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Diffusional Growth Kinetics of Boride Layers on Iron-Chromium Alloys

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Abstract. Two boride layers were found to form at the interface of iron-chromium alloys (10 and 25% Cr) or an industrial 13% Cr steel and boron at 850-950 °C and reaction times in the range 1-12 h. In the case of a Fe-10% Cr alloy and the steel, the layers are based on the FeB and Fe_2B compounds. With a Fe-25% Cr alloy, the constituent phases are FeB and CrB for the outer layer and Fe_2B and Cr_2B for the inner layer. Both layers are characterized by a pronounced texture. 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. The temperature dependence of the layer growth-rate constants obeys a relation of the Arrhenius type.

Introduction

Iron borides Fe_2B and FeB exist in the Fe–B binary system [1]. With iron, its alloys and steels, either one-layer or two-layer coatings can therefore be obtained, depending on boriding media employed and temperature-time conditions of a boriding procedure.

It should be noted 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 [2]. It contradicts diffusional considerations [3] predicting the simultaneous formation and subsequent parabolic growth of the layers of all compounds of any multiphase binary system, whatever their number, but agrees with a physico-chemical viewpoint [4], 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.

In this work, the results on the interaction of iron-chromium alloys (10 and 25% Cr) and industrial 13% Cr steel with boron in a mixture of amorphous boron powder and 5% KBF_4 at 850-950 °C are presented. The main attention is paid to an analysis of the boride layer-growth kinetics.

Experimental Procedure

Materials and Specimens. The materials used included high-purity iron powder (99.98% Fe), electrolytic-grade chromium platelets (99.98% Cr), a commercial 13% Cr steel rod (13 mm in diameter) in the as-received condition (without any additional heat treatment), amorphous powder boron (98.3% B) and analytical-grade KBF_4. 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. All contents are given in mass percent unless otherwise stated. The steel microstructure consisted of the body centered cubic α-phase (ferrite) with fine inclusions of carbides $Me_{23}C_6$ (Me = Cr, Fe).

Cylindrical rods (13 mm in diameter) of Fe-Cr alloys were prepared by arc-melting of appropriate metals under argon, with subsequent casting of the melts into water-cooled copper crucibles. The rods were annealed to ensure their homogenization at a temperature of 1100 °C for 2 h in an argon atmosphere at a pressure of 2.5×10^4 Pa. Specimens in the form of tablets, 11.28 mm in diameter and 5.5 mm high, were machined from the alloy or steel rods. Flat sides (1 cm^2 area) of the tablets were ground and polished mechanically.

Experimental Methods. The vacuum device VPBD-2S employed for boriding solid samples has been described elsewhere [5]. The experiment was carried out in an alumina crucible, 13 mm inner diameter and 40 mm high. A solid tablet was embedded into a mixture of boron powder with 5% KBF_4 as an activator. This amount of KBF_4 appears to be optimum [2,6].

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 2.5×10^4 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 ^{o}C had been reached in the furnace, the crucible, pre-heated to about 400 ^{o}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 constant within ± 1^{o}C. The temperature measurements were carried out using a Pt-PtRh thermocouple. The experiments were performed at temperatures of 850, 900 and 950 ^{o}C. Their duration was 3600-43200 s (1-12 h). After the experiment, the 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 initial materials and boride layers was carried out with the help of metallography, X-ray and chemical analyses, and electron probe microanalysis.

Results and Discussion

Phase Identity and Chemical Composition of Boride Layers. Two boride layers are formed at the interface of iron-chromium alloys or the steel and boron at 850-950 ^{o}C and reaction times up to 12 h (Fig. 1). Layer-by-layer X-ray analysis [5,7] and a further comparison of our and literature [8] data showed that with a Fe-10% Cr alloy and the steel the outer layer bordering the boriding agent was the FeB phase, while the inner layer adjacent to the tablet base was the Fe_2B phase.

