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The mechanism of reaction sintering of iron–iron boride cermets

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The process of reaction sintering of iron and boron in a vacuum has been analysed, as a result of which iron–iron boride cermets have been produced. They constitute a composite material in which iron boride, Fe_2B, with a hardness of about 1800 HV plays the role of the reinforcement, while iron–iron boride, Fe–Fe_2B, with a hardness of about 500 HV plays the role of the matrix. The eutectic filling the spaces between iron boride grains is composed of boron solid solution plates in iron with a hardness of around 250 HV, and iron boride, Fe_2B, plates with a hardness of approximately 1800 HV. The combination of such different materials results in attractive properties of the cermet thus produced: high total hardness (1500 HV), constant over the whole section, and ductility. The properties mentioned, resulting from the cermet structure, depend (apart from the chemical composition) on the phenomena occurring while sintering: the boron diffusion in iron, the formation of the liquid phase and the processes of dissolving powder components in it, and finally upon the crystallization of the boride phase from the liquid. These all determine the unique character of the reaction sintering of iron and boron. The mechanism of this process is reported.

1. Introduction

Interest in cermets as constructional materials and for cutting tools continues to grow. Cermets of the group of sintered carbides, e.g. WC–CO, or aluminium oxides in a metallic matrix, e.g. Al_2O_3–Cr–Mo, are widely used. At the same time, research is being performed into other kinds of such materials.

So far little attention has been paid to iron–iron boride, Fe–Fe_2B, sinters as materials of high hardness, with resistance to wear and corrosion [1]. The resistance to wear of iron borides in the process of dry sliding friction has been studied only in the case of diffusive boronized layers on steels [2, 3]. Nowacki and Klimek [4] reported the possibility of producing Fe–Fe_2B cermets by means of reaction sintering of iron and boron powders. These sinters have the structure of composite materials in which a solution of boron in iron or the Fe–Fe_2B eutectic, constitute the matrix, while the intermetallic phase (iron boride, Fe–Fe_2B) is the hard reinforcement.

Depending on the boron concentration and sintering parameters, cermets of a different structure can be made. It has been shown that Fe–Fe_2B cermets of boron concentration above 8% by weight have a high hardness of about 1500 HV, good ductility, as well as high resistance to wear in the process of dry sliding friction.

Apart from their chemical composition, the phenomena occurring during sintering have a decisive effect upon the properties of the materials mentioned, such as the processes of diffusive boronizing of iron particles, the formation of the Fe–Fe_2B eutectic, the processes of iron, boron and iron boride dissolution in the eutectic, and the crystallization of iron boride. These phenomena contribute to the unique character of the mechanism of reaction sintering of iron and boron powders. The present investigation of this mechanism is a continuation of previous studies [4].

2. Experimental procedure

Iron–iron boride cermets were produced from a mixture of sprayed iron powders of particle size 0.08–0.1 mm, and amorphous boron of particle size 0.005–0.01 mm. The large size of the iron particles made it possible to lengthen the pathway, thus prolonging the period of diffusion of boron into their surface layers, which facilitated observation of this process [5].

The investigations were carried out using matrix profiles pressed under a pressure of 700 MPa, which were then subjected to reaction sintering in a vacuum at 1373 and 1433 K. The first temperature is below the temperature of the eutectic change in the Fe–B equilibrium system, which corresponds to sintering solely in the solid phase. The other temperature corresponds to sintering with participation of the liquid phase of the eutectic composition: iron–iron boride, Fe–Fe_2B [6]. The sintering time was selected so as to allow observation of the effects of the initial and advanced phases of sintering.

Sinters of three boron concentrations were produced: the eutectic (3.8 wt%B), the hypereutectic (6.3 wt%B) and one corresponding to the composition of iron boride, Fe_2B (8.8 wt%B). The sinters made were subjected to metallographic quantitative and qualitative [7, 8] X-ray-structural fractographic investigations, as well as to measurements of hardness distribution.

3. Results

Sintering in the solid phase at a temperature of 1373 K resulted in the formation of cermets composed of sintered particles of iron powder diffusively boronized. The surface of these particles is covered with a thin layer of iron boride, Fe_2B, under which is a solid solution of boron in iron (Fig. 1). These sinters manifest considerable porosity (8%–14%), and the pores are filled with boron powder which has failed to diffuse into the boron particles. The formation of iron boride in the form of needles on the surface of the iron particles is a characteristic feature in the process of the diffusive boronizing of iron and its alloys. The distribution of microhardness of the iron particles in the cermets sintered at 1373 K for three different times is shown in Fig. 2. An increase in the hardness of the iron particle surface results from the formation of the solid solution of boron in iron.

