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Preferred orientation of boride crystals in the borided layers: a quantitative method of evaluation

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A method is proposed to quantitatively evaluate the preferred orientation of FeB and Fe_2B crystals, constituting the borided layer obtained on iron. The preferred orientation is expressed by an empirically calculated factor σ, which allows a fair fit of calculated with observed peak intensities by X-ray diffraction analysis of the layer (R value $\leqslant 0.15$). In a further investigation, this coefficient (σ) was used to quantitatively examine the influence of temperature and reagent composition on the degree of orientation of the phases obtained by boronizing pure iron.

1. Introduction

In the last years, a new thermochemical treatment based on the diffusion of boron in steel, which improves its hardness and wear resistance has been the subject of several studies. This surface treatment can be conducted using solid, liquid or gaseous reagents [1–3].

Pack boronizing is one of the more common boriding methods because it requires very simple equipment. The samples are dipped into a powdery reagent which is contained either in a steel box or in a ceramic crucible, then they are heated in an oven at 1123 to 1273 K (850–1000° C) for 2 to 8 h. Boriding powders are constituted of a reagent which can give out boron (amorphous boron or boron carbide B_4C), an activating reagent (generally KBF_4) and an inert diluent (silicon carbide and/or graphite). Because of the high temperatures reached during the boriding treatment, KBF_4 decomposes to gaseous boron fluoride which is restored by boron carbide.

Surface layers of elevated hardness can be obtained by boronizing various metals [4, 5] but this treatment is principally used for steel hardening.

Boriding layers obtained by steel treatment are constituted of solid solutions of (Fe, M)B and $(Fe, M)_2B$ type. These form when some transition elements partially substitute iron in the borides FeB and Fe_2B. The phases derived from FeB and Fe_2B borides, have the same crystal symmetry as the compounds [6]. The boride FeB is orthorhombic with lattice parameters $a_0 = 0.4059$ nm, $b_0 = 0.5503$ nm and $c_0 = 0.2947$ nm; its space group is Pbmn (V_h^{16}) [7]. The Fe_2B boride is tetragonal, it has lattice parameters $a_0 = 0.510$ nm and $c_0 = 0.424$ nm, and belongs to the I4/mcm (D_{4h}^{18}) space group [8]. In this work we have oriented the elementary cell of the FeB boride according to the standard setting of Pnma space group. For this reason the lattice parameters of this phase become $a_0 = 0.551$ nm, $b_0 = 0.295$ nm and $c_0 = 0.406$ nm [9].

The (Fe, M)B phase, which is richer in boron, constitutes the outermost part of the surface layer; its quantity, in regard to all the borides present, depends on the boronizing conditions as well as on the chemical composition of the steel [10]. The indentation of the phase boundaries between either FeB and Fe_2B borides or Fe_2B and the metallic matrix, increases as the content of alloying elements in the steel decreases. In the borided layers, in zones corresponding to the boundaries, it is normally possible to find mixed crystals of different phases (Fig. 1). By roentgenographic analysis of the phases present in the borided layers obtained during steel treatment, it is possible to ascertain that the boride crystals have an ordered orientation. Crystals of the FeB type preferentially align themselves with the *y*-axis perpendicular to the sample surface, whilst those of the Fe_2B type orientate themselves with the *z*-axis perpendicular to this surface. Consequently, the peaks of the FeB and Fe_2B type phases corresponding to crystallographic planes, with deviation from zero of the k or l index respectively, show increased intensities in the X-ray diffraction spectra.

Kunst and Schaaber [11], in agreement with other authors [12], proposed a theory to explain this behaviour. They pointed out that, when the crystalline structures of these two borides are projected on the (0 1 0) plane (for the FeB type phase) or on the (0 0 1) (for the Fe_2B type phase), it is possible to establish that the boron atoms are connected in chains. These chains oriented in the direction of y or z axes (Figs. 2, 3) are not interrupted by metallic atoms. According to Kunst and Schaaber [11], boron diffusion through boride crystals occurs more readily when the atoms jump between neighbouring lattice positions along these chains. In order to allow the above mentioned diffusion mechanism, a part of the lattice positions in the boron atom chains must be vacant. This was experimentally verified by Kunst *et al.* [11].

