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Mechanism of thermochemical growth of iron borides on iron

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The mechanism of thermochemical growth of iron borides on iron was studied by analysing the products which form on samples placed in contact with B_4C-base powder mixtures with different boronising potential. The analyses were carried out by means of metallographic and X-ray diffraction techniques. Three subsequent stages of growth were observed which explain the occurrence of typical properties of the thermochemically grown boride coatings, such as preferred crystallographic orientations and textures, as well as mechanical compactness and hardness, which play a determining role in the tribological behaviour of borided components. © *2004 Kluwer Academic Publishers*

1. Introduction

Thermochemical boriding of iron alloys allows both single Fe_2B phase and FeB-base polyphase coatings to be obtained and then used mainly to improve surface hardness and wear resistance of components for tribological applications [1–3]. Boride coatings, in fact, display considerable hardness and compactness except for the outermost, few micrometers thick region which, being constituted by differently oriented crystals, is friable and, consequently, should be removed from the component by means of a surface finishing procedure. Single Fe_2B phase coatings can be produced by limiting the boron potential of the boronising media, thus avoiding complications possibly arising by the formation of the much harder but even more brittle product FeB and by the high intensity stress states generally establishing at the FeB-Fe_2B interface [3, 4]. The best results have been obtained using pack cementation processes involving the use of powder mixtures. The fact that continuous, automated and reliable gas processes are not yet commercially available has considerably hindered a larger diffusion of boriding in surface engineering practice, as an alternative to more traditional treatments such as carbon cementation and nitriding.

The phase composition, microstructure and mechanical properties of boride coatings have been widely investigated, and the compactness of the boride layers has been related to the establishing of a preferred crystallographic orientation [5]. The main components of the coatings (Fe_2B and FeB) generally display a strong (002) preferred orientation [5–11]. It has been also reported that the compactness of iron borides is significantly influenced by the kind of the alloying elements which, diffusing from the base metal, enter the coating as a consequence of redistribution phenomena: because of the differences in the alloying processes, the boride coatings display significant differences in total thickness, orientation strength and morphology at the Fe_2B/Fe and FeB/Fe_2B interfaces [12]. However, a satisfactory explanation is missing for the growth mechanism of coatings which (i) consist of a thin, outer region of differently oriented crystals and a thick inner region of (002) oriented crystals, and (ii) display a preferred orientation whose strength increases with increasing depth [5].

In the present work, the growth mechanism of iron borides was investigated by means of boriding treatments carried out on iron using powder mixtures with a controlled boronising potential, selected in order to allow the different stages of the process to be observed.

2. Experimental details

Samples of 99.9% pure iron were treated at 850°C for times up to 15 h using three different B_4C-base powders, the boronising potentials of which can be conventionally defined as low, intermediate and high, respectively. The powder compositions are reported in Table I.

The considerable dilution of B_4C with SiC (powder No. 1 in Table I) lowers the boriding rate and allows the early stages of Fe_2B growth to be studied in detail. The use of pure B_4C (powder No. 2) allows thicker single Fe_2B phase coatings to be obtained. On the other hand, the treatments carried out under the same conditions of temperature and time of exposure using KBF_4-activated B_4C (powder No. 3) extend the investigation to the subsequent stages of growth, which are associated with the formation of thicker, polyphase boride coatings. All the treatments were carried out using boats of fused silica sealed under vacuum in order to avoid any presence

TABLE I Composition and boronising potential of the B_4C-base powders

Powder no.	Boronising potential	B_4C	SiC	KBF_4
1	Low	10	90	–
2	Intermediate	100	–	–
3	High	90	–	10