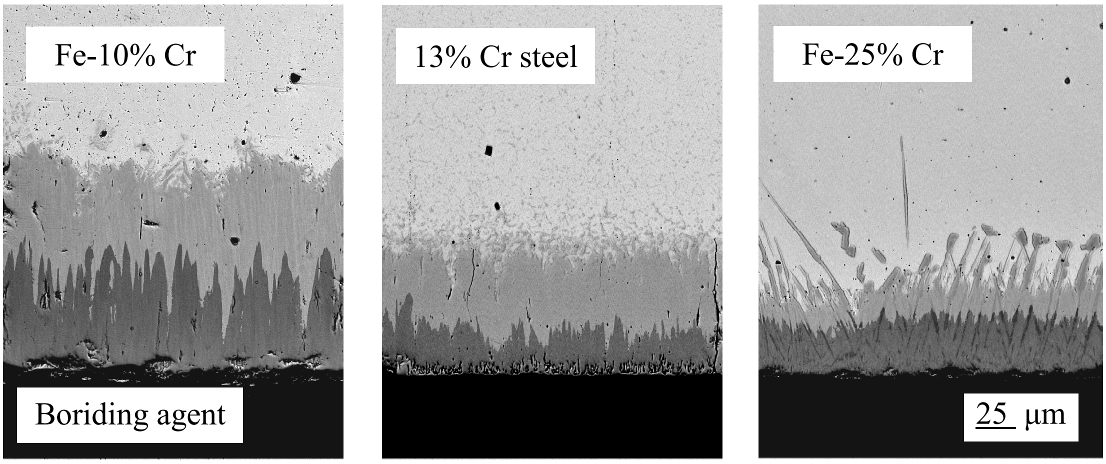


Fig. 1 Backscattered electron images of boride layers formed at the interface of Fe-Cr alloys or the steel and boron at a temperature of 950 ^{o}C.

The structure of boride layers on the surface of Fe-25% Cr alloy samples proved to be more complicated. Each of them consists of two phases. As seen from plain-view micrographs of Fig. 2, the outer boride layer consists of distinct brighter and darker regions, with the latter having a peculiar regular arrangement. EPMA measurements indicate that iron prevails in brighter regions, while chromium is dominant in darker regions. Hence, compositionally the outer boride layer actually comprises the (Fe,Cr)B and (Cr,Fe)B phases, although X-ray diffraction analysis practically does not show the presence of the CrB phase, probably because, firstly, the FeB and CrB phases have very similar crystal structures [1,8] and, secondly, under non-equilibrium conditions the lattice rearrangement is not completed in view of time limitations. Being far from equilibrium, this layer appears to be single-phase structurally and two-phase compositionally.

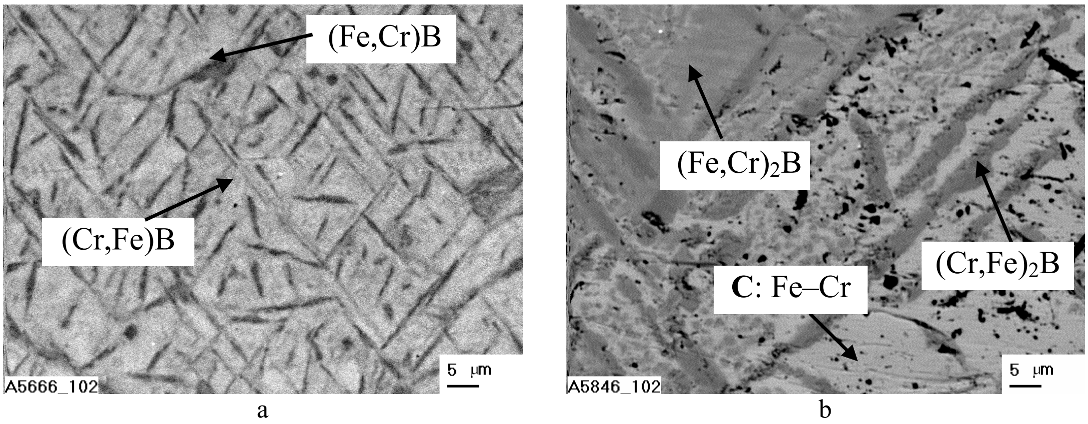


Fig. 2 Plain-view micrographs of sections crossing (a) the outer and (b) inner boride layers.