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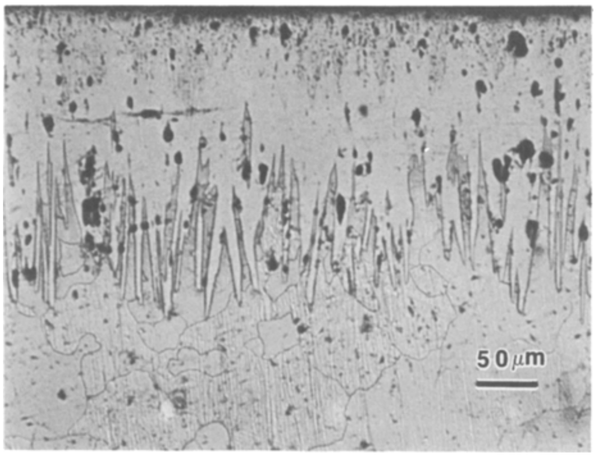

Figure 1 Armco iron sample borided for 7 h at 1223 K with powders (B_4C = 20%; KBF_4 = 5%; SiC = 75%), etching 5% nital.

As a result of this diffusion mechanism the boride crystals, which are arranged with their boron atom chains parallel to the non-metal diffusion direction (i.e. perpendicular to the sample surface), grow more quickly than the others. The preferred orientation of crystals constituting the surface layers obtained by boronizing steels also depends on the treatment conditions (e.g. the temperature).

In this paper a method is described to quantitatively evaluate the degree of orientation of boride crystal grains along a preferred direction. This method is based on X-ray diffraction analysis and involves comparison between the experimental peak intensities measured on the diffraction curves, and those theoretically computed according to a model which takes into account the preferred orientation of crystal grains. We have used this method to study the influence that boriding conditions exert on the texture of the surface layer.

2. Experimental conditions

2.1. Sample preparation

Boriding was carried out on discs of Armco iron, with a diameter of 30 mm and a thickness of 4 mm. The surface of the samples were ground accurately and levigated by means of abrasive papers and cloths before boronizing. The treatment was carried out at 1123, 1173 and 1273 K using powdery reagents of variable composition. The treatment conditions are shown in Table I.

For each set of process conditions two samples were borided in a ceramic crucible. The crucibles were sealed by means of a mixture of sodium silicate pentahydrate and alumina which was placed on the surface of the reacting powder and heated to the treatment temperature at which melting of this mixture occurred. Boronizing was carried out for periods of 24 h with the purpose of obtaining, for all the temperatures and the reacting powder compositions used, a two-phase layer (FeB + Fe_2B) of appreciable thickness. Borided samples were polished by slight abrasion on papers then analysed by means of X-ray diffraction (FeK_α $\lambda = 193.73$ pm), using an automatic computerized Philips PW1710 with detraction of the instrumentation background.

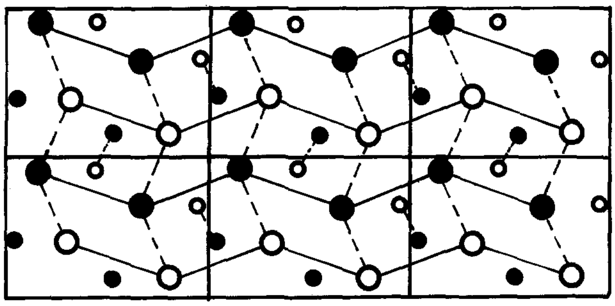

Figure 2 FeB structure projected on the (0 1 0) crystallographic plane: ○ = Fe atom in 1/4b; ● = Fe atom in 3/4b; o = B atom in 1/4b; • = B atom in 3/4b.