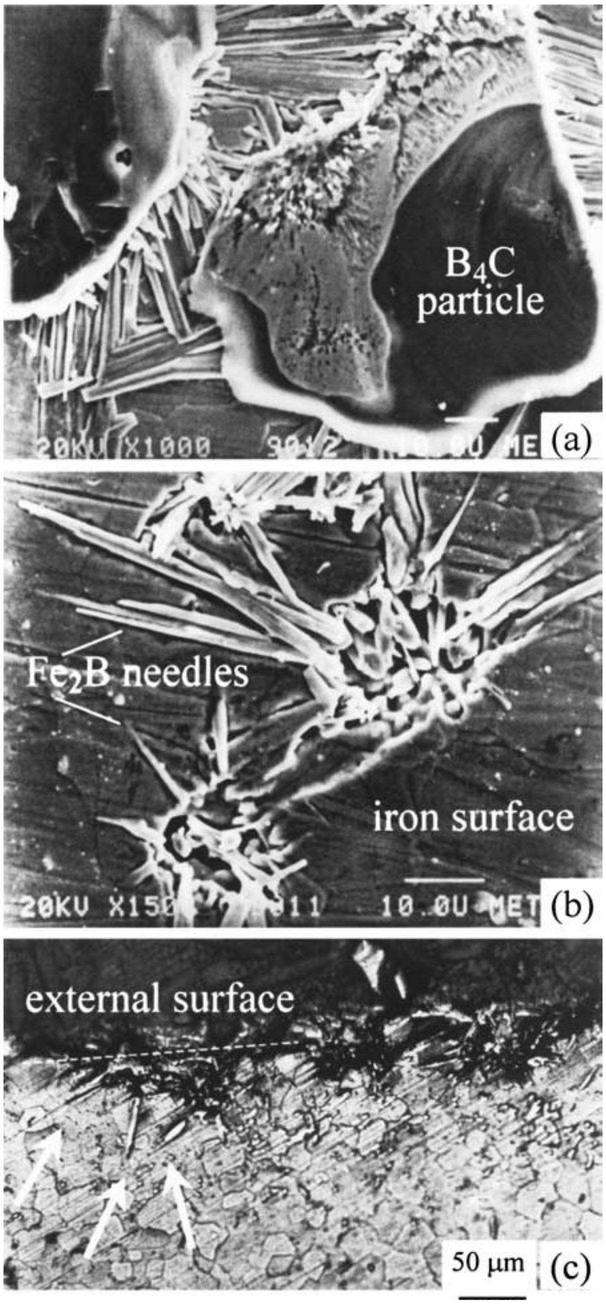

Figure 1 Iron sample treated for 1 h at 850°C in contact with a low boron potential medium (powder No. 1 in Table I): (a) SEM image of B_4C crystals (dark areas) on iron and of acicular crystals of Fe_2B grown on the metal surface starting from the carbide-metal contact zones; (b) details of the Fe_2B crystals shown in (a), after removal of the carbide particles; (c) metallographic cross section of the same sample showing (i) surface cavities due to localised iron boriding and subsequent removal of reaction products, and (ii) some Fe_2B crystals (white arrows) grown inside the iron substrate.

of oxygen in the reaction environment. As previously shown, in fact, oxygen considerably reduces the iron-boron reactivity [13].

The borided samples were characterised by means of X-ray diffraction analysis (XRD), optical microscopy (OM) and scanning electron microscopy (SEM). The XRD measurements were carried out using a computer controlled goniometer and Co K_α radiation. The compactness of the boride layers was evaluated by means of fractographic analyses carried out on coated samples submitted to V-notching and bending machining operations.

3. Results and discussion

The growth dynamics of the boride coating will be described distinguishing between three subsequent stages. During the first stage, crystals of Fe_2B (the first product to form) grow on the metal surface up to a complete coverage. During the second stage, significant amounts of Fe_2B crystals form and grow inside towards the metal bulk . During the third stage, all Fe_2B crystals form and grow inside assuming a preferred crystallographic orientation. Finally, the growth of a layer of FeB on the inner layer of Fe_2B will be examined in order to extend the analysis to polyphase boride coatings.

3.1. Coverage of the metal surface (stage 1 of growth)

When iron is kept in contact with a low boron potential medium (powder No. 1 in Table I), the reaction products grow at a rate which is low enough to allow the growth behaviour to be observed carefully. Fig. 1a and b show the morphology of an iron sample treated at 850°C for an exposure time as short as 1 h. In the early stage of growth, acicular Fe_2B crystals grow in radial directions starting from the contact zones between the metal surface and B_4C particles (Fig. 1a), lengthening upon the surface of the base metal (Fig. 1b). These features can be explained considering that (i) only solid state reactions occurred and, consequently, active boron was supplied only at the contact zones between the metal surface and B_4C particles; (ii) Fe_2B crystals preferentially grow along their [001] crystallographic direction, i.e., the direction which has the shortest distance between neighbouring B atoms and, consequently, constitutes the easier path for the boron diffusion in the body centred tetragonal lattice of Fe_2B; and (iii) the Fe_2B needles growing upon the metal surface find a minimum of mechanical resistance from the base metal, because of the considerable increase in volume ($\sim$16%) associated with the transformation of Fe into Fe_2B. This kind of growth leads to the formation of a first layer of differently oriented crystals, i.e., an outermost, mechanically inconsistent layer.