The inner boride layer was also found to be non-homogeneous (see Fig. 2b). Like the outer layer, it consists of the $(Fe,Cr)_2B$ and $(Cr,Fe)_2B$ phases. Note that the Fe_2B and Cr_2B phases are isomorphous [1,8]. Both boride 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) for the orthorhombic FeB phase, and {002} ($d = 0.212$ nm) for the tetragonal Fe_2B 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 [6,9]. 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.

Layer-Growth Kinetics. 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 the time [3,10]. For thick layers, such equations produce a quite satisfactory fit to the experimental data (Fig. 3). In fact, however, growth kinetics of the FeB and Fe_2B layers at the diffusional stage of their formation are somewhat more complicated. After compact layers of both borides have formed, their subsequent diffusional growth is due to two partial chemical reactions

$$B_{dif} + Fe_2B = 2FeB \tag{1$_1$}$$

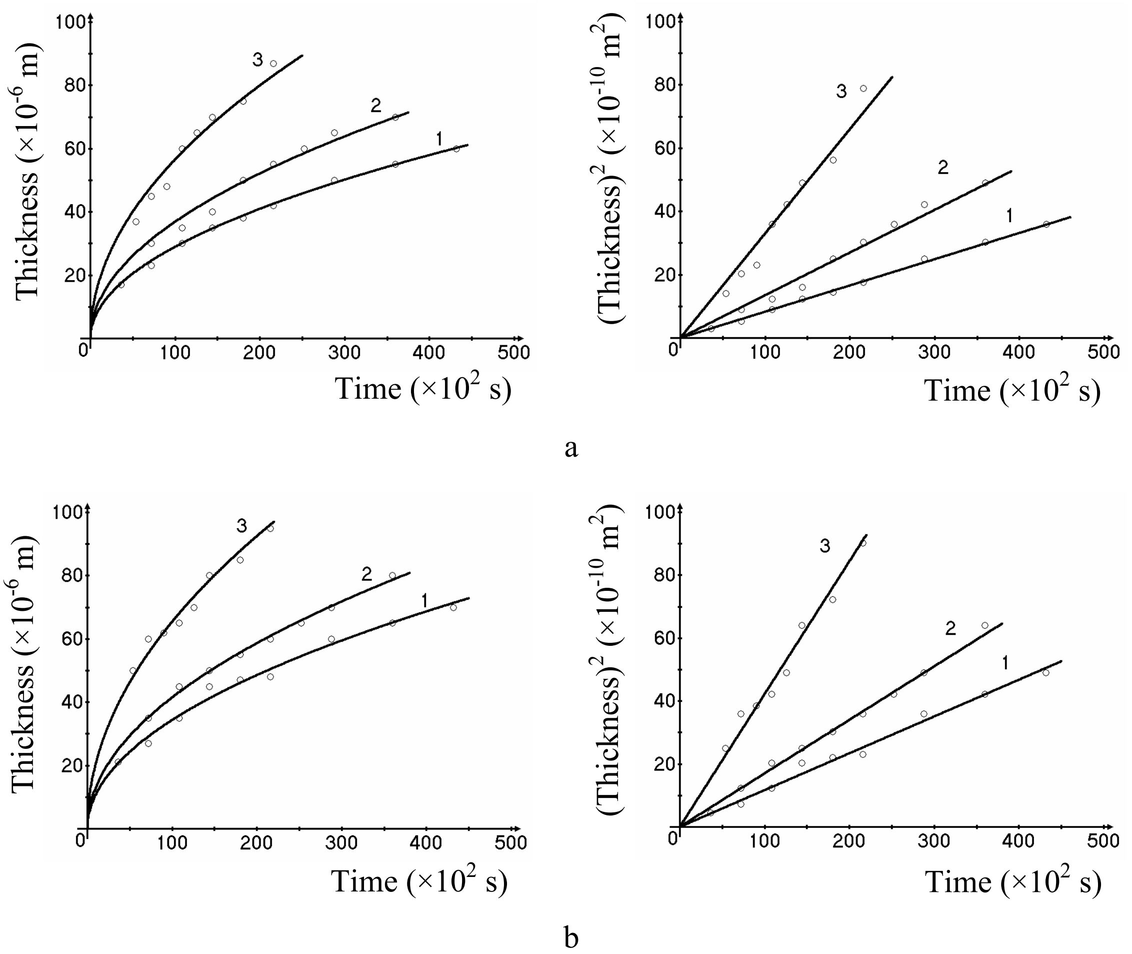
$$Fe_{dif} + FeB = Fe_2B \tag{1$_2$}$$

taking place at interface 2 (Fig. 4). Layer-growth kinetics are described by a system of two non-linear equations [4,11,12]

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

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

where x is the FeB layer thickness, y is the Fe_2B layer thickness, k_B is the FeB layer growth-rate constant, k_{Fe} is the Fe_2B layer growth-rate constant, g is the ratio of the molar volumes of the FeB and Fe_2B compounds, $p = q = r = 1$ and $s = 2$ (factors from the formulae of FeB and Fe_2B).



