h at each temperature).

Specimens in the form of tablets, 11.28 mm diameter and 5.5 mm high, were machined from the steel rod. Flat sides (1 cm<sup>2</sup> area) of the tablets were ground and polished mechanically.

**Experimental methods.** The vacuum device VPBD-2S employed for boriding steel samples has been described elsewhere [12]. The experiment was carried out in an alumina crucible, 13 mm inner diameter and 40 mm high. A steel tablet was embedded into a mixture of boron powder with 5%  $\text{KBF}_4$  as an activator. This amount of  $\text{KBF}_4$  appears to be optimum [1, 8].

The chamber was pumped to a pressure of about 10 Pa and filled with high-purity argon (99.999 vol.% Ar). This procedure was repeated twice. Then, the chamber was again pumped and filled with argon at a pressure of  $2.5 \times 10^4$  Pa, and heating was started. During heating, the crucible with its contents was in the cold zone above the furnace. After the required temperature in the range of 850-950 °C had been reached in the furnace, the crucible, pre-heated to about 400 °C, was moved into its middle part. After an initial drop, the temperature attained its pre-determined value in 4-5 min and was then maintained constant within  $\pm 1^\circ\text{C}$  with the help of an automatic thermoregulator VRT-3. The temperature measurements were carried out using a Pt-PtRh thermocouple. The experiments were performed at temperatures of 850, 900 and 950 °C. Their duration was 3600-43200 s (1-12 h).

After the experiment, the steel tablet coated with boride layers was cut along the cylindrical axis into two unequal parts (4 and 7 mm) using an electric-spark machine. The greater part of the tablet was embedded into a cold-setting epoxy resin and used to prepare a metallographic cross-section. The lesser part was used for X-ray diffraction investigations (plain-view samples).

Characterization of the steel and boride layers was carried out with the help of metallography (optical microscope MIM-7 equipped with a HP Photosmart 720 camera), X-ray (DRON-3) and chemical analyses, and electron probe microanalysis (JEOL Superprobe 733 and CAMECA Camebax SX50).

X-ray diffraction patterns were taken immediately from the surface of tablet samples on a apparatus using  $\text{Cu K}_\alpha$  radiation. When taking the first pattern, no polishing of a borided steel sample was applied (section 0 in Fig. 1). Then, about 40  $\mu\text{m}$  of a boride layer was removed by grinding and subsequent polishing, and another X-ray diffraction pattern was taken (section I). This procedure was repeated at a step of 20-30  $\mu\text{m}$  until the steel base was reached (sections II-V). Six X-ray diffraction patterns were thus taken on each borided steel sample.

## Results and discussion

**Phase identity and chemical composition of boride layers.** As seen in Fig. 1, two boride phases are formed as separate layers at the steel-boron interface at 850-950 °C and reaction times up to 12 h. Layer-by-layer X-ray analysis and a further comparison of our and literature [13] data showed the outer layer bordering the boriding agent to be the FeB phase, while the inner layer adjacent to the steel base to be the  $\text{Fe}_2\text{B}$  phase.

Both layers consist of columnar crystals oriented preferentially in the direction of diffusion. Their characteristic feature is a pronounced texture. The strongest reflections are {002} (spacing,  $d = 0.148$  nm) and, to a lesser extent, {020} ( $d = 0.275$  nm) for the orthorhombic FeB phase, and {002} ( $d = 0.212$  nm) for the tetragonal  $\text{Fe}_2\text{B}$  phase.

The larger orientation order is characteristic of the inner portions of both boride layers compared to their near-interface portions, in agreement with findings of other researchers [1, 14, 15]. This is easily explainable because near-interface portions of any boride layer are less equilibrated compared to its inner portions. Therefore, near-interface crystals have less time to align in the preferred direction.