During the first stage of growth, some needles of Fe_2B can also grow inside the substrate along different directions, as shown by metallographic cross-sections (Fig. 1c). This can be explained on the basis of a previously proposed tip-enhanced mechanism of growth [5, 14]. These crystals, in fact, induce in the base metal stresses and lattice distortions which are particularly high in the metal regions located in front of needle tips.

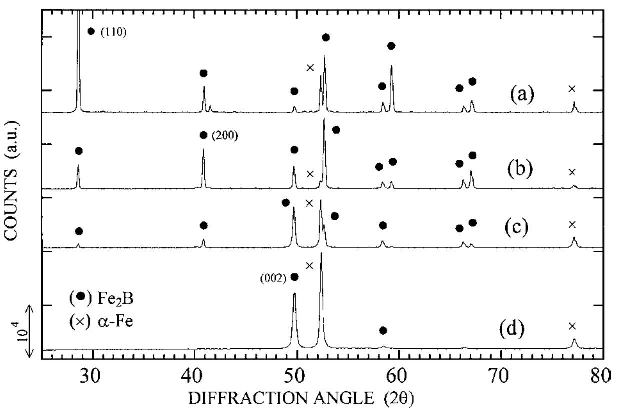

Figure 2 XRD patterns (Co K_α radiation) for an iron sample treated for 15 h at 850°C in contact with a low boron potential medium (powder No. 1 in Table I): (a), (b), zones of Fe_2B crystals with (110) or (200) preferred orientations, respectively; (c), (d), patterns measured after removal of the outermost, mechanically inconsistent layer (c), and for an Fe_2B region near the Fe_2B-Fe interface (d).

The higher availability of locally stored energy makes these regions more reactive sites, i.e., sites of easier growth for the iron boride. However, the boride growth inside the metal is limited by the low amount of active boron diffusing through the coating down to the needle tips. In this stage, the main part of boron is consumed by the crystals growing more quickly on the metal surface.

The XRD patterns reported in Fig. 2 show that, after 15 h under the same boriding conditions, the metal surface is fully covered by a layer which (i) consists entirely of Fe_2B , and (ii) is thin (5–15 μm), as shown by the presence in the patterns of peaks of the metal substrate (α-Fe). Moreover, XRD mapping of the surface shows the presence in the layer of zones rich in (110) oriented or (200) oriented crystals (Fig. 2a and b, respectively). Therefore, as schematised in Fig. 3 (stage 1), Fe_2B crystals can grow in different zones of the same layer with their [001] axes parallel to the external surface, assuming orientations which can change as a consequence of local differences in the accomodation process on the underlying metal.

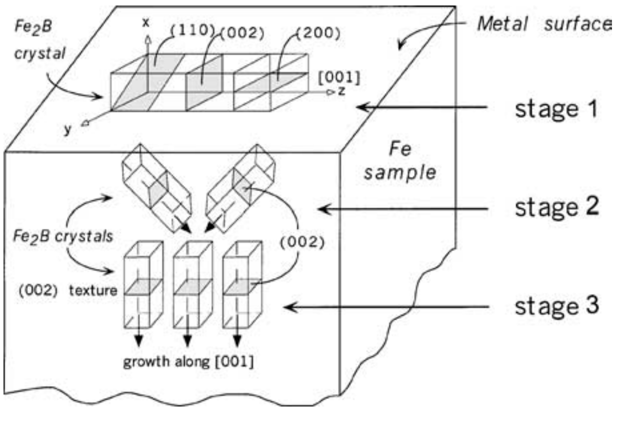

Figure 3 Schematic representation of the stages of thermochemical growth of Fe_2B crystals: stage 1, growth on the metal surface; stage 2, growth inside the outer regions of the metal sample; and stage 3, growth in depth leading to a strong (002) preferred orientation.

3.2. Growth of Fe_2B crystals inside the metal (stage 2 of growth)

The growth of Fe_2B crystals inside the metal is prevailing during this stage, as shown by XRD analyses carried out on thicker (15–50 μm), single Fe_2B phase coatings grown at the same temperature using a medium with an intermediate boronising potential (powder No. 2 in Table I). The patterns reported in Fig. 2c and d and recorded after mechanical removal of the outermost, few micrometers thick parts of the boride layer, show a (002) preferred orientation whose strength increases as the depth of analysis is increased. In particular, the boride grown near the coating-metal interface only shows the (002) Fe_2B diffraction peak, in addition to α-Fe peaks (Fig. 2d). Therefore, the second stage of Fe_2B growth is characterised by the transition from an outer, thin and mechanically inconsistent region of crystals which are randomly oriented or locally oriented (110) or (200), to an inner, thick and compact region of (002) oriented crystals. As the metal surface is covered by reaction products, there is an increasing number of crystals (each one growing on the metal surface along its [001] axis) which, coming in contact with adjacent, non-parallel crystals, undergo strong mechanical stresses. Because of these obstacles, some crystals stop their growth (Fig. 4a), while other crystals only can grow after changing direction on the metal surface