a

b

Fig. 3 Plots of layer thickness (left) and squared layer thickness (right) against time for (a) the FeB layer and (b) the Fe_2B layer formed at the interface of a Fe-10% Cr alloy and boron at a temperature of 850 °C (line 1), 900 °C (line 2) and 950 °C (line 3).

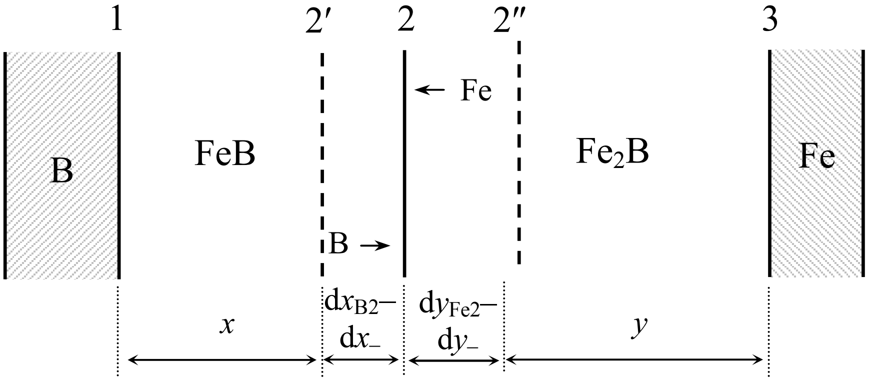


Fig. 4 Schematic diagram to illustrate the growth process of two iron boride layers under conditions of diffusion control. Both layers thicken at their common interface 2.

Under conditions of diffusion control, both boride layers thicken at their common interface 2, as shown in Fig. 4. 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 macroscopic defects and therefore growing by the volume-diffusion mechanism.

Table 1 Kinetic data for the FeB and Fe_2B layers formed at the steel-boron interface at 850 °C.

Time ($\times10^2$ s)	**Layer thickness** ($\times10^{-6}$ m)			**Growth constant from a relation $x^2 = 2k_1t$** k_1 ($\times10^{-14}$ m^2 s^{-1})			**Growth constant from Eqns. (2)** k ($\times10^{-13}$ m^2 s^{-1})	
	total	**FeB**	**Fe_2B**	**total**	**FeB**	**Fe_2B**	**k_B**	**k_{Fe}**
36	25	12	13	8.7	2.0	2.3		
72	35	15	20	8.5	1.6	2.8	1.54	3.13
144	50	20	30	8.7	1.4	3.1	0.94	2.01
216	60	25	35	8.3	1.5	2.8	0.94	1.88
288	70	28	42	8.5	1.4	3.1	1.03	2.23
324	75	30	45	8.7	1.4	3.1	1.19	2.46
360	80	33	47	8.9	1.5	3.1	1.31	2.56
396	85	35	50	9.1	1.5	3.2	1.53	2.83
432	90	40	50	9.4	1.9	2.9		