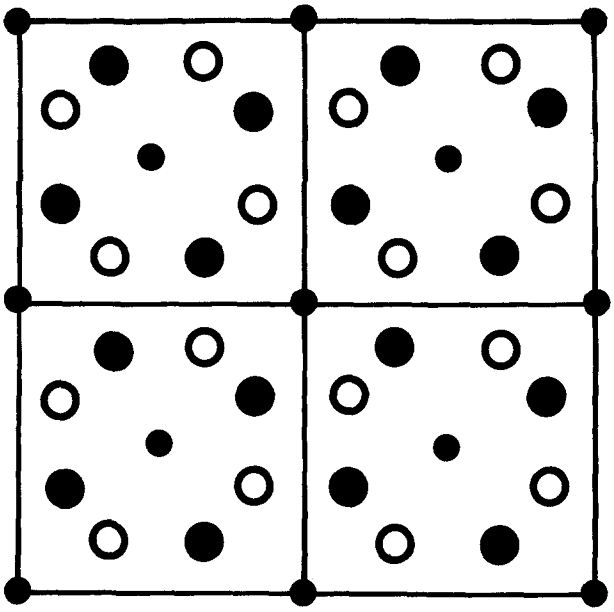

Figure 3 Fe_2B structure projected on the (0 0 1) crystallographic plane: ○ = Fe atom in 1/4c; ● = Fe atom in 3/4c; • = 3 B atoms in 0, 1/2, lc.

The analyses were first carried out on the surface of the samples then repeated several times after progressive mechanical removal of a measured part of the surface layer. In such a way the phases constituting the borided layer were characterized at different distances from the surface of the sample. The analyses were carried out on both plane surfaces of the two samples for each set of treatment conditions and for each episode of material removal. The peak intensities of the X-ray diffraction pattern were calculated as an average of these four determinations.

Evaluation of the thickness of the removed material was made by means of weight loss measurements. This was computed from the weight reduction of the sample,

TABLE I Treatment conditions for sample preparation

Sample no	Temperature (K)	Boriding powder composition (wt. %)		
		B_4C	KBF_4	SiC
1	1123	20	5	75
2	1123	40	10	50
3	1173	30	7.5	62.5
4	1173	20	5	75
5	1273	20	5	75
6	1273	40	10	50

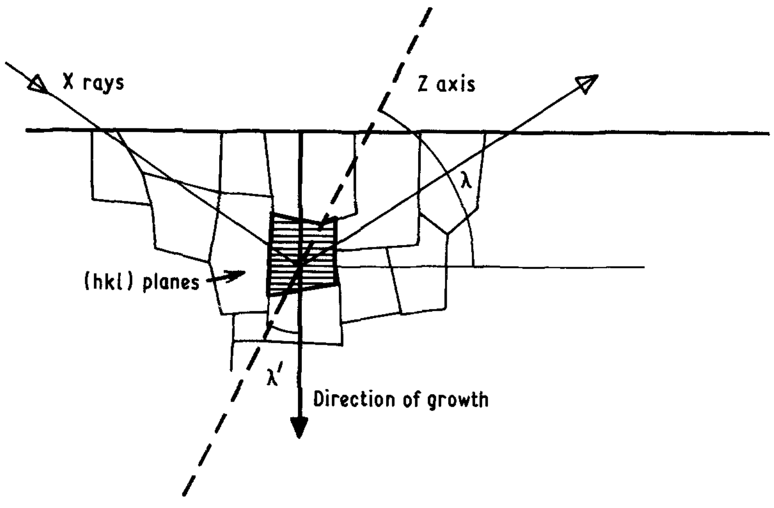

Figure 4 Geometry of the diffraction process: relationship between λ and λ' angles.

knowing both its geometric shape and the absolute gravity of the borides.

As we are going to demonstrate later in this paper, the degree of preferred orientation developed increases from the edge of the samples towards the centre. The experimental X-ray diffraction patterns regards a certain thickness of the investigated layers because X-rays have a significant depth of penetration in borides; therefore this analytical method averages the information about the preferred orientation of boride crystals. In spite of this, by using this method it is possible to carry out a comparison between samples treated under different conditions.