As the sintering time increases, the depth and hardness of the diffusive surface layer increase. At the same time, there is an increase in the fraction of iron boride formed on the surface, which manifests itself, for instance, by an increase in the intensity of the diffraction lines of this phase on the diffraction patterns (Fig. 3).

While sintering at 1433 K, the liquid phase (the iron–iron boride, Fe–Fe_2B eutectic) is formed. The microstructure of the sinters produced under these conditions is composed of diffusively boronized particles of a hardness 130–280 $HV_{0.05}$ embedded in the iron–iron boride (Fe–Fe_2B) eutectic of hardness 500 $HV_{0.1}$ (Figs 4 and 5) and a small number of pores.

The volume fraction of the components in the cermet changes depending on the sintering time (Fig. 6). With an increase in sintering time, the fraction of iron particles decreases, the porosity is reduced, while the fraction of the eutectic increases.

Fe–Fe_2B cermets of a concentration of 6.3 and 8.8 wt%B have a different microstructure. They are made up of iron boride (FeB) grains with a hardness of around 1800 $HV_{0.2}$ embedded in the iron–iron boride (Fe–Fe_2B) eutectic. A comparison of scanning images of the above sinters in the light of reflected and secondary electrons shows the presence of undissolved

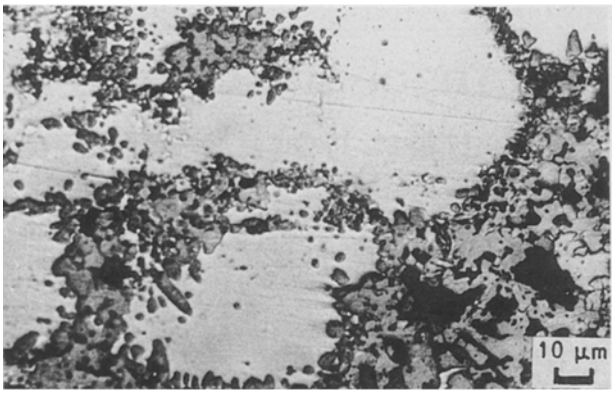

Figure 1 Microstructure of the Fe–Fe_2B cermet of 8.8 boron concentration sintered at 1373 K for 0.25 min, showing iron boride, Fe_2B, on the surface of iron powder particles and pores filled with boron, unetched.

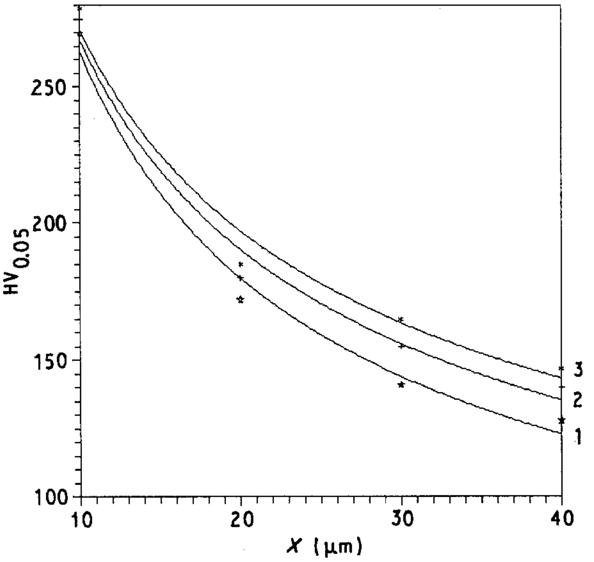

Figure 2 Distribution of hardness inside the iron powder particles in the Fe–Fe_2B cermet of 8.8 wt% boron concentration sintered at 1373 K for (1) 0.25, (2) 60 and (3) 120 min.