An obvious criterion of the applicability of Eqns. (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, $\rho_1 = 6.70 \times 10^3$ kg m^{-3} and $\rho_2 = 7.34 \times 10^3$ kg m^{-3}, of the FeB and Fe_2B compounds [6] and their molecular masses, $M_1 = 66.65$ g mol^{-1} and $M_2 = 122.49$ g mol^{-1}: $g = M_1\rho_2/M_2\rho_1 = 0.60$. The derivatives were found from the experimental layer thickness-time dependences by the numerical three-point method using a conventional computer program (linear approximation). To find a derivative for a given experimental point, (x_i, t_i), like those on left-hand plots of Fig. 3, data for two neighboring points, (x_{i-1}, t_{i-1}) and (x_{i+1}, t_{i+1}), were also used. Left-hand and right-hand derivatives, $(x_i - x_{i-1})/(t_i - t_{i-1})$ and $(x_{i+1} - x_i)/(t_{i+1} - t_i)$, were first found for this point and a mean value was then calculated. The derivatives could thus be found for all experimental points, excepting clearly end ones, for which a neighboring point is lacking. As seen in Table 1, the results of calculations of k_B and k_{Fe} are strongly dependent upon a scatter of experimental points. To avoid this, approximation of experimental data with any suitable analytical function is therefore advisable. 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). Since the experimental $x - t$ dependences become smoothed as a result of this procedure (solid lines on left-hand plots of Fig. 3), all values of k_B thus found are identical. The same applies to k_{Fe}. 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. Note that parabolic relations only predict a gradual growth of both compound layers with increasing time. According to Eqs. (2), however, one of them may shrink, while the other grows, as often observed in practice [4].

The temperature dependence of layer growth-rate constants, K, is described in the 850-950 °C range by the Arrhenius equation $K = K_0 \exp(-E/RT)$, where E is the activation energy, R is the gas constant and T is the absolute temperature. Values of K_0 and E are listed in Table 3.

Summary

Two boride layers based on the phases FeB and Fe_2B occur at the interface of a Fe-10% Cr alloy or an industrial 13% Cr steel and boron at 850-950 °C and reaction times up to 12 h. With a Fe-25% Cr alloy, the constituent phases are FeB and CrB for the outer layer and Fe_2B and Cr_2B for the inner layer. The characteristic feature of both layers is a pronounced texture.

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

Table 2 Values layer growth-rate constants found from a parabolic relation, k_1, and from Eqns. (2), k.

Alloy	Temperature (°C)	k_1 ($\times10^{-14}$ $m^2 s^{-1}$)			k ($\times10^{-13}$ $m^2 s^{-1}$) from experimental		k ($\times10^{-13}$ $m^2 s^{-1}$) from approximated	
		total	FeB	Fe_2B	k_B	k_{Fe}	k_B	k_{Fe}
10% Cr	850	19.8	4.1	5.9	2.8	4.6	2.5	4.2
	900	30.4	6.6	8.6	4.5	7.1	4.0	6.3
	950	72.4	15.4	21.4	11.0	18.2	9.4	15.4
25% Cr	850	5.3	1.6	1.1	0.92	1.02	0.86	0.96
	900	8.9	3.1	1.7	1.69	1.71	1.60	1.59
	950	16.0	5.0	3.1	2.49	2.69	2.63	2.79
Steel	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

Table 3 Values of K_0 ($m^2 s^{-1}$) and E (kJ mol^{-1}) for Arrhenius-type equations.

Alloy	k_1						k_B		k_{Fe}	
	total		FeB		Fe_2B					
	K_0	E	K_0	E	K_0	E	K_0	E	K_0	E
10% Cr	1.32×10^{-6}	147.5	3.89×10^{-7}	150.6	3.46×10^{-7}	146.4	2.16×10^{-6}	149.8	2.79×10^{-6}	147.5
25% Cr	3.74×10^{-8}	125.9	1.86×10^{-8}	130.2	3.27×10^{-9}	118.0	8.07×10^{-8}	128.3	4.32×10^{-8}	121.7
Steel	1.36×10^{-7}	132.8	1.46×10^{-7}	149.4	7.87×10^{-9}	116.4	4.40×10^{-7}	142.2	1.24×10^{-7}	124.3

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