2.2. Description of the model and data processing

This model was used in order to quantify the preferred orientation of both FeB and Fe_2B compounds. For reasons of simplicity we shall first describe its application to Fe_2B, for which the direction of preferred growth is coincident with the z-axis of the tetragonal cell.

From the above it can be inferred that the crystal grain growth is supported by boron supplied through a layer of pre-formed boride which strongly affects the orientation of the crystals under formation. The prerequisite of a random orientation of crystals, typical of powder diffraction measurements, is invalid.

In the diffraction geometry of a plane sample (according to Seeman–Bohlin) a generic *hkl* lattice plane of a crystal grain, must lie parallel to the surface of the sample in order to display a diffraction capability for the incident X-ray beam. Therefore the same *hkl* plane has to be found in a perpendicular position relative to the direction of both boron diffusion and of layer growth. For the prepared samples these are perpendicular to the plane surface of the sample. For example the *hkl* lattice planes of the $(0\,0\,l)$ type, which form an angle of 90° with the z-axis, will be in the correct position for diffraction when the z-axis of the unit cell is alligned with the diffusion direction. For a generic *hkl* lattice plane a proper λ' angle between the z-axis of the unit cell and the growth direction will be formed, so as to allow a diffraction capability for the same lattice plane (Fig. 4). Under conditions of preferred crystal growth, the probability of finding a crystal grain with a family of *hkl* planes in a suitable position for diffraction will depend on the λ' angle and will decrease as the latter increases. As a result, we should see a weakening of the intensities corresponding to those *hkl* reflexions for which the λ' angle deviates from nil, in respect to reflexions of $(0\,0\,l)$ type (Table II). λ is the angle formed between the generic lattice plane *hkl* and the z-axis (Fig. 4), whilst λ' is the angle between the z-axis and the direction of growth. For each reflection this λ angle can be computed using a known formula of spatial trigonometry and therefore the λ' angle is deduced as follows

$$\lambda = \arccos \frac{l/c_0}{\sqrt{h^2/a_0^2 + k^2/b_0^2 + l^2/c_0^2}}$$

$$\lambda' = 90 - \lambda \qquad (1)$$

The relative peak intensities for a sample without preferred crystal orientation have to coincide with those of a powdered sample. We have calculated these values instead of taking them from the literature or measuring them on the powdered samples of borides, because it is difficult to be sure that a completely random crystal arrangement occurs in a powdered sample. Theoretical peak intensities for samples with no preferred orientation have been calculated and compared with measured intensities. They were calculated from the atomic coordinates of FeB and Fe_2B [9], from their space group, from the Lorenz and Polarization factors and from the multiplicity of each reflection, as follows

$$I_{\text{powder}} = m(1 + \cos^2 2\Theta)(\sin^2\Theta \cos\Theta)^{-1} \times (\Sigma_n F e^{-B\sin 2\Theta/\lambda^2} gf)^2 \qquad (2)$$

where
m = multiplicity of the reflection
F = scattering factor [13]
g = occupation
f = geometric structure factors [14]
n = number of independent atomic positions
λ = wave length
Θ = diffraction angle
B = thermal factor
e = base of natural logarithms

The computer programme was developed in this Department.

In a further step it was assumed, and the hypothesis was confirmed *a posteriori* by the fair fit with experimental data, that the weakening of the intensities of the different *hkl* reflections in respect to those computed for a powdered sample, are to be related to λ' according to an inverse exponential law.

$$I_{\text{preferred}} = I_{\text{powder}}\, e^{-\sigma\lambda'/100} \qquad (3)$$

Where σ is a coefficient which increases as the preferred orientation is enhanced. The factor 100 was inserted with the purpose of bringing the σ values to a definite range (i.e. 0 to 10). The value of this exponential function decreases from 1 toward zero when the λ' angle increases. Therefore it decreases when the probability of finding crystals with the *h k l* plane (in relation to which the peak intensity is calculated) parallel to the surface decreases. The slope of this function is determined by the σ coefficient.