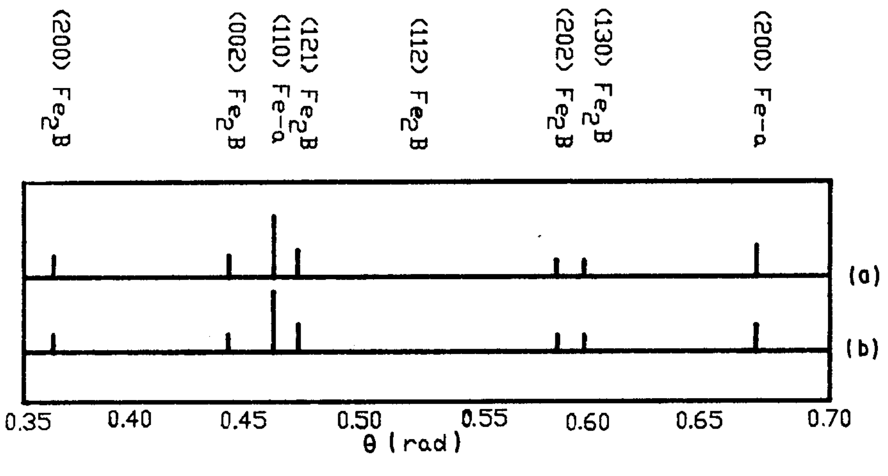

Figure 3 Diffraction pattern of the Fe–Fe_2B cermet of 8.8 wt% boron concentration sintered at 1373 K for (a) 0.25, (b) 120 min.

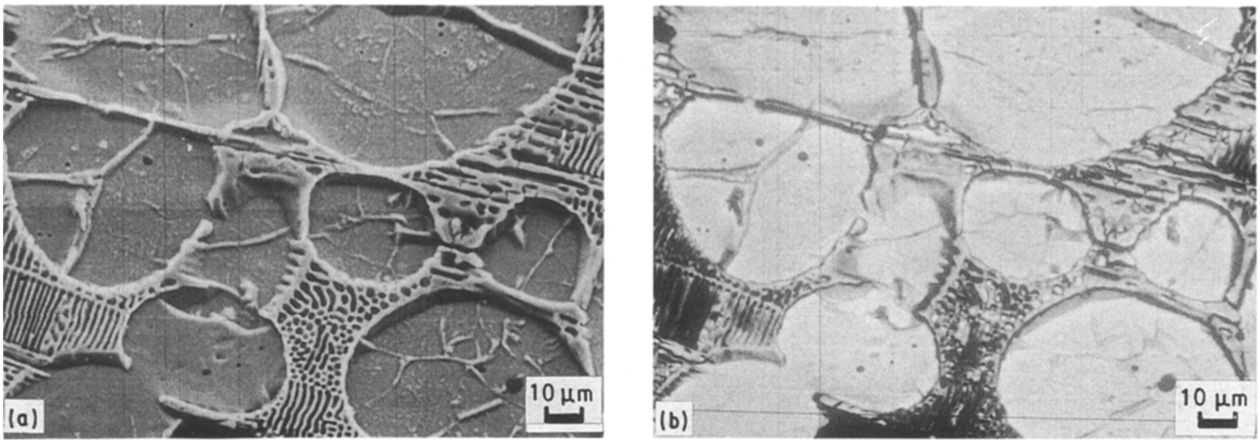

Figure 4 Microstructure of the Fe–Fe_2B cermet of 3.8 wt% boron concentration sintered at 1433 K for 3 min, showing iron powder particles on the background of the Fe–Fe_2B eutectic; visible precipitation of Fe_2B around iron powder particles and along the iron grain boundaries in powder particles. (a) Secondary electron image, (b) reflected electron image, etched in 3% HNO_3 in alcohol.