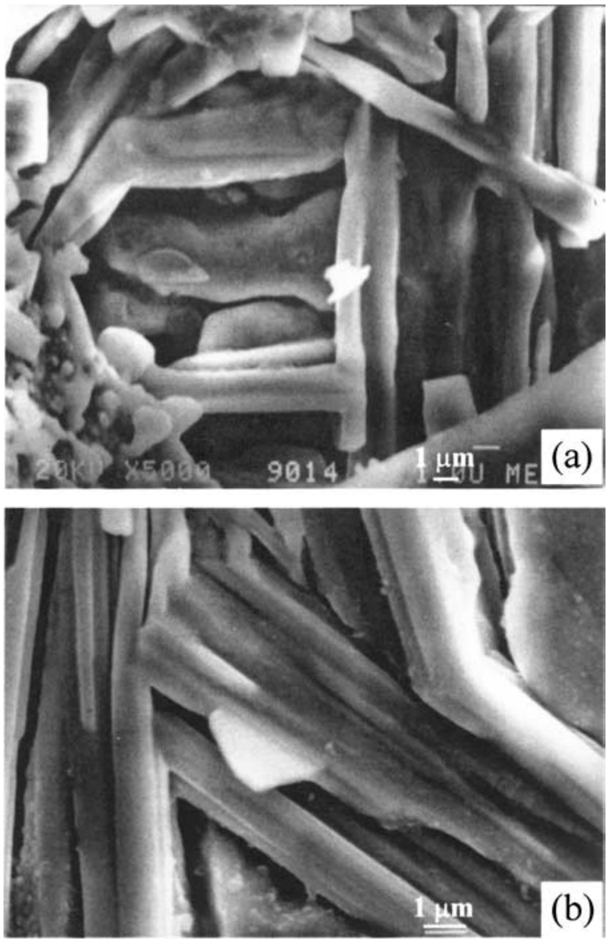

Figure 4 SEM micrographs showing Fe_2B crystals which, while growing on the metal surface, were (a) stopped, or (b) forced to change in growth direction as a consequence of contacts with adjacent boride crystals.

(Fig. 4b). In this stage, schematised in Fig. 3 (stage 2), an increasing number of crystals is forced to grow inside the metal, i.e., with their [001] axis of easier growth non-parallel to the metal surface. Moreover, the growth of boride needles inside the metal is further favoured by the fact that the boron amount consumed by crystals growing on the metal surface decreases and, consequently, more boron can diffuse down at the tips of needles growing inside.

3.3. Establishing of a strong (002) Fe_2B texture (stage 3 of growth)

During the stage 2 several Fe_2B crystals growing inside along different directions can come in contact hindering each other. Consequently, an increasing number of crystals is forced to grow along a path of minimum resistance, i.e., with their [001] axis parallel. Therefore, a third stage of growth occurs where all the boride needles tend to grow perpendicularly to the external surface (Fig. 3, stage 3). This fully explains (i) the formation of Fe_2B crystals oriented with their (002) planes parallel to the external surface, and (ii) the increasing strength of this orientation as the depth towards the Fe_2B-Fe interface increases. The formation of increasingly iso-oriented crystals also accounts for the mechanical compactness of these regions in the boride layers.

It is worth noting that, if a pure B_4C powder is used, the boronising potential and the growth rate of Fe_2B are too high to allow the early stage of the process to be studied in detail.

3.4. Formation of polyphase boride coatings

Boride treatments carried out using media with a high boronising potential (powder No. 3 in Table I) lead to the formation of polyphase coatings, constituted by an FeB-base outermost layer grown on an inner (002) oriented Fe_2B layer. The 'FeB-base' definition is because these coatings generally contain a high boron product (FeB_x with $x > 1$) in their outermost part [15–17]. The SEM observations show that the outermost crystals of the FeB layer are differently oriented and mechanically inconsistent, coming from the transformation of the outer, inconsistent region of the Fe_2B layer. On the contrary the deeper regions of FeB, coming from the transformation of compact regions of (002) oriented Fe_2B crystals, are textured and mechanically very compact. Moreover, the strength of the (002) FeB orientation increases at increasing depths towards the FeB-Fe_2B interface, according to the texture profile of the Fe_2B regions transformed into FeB.