Before comparison with measured intensities, the calculated intensities were scaled in respect to the first by multiplying them with a proper value, chosen in such a way as to allow that

$$\Sigma_n I_{\text{observed}} = \Sigma_n (I_{\text{powder}}\, e^{-\sigma\lambda'/100}) \qquad (4)$$

where the summation is carried out on all the n peaks of the experimental spectrum. This enables direct comparison of the calculated peak intensities with the observed ones using correlation factor (R), usually computed for powder diffraction. This is defined as follows

$$R = \frac{\Sigma_n |I_{\text{preferred}} - I_{\text{observed}}|}{\Sigma_n I_{\text{observed}}} = \frac{\Sigma_n |I_{\text{powder}}\, e^{-\sigma\lambda'/100} - I_{\text{observed}}|}{\Sigma_n I_{\text{observed}}} \qquad (5)$$

The σ factor of preferred orientation was determined for each sample and for each set of measured intensities by finding which factor value corresponds to the lowest R value. To this purpose σ was varied with 0.1 steps starting from 0 up to the value which makes R lowest. The intensities computed above always agree with the observed ones, with R values less than 0.15 for every examined sample.

TABLE II Angles λ' for the lattice planes of FeB and Fe_2B phases (for FeB λ' is the angle between the y-axis and the growth direction of the layer)

FeB phase		Fe_2B phase	
lattice plane	λ' angle	lattice plane	λ' angle
101	90	110	90
200	90	200	90
011	36.3	002	0
201	90	211	61.7
111	42.3	112	30.4
210	47.0	220	90
102	90	202	39.7
211	52.4	130	90
301	58.1	222	49.6
112	57.4		
020	0		
311	60.5		

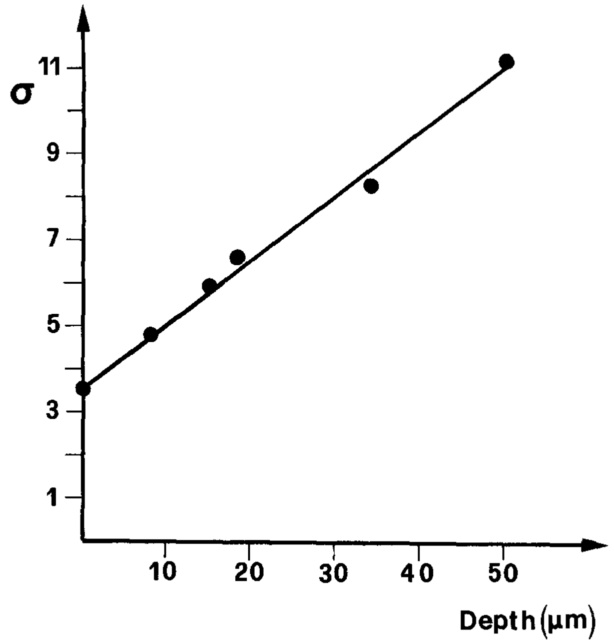

Figure 5 Trend of the σ coefficient values for FeB against the distance from the sample surface.

3. Results and discussion

Measurements of preferred orientation on borided samples of Armco iron were carried out firstly at progressively increasing distances from the surface. To such purposes the samples were grinded removing measured thicknesses of borided layer. The results, obtained on sample no 4 (Table I) after 24 h treatment, are resumed in Table III. They clearly show an increasing orientation (in respect to the y-axis of the orthorhombic unit cell of FeB) with the thickness of removed layer (i.e. with the distance from the surface) (Fig. 5).

The relative diffraction patterns are also shown in Fig. 6; the intensity variations are clearly evidenced for the FeB, while the intensities of the underlying Fe_2B gradually increase.