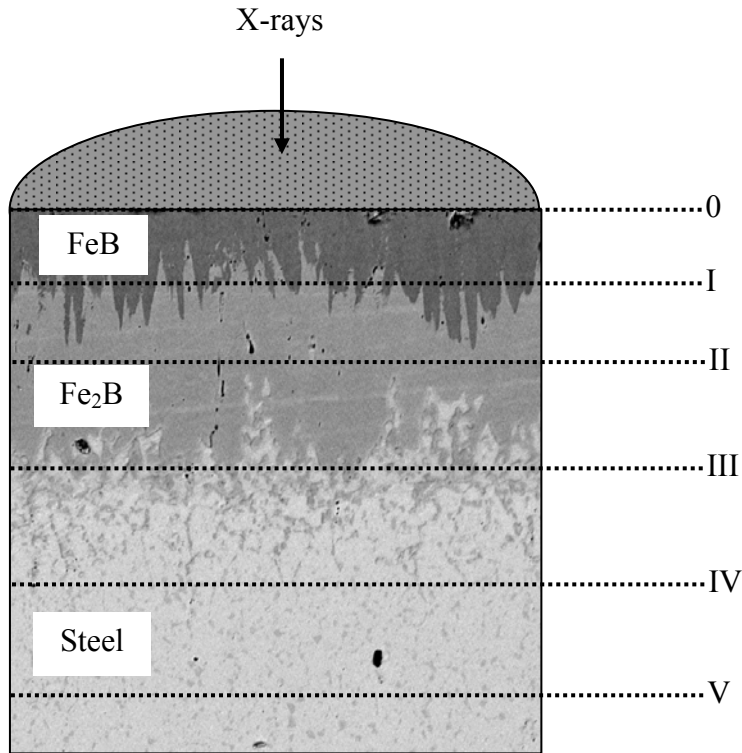


Fig.1. Backscattered electron image of boride layers formed at the steel-boron interface at a temperature of 950 °C (reaction time 6 h) and a scheme of X-ray diffraction experiments.

X-ray investigations were followed by electron probe measurements. Sections 0 of a borided steel sample corresponded to the FeB phase. Section I crossed both the FeB and Fe<sub>2</sub>B phases. Section II crossed the Fe<sub>2</sub>B phase. Inclusions of FeB in Fe<sub>2</sub>B were fine and rare. The microstructure of sections III and IV consisted of the steel base with fine inclusions of the FeB phase and an Fe–Cr phase containing 33-53 at.% chromium. Section V was entirely the steel base of nominal composition.

The FeB and Fe<sub>2</sub>B phases dissolve considerable amounts of chromium. Its distribution within the boride layers is rather irregular, due probably to non-equilibrium conditions of layer formation. The average chromium content is 8 at.% in the (Fe,Cr)B layer and 9 at.% in the (Fe,Cr)<sub>2</sub>B layer. These values agree fairly well with literature ones [14].

**Layer-growth kinetics.** Compared to other boriding agents mentioned in Introduction, mixtures of amorphous boron and KBF<sub>4</sub> allow much thicker and more regular boride layers to be obtained under similar conditions of temperature and time. After continuous layers of both iron borides have formed, their subsequent diffusional growth is due to two partial chemical reactions taking place at appropriate layer interfaces (Fig. 2):



The growth kinetics of compound layers are usually treated using parabolic equations of the type  $x^2 = 2k_1t$ , where  $x$  is the layer thickness,  $k_1$  is the layer growth-rate constant and  $t$  is time [9, 16, 17]. For sufficiently thick layers, such equations produce a quite satisfactory fit to the experimental data (Table 1).

In fact, however, growth kinetics of the FeB and Fe<sub>2</sub>B layers at the diffusional stage of their formation are somewhat more complicated and can alternatively be described by a system of two non-linear equations [10, 18-21]

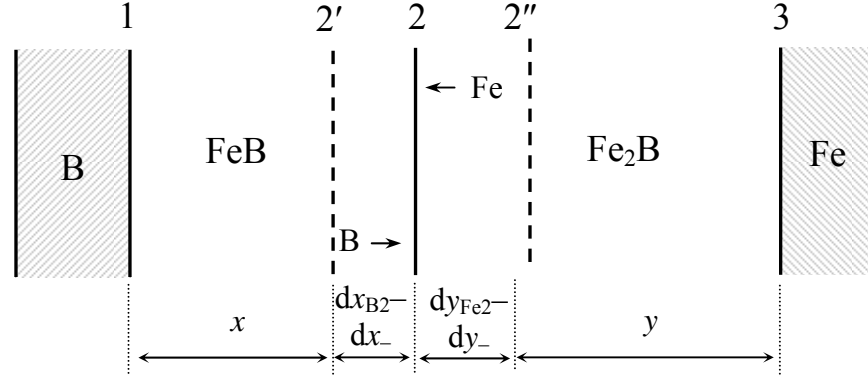


Fig. 2. Schematic diagram to illustrate the growth process of two iron boride layers under conditions of diffusion control. Both layers thicken at their common interface 2. No reactions can take place at interfaces 1 and 3 in view of the lack of appropriate diffusing atoms.