It is to be noted that, in contrast with some opinion reported in the literature [18], no relationship was found between the preferred orientation of FeB and Fe_2B borides and the columnarity which, as is known, characterises both FeB-Fe_2B and Fe_2B-Fe interfaces of polyphase coatings grown on iron (Fig. 5a). In fact, preferred orientations of the same type have been found to characterise boride coatings grown on high chromium iron alloys [9, 12, 19], which usually display almost flat interfaces (Fig. 5b).

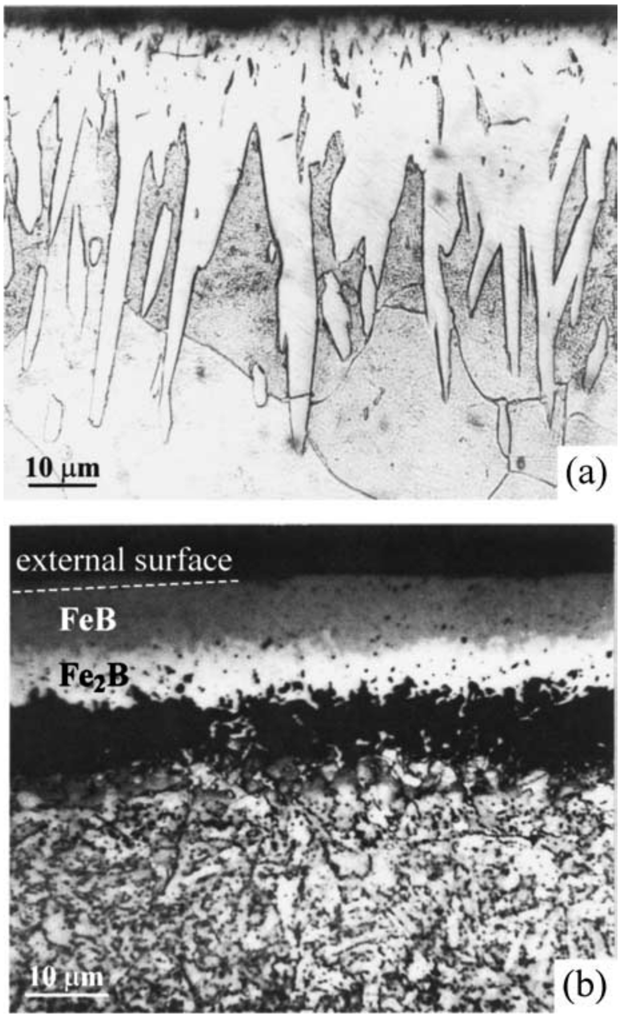

Figure 5 Cross sections of polyphase boride coatings grown at 850°C using a 2.5 wt% B_4C powder mixture. Typical differences in the morphology of FeB-Fe_2B and Fe_2B-Fe interfaces are shown for substrates very differing in composition: (a) pure iron, and (b) high Cr steel (X32 Cr 13). In both cases the Fe_2B layer displayed a (002) preferred crystallographic orientation.

4. Conclusions

Boride coatings were grown on iron at 850°C using powder mixtures of different boronising potential in order to control the growth rate and get information on the growth mechanism. The results of XRD analysis and metallographic observations led the following conclusion to be drawn:

1. Fe_2B is the first product to form with a growth mechanism involving three subsequent stages:
   - The first, acicular crystals of Fe_2B preferentially grow on the metal surface with their [001] axis mainly oriented parallel to the reaction surface, forming a surface layer of differently oriented crystals.
   - As the metal surface is covered, an increasing number of Fe_2B crystals comes in contact with adjacent crystals and are forced to grow inside the metal, retaining an acicular shape.

– Finally, an increasing number of Fe_2B crystals are led to develop oriented with their [001] axis of easier growth normal to the external surface, in order to minimise the mechanical resistance to growth between adjacent crystals. This stage leads to formation in the coating of strongly (002) oriented and mechanically compact Fe_2B regions.

The growth mechanism described above well accounts for the typical properties generally displayed by thermochemically grown Fe_2B layers.

2. In the case of polyphase coatings grown using high boronising potential media, the compactness of the outer FeB layers forming by reaction between Fe_2B and active boron, is determined by the strength of crystallographic texture of the reacting Fe_2B regions which, consequently, is determining to attain adequate levels of mechanical compactness and hardness for the whole boride coating.

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