These results can be explained with the aid of the theory of "diffusion channel" as proposed by Kunst *et al.* [11], by supposing different stages in the boriding process. Firstly, boron diffuses into the metal with a velocity slightly dependent on the lattice type: face or body centred (the respective diffusion coefficients as reported in the literature are $1.53\ 10^{-7}\,cm^2\,sec^{-1}$ at 950° C and $1.45\ 10^{-7}\,cm^2\,sec^{-1}$ at 900° C) [11]. These rather high diffusion coefficients are of the same magnitude as those competing for other small size elements (like C and N). On the contrary boron solubility in

TABLE III Perferred orientation of the FeB phase crystals at increasing distances from the surface (sample no 4)

Measurement no	Distance from the surface (μm)	Preferred orientation coefficient (σ) of the FeB phase	Correlation factor (R)
1	0	3.5	0.12
2	8	4.8	0.08
3	15	5.9	0.11
4	18	6.6	0.08
5	34	8.2	0.03
6	50	11.1	0.04

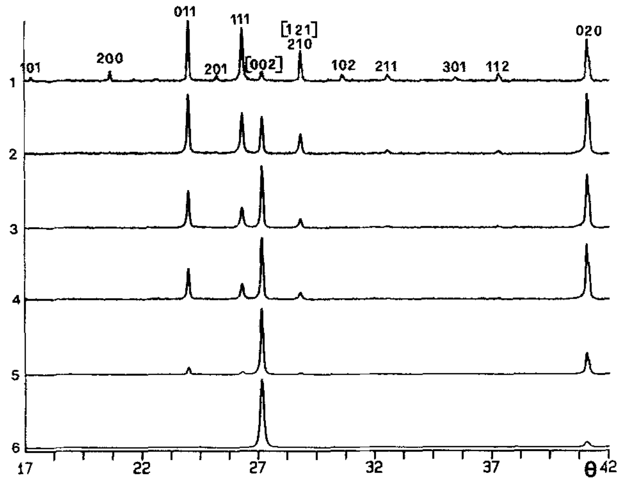

Figure 6 X-ray diffraction patterns carried out on sample no 4 at increasing distances from the surface; some peaks of the phases FeB and Fe_2B are labelled with their reflexion indexes (in brackets for Fe_2B), the number of each spectrum refers to Table III.

iron is very low and strongly dependent on irregularities in the crystal lattice and therefore also on the purity of the same metal. When a suitable boron concentration is reached at some points on the surface of the metal, Fe_2B crystals begin to nucleate. Secondly, a surface layer composed of Fe_2B is obtained, under which a wide boron diffusion zone is located. The crystals constituting the above surface layer are statistically oriented in every possible direction.

Kinetic studies have shown that the boron diffusion coefficient in the Fe_2B boride ($9.25\ 10^{-9}\,cm^2\,sec^{-1}$ at 900° C) [11] is lower than that encountered in pure iron. Therefore, once the formation of the compound in a thin surface layer has been completed, the growth rate of the same layer is strongly affected by the velocity of boron diffusion through it. According to the theory of "diffusion channel" diffusion of boron through each of the Fe_2B crystal grains occurs more readily as the angle between the z-axis and the direction perpendicular to the sample surface (Fig. 4) decreases. Therefore while some crystals grow rapidly, others grow more slowly and are incorporated by the rapidly growing nuclei at high temperatures. As a result increased orientation along z-axis takes place, contemporary to the growth of the composition layer.

Operating at higher temperatures and employing a boronizing agent of proper composition it is possible to obtain on the outermost part of the surface the boride FeB richest in boron. On the superficial area of the sample on which a sufficient boron concentration is reached, the nucleation and growth of the latter phase occurs. This first layer possesses a random orientation of single grains. According to Kunst and Schaaber [11], boron diffusion into this phase is similarly affected by orientation, as for Fe_2B. It occurs with preference through those crystals displaying a lesser angle between the diffusion direction and y-axis. This provokes a progressive orientation of crystal grains inside the FeB layer during the growth of the same layer. According to the above, the hardened surface layer obtained by boriding Armco iron is constituted by an outermost zone of FeB composition, inside which the crystals show a trend to progressively ordered orientation starting from the surface towards the inside of the sample. The underlying zone of Fe_2B composition shows to a higher degree the particular texture described above.