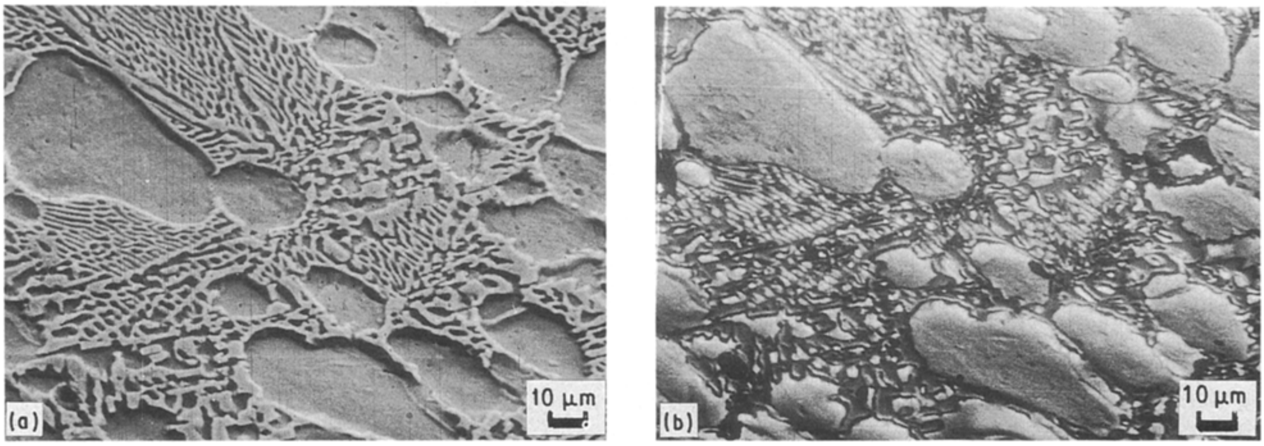

Figure 5 Microstructure of the Fe–Fe_2B cermet of 3.8 wt% boron concentration sintered at 1433 K for 120 min; the description of the microstructure is as in Fig. 4. (a) secondary electron image, (b) reflected electron image, etched in 3% HNO_3 in alcohol.

iron powder particles in the eutectic (Figs 7 and 8) for short sintering times. These particles dissolve completely in the eutectic as the sintering time increases. As a result of the dissolution processes of iron and boron in the eutectic and the crystallization of iron boride, the fraction of iron boride, Fe_2B, increases in these sinters. The increase in the fraction of Fe_2B in the sinters with sintering time is illustrated by an increase in the intensity of the reflections from this phase on the diffraction patterns (Fig. 9). The reflections in the diffraction patterns presented in Fig. 9 constitute the total effect of diffraction of an X-ray beam in the Fe_2B crystals occurring separately and in the eutectic.

The metallographic, diffractometric investigations and hardness measurements were complemented by fractographic investigations which broaden the views of the structure of the cermets discussed (Figs 10–12). These investigations show that at a lower sintering temperature of 1373 K or over short sintering times (independent of the temperature), the cermets reveal fractures running along the boundaries of the iron powder particles. This indicates an insufficient degree of progression of the sintering process. With an increase in sintering time, the fracture character changes to the transcrystalline one, indicating considerable advancement of diffusive processes while sintering. This fracture contains elements of both brittle and ductile fracture. The brittle fractures occur in the iron boride grains, while the ductile fractures occur in the iron–iron boride eutectic.

4. Discussion and conclusion

An analysis of the results obtained allows us to suggest a model of the sintering process of an iron and boron powder mixture. This process consists of several stages.

In the first stage, which comprises the period of heating up the profile pressed from iron and boron powders (Fig. 13) to the eutectic temperature in the Fe–B equilibrium system (1423 K), only diffusion processes in the solid phase occur. They consist in the diffusion of boron into the surface of iron powder