$$\frac{dx}{dt} = \frac{k_B}{x} - \frac{rg}{p} \frac{k_{Fe}}{y} \quad (2_1)$$

$$\frac{dy}{dt} = \frac{k_{Fe}}{y} - \frac{q}{sg} \frac{k_B}{x} \quad (2_2)$$

where  $x$  is the FeB layer thickness,  $y$  is the Fe<sub>2</sub>B layer thickness,  $k_B$  is the FeB layer growth-rate constant,  $k_{Fe}$  is the Fe<sub>2</sub>B layer growth-rate constant,  $g$  is the ratio of the molar volumes of the FeB and Fe<sub>2</sub>B compounds,  $p = q = r = 1$  and  $s = 2$  (factors from the chemical formulae of FeB and Fe<sub>2</sub>B).

Under conditions of diffusion control, both boride layers thicken at their common interface 2, as shown in Fig. 2. The FeB layer grows at the expense of diffusion of the boron atoms across its bulk and their subsequent reaction with the Fe<sub>2</sub>B compound. As a result, its thickness increases during  $dt$  by  $dx_{B2}$ . The Fe<sub>2</sub>B layer grows at the expense of diffusion of the iron atoms across its bulk and their further reaction with the FeB compound. During the same time  $dt$ , its thickness increases by  $dy_{Fe2}$ . Since the FeB and Fe<sub>2</sub>B compounds are consumed in the formation of each other, the thickness of the FeB layer simultaneously decreases by  $dx_{-}$ , while that of the Fe<sub>2</sub>B layer by  $dy_{-}$ . The net change of the FeB layer thickness during  $dt$  is the difference between  $dx_{B2}$  and  $dx_{-}$ , while that of the Fe<sub>2</sub>B layer thickness is the difference between  $dy_{Fe2}$  and  $dy_{-}$ . Therefore, Eqs. (2<sub>1</sub>) and (2<sub>2</sub>) contain two terms on their right-hand parts.

Even though both boride layers are often considered to grow at the expense of diffusion of the single component boron across their bulks, it is hardly possible with compact layers having no macrodefects and therefore growing by the volume-diffusion mechanism. During diffusional growth, by definition, diffusion across the layer bulks is the rate-determining step, the interface reactions being very fast. It means that all the boron atoms reaching interface 2 react with Fe<sub>2</sub>B to form FeB at that interface. Since the ability of interface 2 to combine those atoms exceeds their diffusional transport across the FeB layer, none of them can diffuse further to interface 3 and react with Fe to form Fe<sub>2</sub>B. Similarly, all the iron atoms diffusing across the Fe<sub>2</sub>B layer are combined into Fe<sub>2</sub>B by their reaction with FeB at interface 2. Hence, iron atoms cannot take part in the formation of the FeB layer at interface 1.

This obvious conclusion is usually overlooked, if the process of formation of compound layers is treated without writing the equations of chemical reactions proceeding at layer interfaces. The neglect of those reactions results in a misleading conclusion about the possibility of simultaneous diffusional growth of multiple layers. Since this is in fact impossible, any calculations based on Fick's laws yield fictitious values of diffusion coefficients, having no physical meaning.