With the aim of studying the influence that the boriding conditions exert on the texture of the surface layer, samples of Armco iron were borided by means of powder reagents of different composition and at different temperatures (Table I). Armco iron was preferred to steels because the alloying elements, which often substitute iron in the boride lattice, can probably influence the growth mechanism described above.

After slight polishing of the surfaces, all the samples were analysed by X-ray diffraction in order to evaluate the preferred orientation of the FeB phases obtained in different treatment conditions. The preferred orientation of the Fe_2B phase was estimated in an analogous way after mechanical removal of the compound FeB from the surface layer. The results reported in Table IV show that the degree of preferred orientation clearly depends on the boriding conditions adopted. The preferred orientation is as much appreciable as the temperature and reactivity of the boriding reagent are higher.

The influence of the temperature was qualitatively observed by Kunst and Schaaber [11]. This behaviour can be explained on the basis of the mechanism for the formation of the layer exposed above.

In fact, when a compound layer is formed with crystals casually arranged, a growth of orientated crystals develops as a consequence of the diffusion mechanism of boron through the borides. We think that the thickness of the part of the layer in which crystals show a disorderly arrangement depends on

TABLE IV Preferred orientation of the crystals constituting the borided layers obtained in different treatment conditions (FeB and Fe_2B phases)

Temperature (K)	1123		1173		1273	
Boriding composition (wt. %)	FeB	Fe_2B	FeB	Fe_2B	FeB	Fe_2B
B_4C = 40%; KBF_4 = 10%; SiC = 50%	$\sigma = 6.4$ R = 0.06	$\sigma = 7.1$ R = 0.07	– –	– –	$\sigma = 9.2$ R = 0.02	$\sigma = 8.9$ R = 0.02
B_4C = 30%; KBF_4 = 7.5%; SiC = 62.5%	– –	– –	$\sigma = 6.2$ R = 0.15	$\sigma = 6.0$ R = 0.12	– –	– –
B_4C = 20%; KBF_4 = 5%; SiC = 75%	$\sigma = 3.4$ R = 0.15	$\sigma = 3.9$ R = 0.12	– –	– –	$\sigma = 5.1$ R = 0.08	$\sigma = 9.1$ R = 0.04

the temperature and on the chemical composition of the reagent. Strong reactivity of the boriding powders (due to increasing temperature or to chemical composition) causes the quick formation of borides on the surface sample. When a weaker reagent is used, boron diffusion happens for a longer time, so that a greater thickness of the material is saturated by boron when boride nucleation occurs. Therefore in this second case the nucleation covers a large area.

4. Conclusions

A computer simulation method for the comparison of experimental peak intensities with calculated X-ray diffraction spectra of FeB and Fe_2B borides may be used to quantitatively evaluate the preferred orientation of the crystals constituting the borided layers. In the course of the simulation the intensities of the diffraction peaks were calculated, taking into consideration the preferred orientation of crystals by correcting the theoretical values of intensities which should be obtained on a powder sample. The diffraction peak intensities were calculated as

$$I_{\text{preferred}} = I_{\text{powder}}\, e^{-\sigma\lambda'/100} \qquad (6)$$

By repeating the X-ray diffraction analysis at various distances from the surface of the borided iron samples we ascertained that the preferred orientation increases, starting from the edge toward the centre of the samples. This is in agreement with the "channel diffusion theory" proposed by Kunst and Schaaber [11] with the aim of explaining the texture of the borided layers.

The treatment conditions used in boronizing also exert an influence on the texture of the surface layer. The preferred orientation of the crystals in the external part of the borided layer increases as the temperature or the strength of the boriding agent increase.

In the outermost part of the layer crystals are placed casually, while in the innermost part a progressive preferred orientation occurs. Consequently the thickness of the outermost disorderly zone can be influenced by the treatment conditions.

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