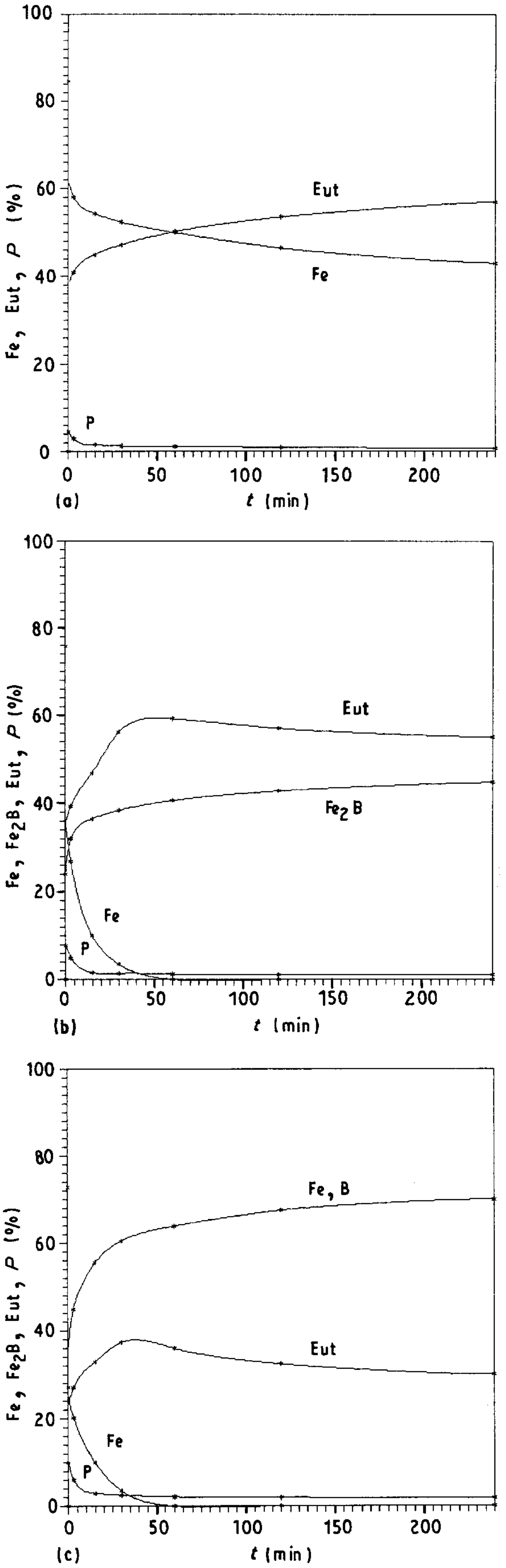

Figure 6 Dependence of the fraction of structural components: iron (Fe), iron boride (Fe_2B), Fe–Fe_2B eutectic (Eut) and porosity (*P*) of the Fe–Fe_2B cermets of boron concentrations of (a) 3.8 wt%, (b) 6.3 wt%, (c) 8.8 wt%, sintered at 1433 K.

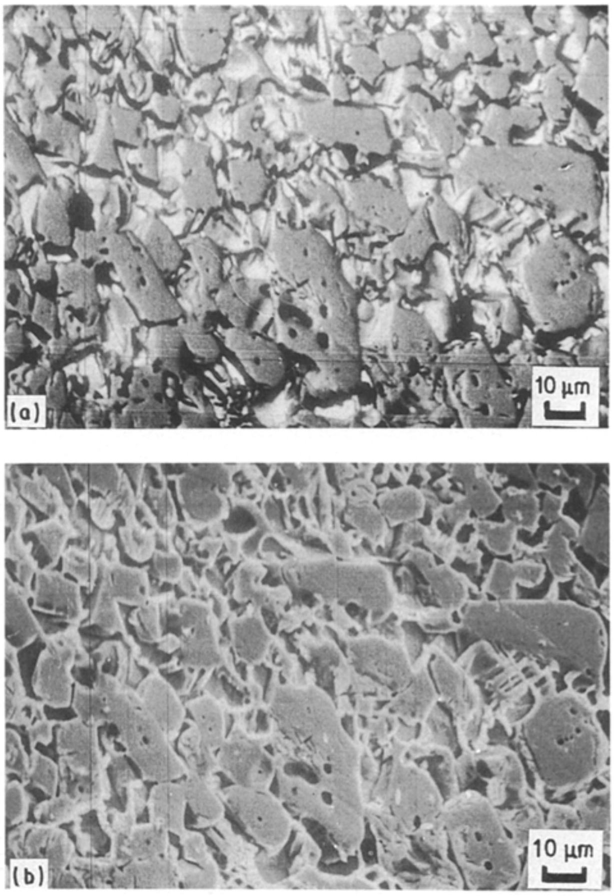

Figure 7 Microstructure of the Fe–Fe_2B cermet of 8.8 wt% boron concentration sintered at 1433 K for 3 min, showing Fe_2B grains on the background of the Fe–Fe_2B eutectic. (a) Secondary electron image, (b) reflected electron image, etched in 3% HNO_3 in alcohol.