Table 1. Kinetic data for the FeB and Fe<sub>2</sub>B layers formed at the steel-boron interface at 950 °C

Time ( $\times 10^2$ s)	$x$ ( $\times 10^{-6}$ m)			$k_1$ ( $\times 10^{-14}$ m <sup>2</sup> s <sup>-1</sup> )			$k$ ( $\times 10^{-13}$ m <sup>2</sup> s <sup>-1</sup> )	
	total	FeB	Fe <sub>2</sub> B	total	FeB	Fe <sub>2</sub> B	$k_B$	$k_{Fe}$
36	45	20	25	28.1	5.6	8.7		
72	65	30	35	29.3	6.3	8.5	4.02	6.60
108	80	35	45	29.6	5.7	9.3	3.30	6.03
144	90	40	50	28.1	5.6	8.7	3.17	5.46
180	100	45	55	27.8	5.6	8.4	3.57	6.00
216	110	50	60	28.0	5.8	8.3	3.60	5.80
288	125	60	65	27.1	6.3	7.3	3.57	5.32
360	140	65	75	27.2	5.9	7.8	1.77	2.98
432	155	75	80	27.8	6.5	7.4		

One of main criteria of the applicability of Eqs. (2) for treating the diffusional layer-growth kinetics is the constancy of  $k_B$  and  $k_{Fe}$  over a given range of time, as is the case with boride layers (Table 1). The value of  $g$  necessary for calculations of  $k_B$  and  $k_{Fe}$  was estimated from the densities of the FeB and Fe<sub>2</sub>B compounds ( $6.706 \times 10^3$  kg m<sup>-3</sup> and  $7.336 \times 10^3$  kg m<sup>-3</sup>, respectively [1]) as 0.60. The derivatives were found from the experimental layer thickness-time dependences by the numerical three-point method.

As seen in Table 1, the results of calculations using the system of Eqs. (2) are strongly dependent upon the accuracy of measuring the layer thickness. Approximations of experimental data with any suitable analytical functions are therefore advisable to obtain more accurate values of  $k_B$  and  $k_{Fe}$ . For example, the use of parabolic relations to approximate the layer thickness-time dependences and then to find the derivatives yields another set of values of  $k_B$  and  $k_{Fe}$  (Table 2). Comparing these with the average values of  $k_B$  and  $k_{Fe}$  found numerically from the experimental points, it may be concluded that both sets of the constants agree fairly well, providing evidence for the validity of the analytical treatment employed.

Table 2. Average values of layer growth-rate constants

Temperature (°C)	$k_1$ ( $\times 10^{-14}$ m <sup>2</sup> s <sup>-1</sup> )			$k$ ( $\times 10^{-13}$ m <sup>2</sup> s <sup>-1</sup> ) from experimental points		$k$ ( $\times 10^{-13}$ m <sup>2</sup> s <sup>-1</sup> ) from approximated dependences	
	total	FeB	Fe <sub>2</sub> B	$k_B$	$k_{Fe}$	$k_B$	$k_{Fe}$
850	8.8	1.6	3.0	1.21	2.44	1.04	2.01
900	17.3	3.5	5.3	2.68	4.70	2.17	3.74
950	28.1	5.9	8.3	3.29	5.45	3.61	5.96

The temperature dependence of the layer growth-rate constants is described in the 850-950 °C range by the following equations of the Arrhenius type:

$$K = K_0 \exp(-E/RT) \quad (3)$$

where  $K$  stands for any layer growth-rate constant,  $E$  is the activation energy,  $R$  is the gas constant and  $T$  is the absolute temperature:

$$\begin{aligned}k_1 &= 1.46 \times 10^{-7} \exp(-149.4 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1} \text{ for the FeB layer,} \\k_1 &= 7.87 \times 10^{-9} \exp(-116.4 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1} \text{ for the Fe}_2\text{B layer,} \\k_1 &= 1.36 \times 10^{-7} \exp(-132.8 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1} \text{ for both boride layers,} \\k_B &= 4.40 \times 10^{-7} \exp(-142.2 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}, \\k_{\text{Fe}} &= 1.24 \times 10^{-7} \exp(-124.3 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}.\end{aligned}$$

## Summary

Two boride phases FeB and Fe<sub>2</sub>B occur as separate layers at the interface between a commercial 13% Cr steel (40X13) and a mixture of amorphous boron with 5% KBF<sub>4</sub> at 850-950 °C and reaction times up to 12 h.

The characteristic feature of both layers is a pronounced texture. The strongest reflections are {002} and {020} for the orthorhombic FeB phase and {002} for the tetragonal Fe<sub>2</sub>B phase.

Diffusional growth kinetics of iron boride layers are close to parabolic and can alternatively be described by a system of non-linear differential equations.

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