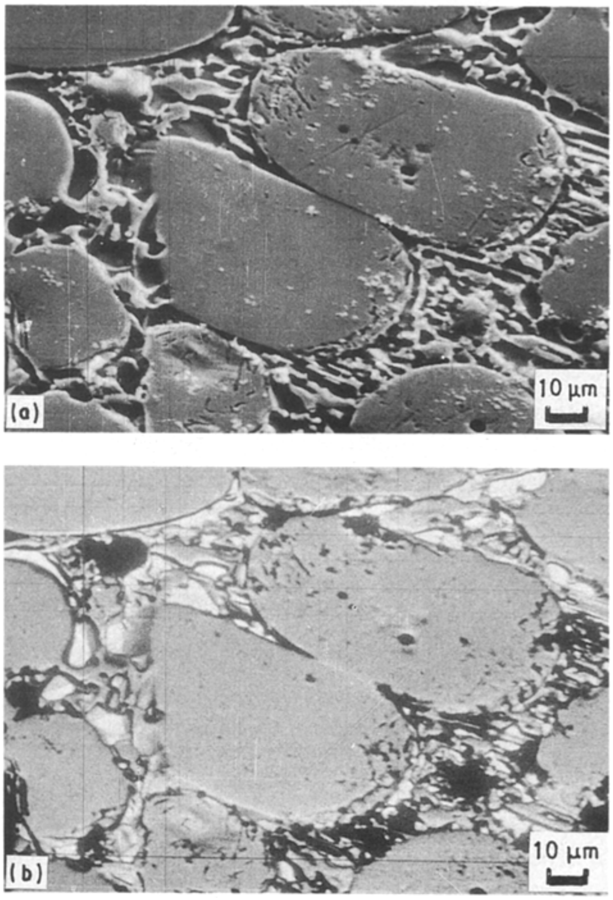

Figure 8 Microstructure of the Fe–Fe_2B cermet of 8.8 wt% boron concentration sintered at 1433 K for 120 min, showing Fe_2B grains on the background of the Fe–Fe_2B eutectic. (a) Secondary electron image, (b) reflected electron image, etched in 3% HNO_3 in alcohol.

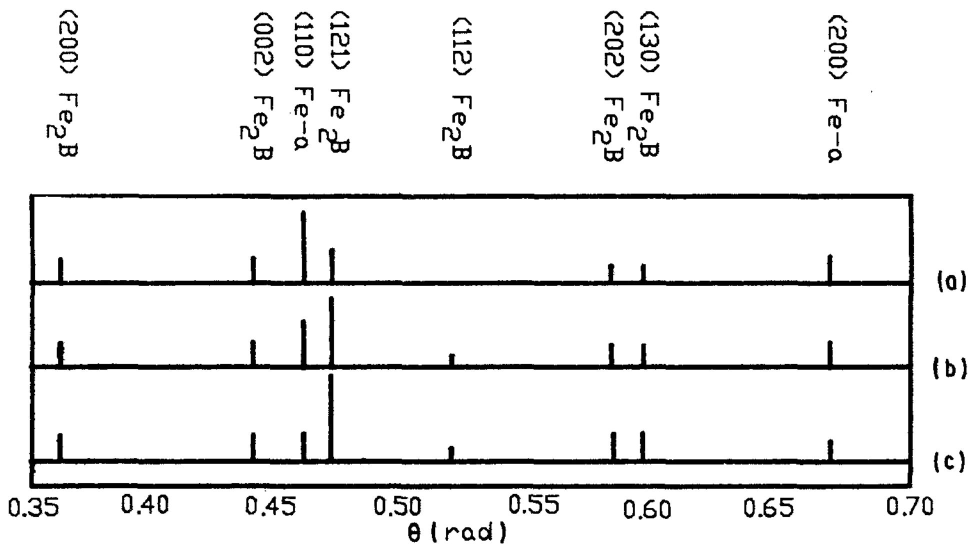

Figure 9 Diffraction patterns of the Fe–Fe_2B cermet of 8.8 wt% boron concentration sintered at 1433 K for (a) 0.25, (b) 3, and (c) 240 min.

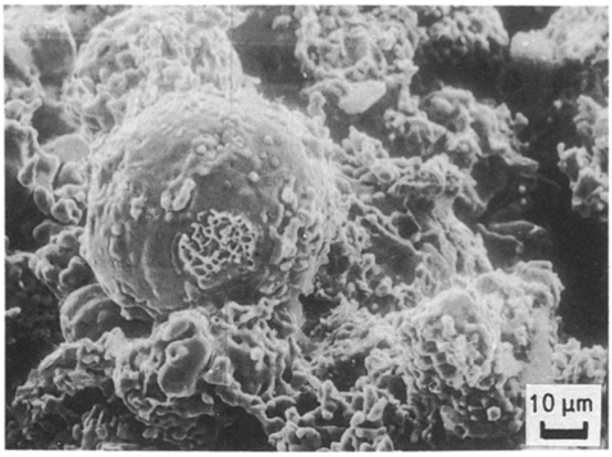

Figure 10 Scanning image of a fracture of the Fe–Fe_2B cermet of 8.8 wt% boron concentration sintered at 1373 K for 0.25 min, showing a fracture between the surfaces of the boronized iron particles.

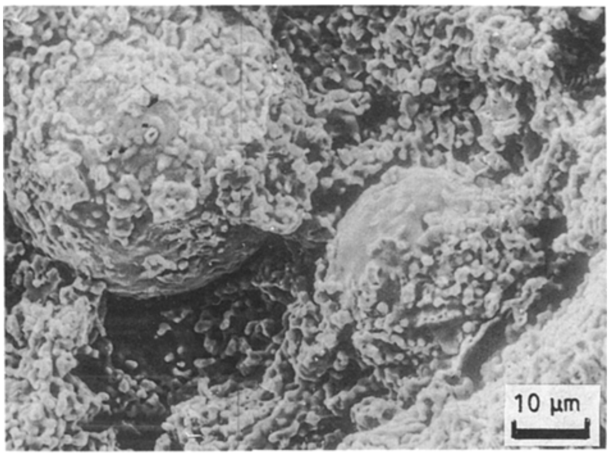

Figure 11 Scanning image of a fracture of the Fe–Fe_2B cermet of 8.8 wt% boron concentration sintered at 1433 K for 3 min, showing a fracture between the surfaces of the boronized iron powder particles.

particles. This diffusion proceeds interstitially through and along the boundaries of iron grains in the powder particles. As a result of this process, under the surface of the iron powder particles as well as along the grain boundaries, a layer of a solid solution of boron in iron is formed, increasing in thickness with increasing

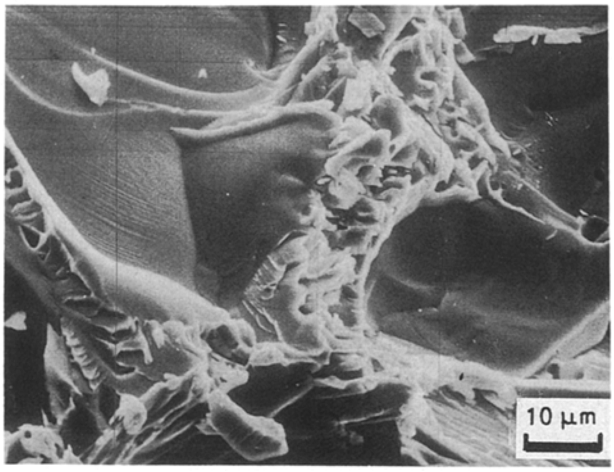

Figure 12 Scanning image of a fracture of the Fe–Fe_2B cermet of 8.8 wt% boron concentration sintered at 1433 K for 120 min, showing a fracture (transcrystalline) with the elements of a ductile fracture.

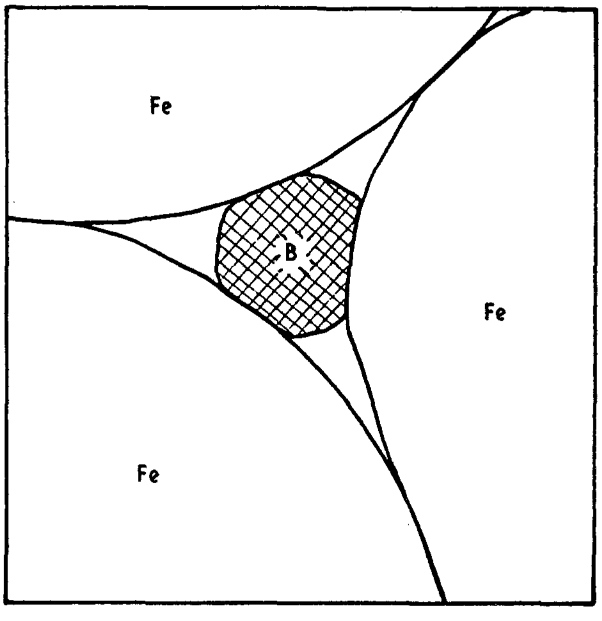

Figure 13 Diagram of the microstructure of a compact from iron and boron powders at 293 K: Fe, iron; B, boron.

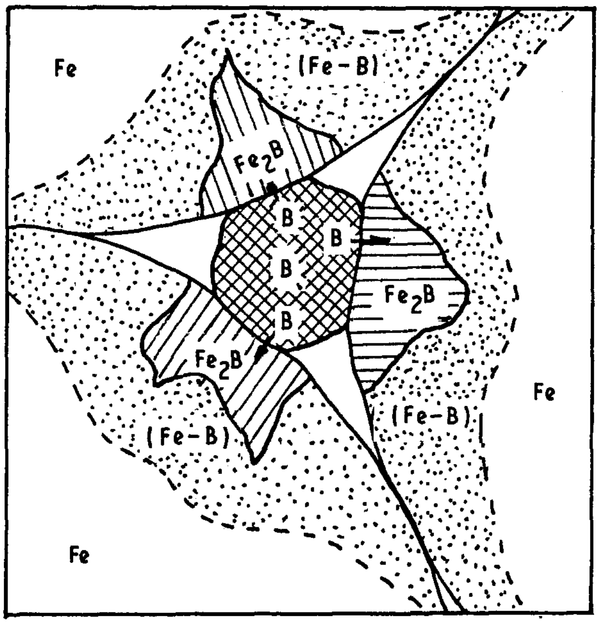

Figure 14 Diagram of the sintering process of the Fe–Fe_2B cermet at a temperature lower than the eutectic temperature in the Fe–B equilibrium system (1422 K): Fe, iron; B, boron; Fe–B, solid solution of boron in iron; Fe_2B, iron boride.

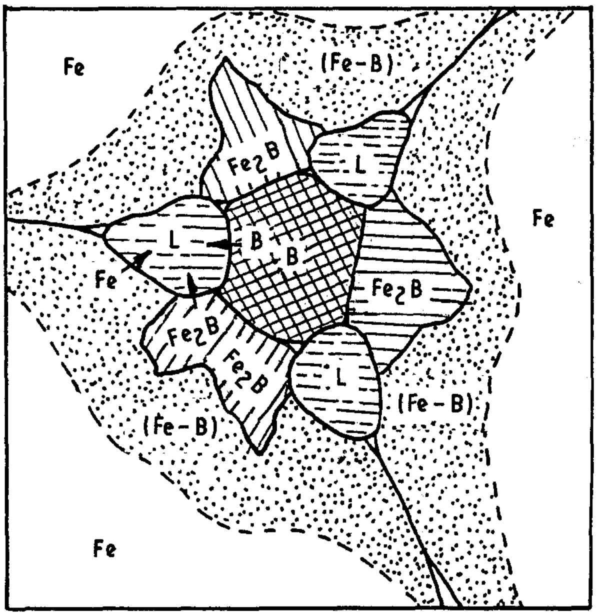

Figure 15 Diagram of the sintering process of the Fe–Fe_2B cermet at a temperature higher than the eutectic temperature in the Fe–B equilibrium system (1422 K). Boron concentration: Fe, iron; B, boron; Fe–B, solid solution of boron in iron; Fe_2B, iron boride; L, liquid.

sintering time. Then, iron boride, Fe_2B, is formed on the surface of the iron particles. At this stage, only boron, being in direct contact with the iron powder surface, participates in the diffusion, which is decisive of a small range of diffusion processes. At the same time, as a result of the typical conversions occurring during the sintering, compression of the compact takes place. This stage is shown in Fig. 14.

The second stage begins when the system reaches the eutectic temperature (1433 K). At this temperature, a liquid with the position of the iron–iron boride eutectic is formed in the iron in microregions where the boron concentration is 3.8 wt%. The greatest probability of the formation of such microregions occurs at the boundary between the solid solution of boron in iron and iron boride or boron.

With the formation of the liquid phase, a number of simultaneous partial processes begin. On the one hand, this is the dissolution of iron particles, boron and iron boride grains formed in the first stage of sintering in the liquid; on the other hand, crystallization of iron boride from the liquid occurs. When the compacts with a boron concentration of 3.8 wt% are sintered, the equilibrium of the processes of dissolution and crystallization shifts toward dissolution (Fig. 15a), which causes an increase in the quantity of the eutectic.

In the iron–boron equilibrium system for a boron concentration of 8.8% by weight, iron boride is a thermodynamically stable phase, therefore while sintering compacts of this boron concentration, the equilibrium shifts toward the crystallization of iron boride. A diagram of the mechanism of this process is presented in Fig. 15b.

On completion of the sintering process, cermets of 3.8 wt% boron concentration should be composed only of the Fe–Fe_2B eutectic, while cermets of the 8.8 wt% boron concentration are composed only of iron boride, Fe_2B. When the state of the equilibrium was not attained in the Fe–Fe_2B. eutectic, a certain amount of iron grains superficially saturated with boron remained in the first case, and a certain amount of Fe–Fe_2B eutectic remained between the iron boride grains, in the other.

From the viewpoint of mechanical properties, hardness and ductility, the second kind of structure is interesting, because it constitutes an advantageous composition of a phase of great hardness, Fe_2B (1800 $HV_{0.1}$), and a mixture of phases of considerable plasticity, the Fe–Fe_2B eutectic of hardness 500 $HV_{0.1}$. The eutectic between the Fe_2B grains plays the role of a relatively plastic matrix and, at the same time, constitutes a specific kind of composite made up of plates of solid solution of boron in iron having a hardness of about 250 $HV_{0.1}$, and plates of iron boride with a hardness of about 1800 $HV_{0.1}$.

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