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Structure and properties of $Fe–Fe_2B$ cermets

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The possibilities of producing $Fe–Fe_2B$ cermets as a result of sintering the pure elements Fe and B in a vacuum have been analysed. Attempts at sintering in the solid phase and with the participation of the liquid phase, the $Fe–Fe_2B$ eutectic, have been made. Metallographic qualitative and quantitative studies, X-ray structural qualitative and quantitative analysis and X-ray microanalysis allowed determination of the structure of Fe_2B cermets as well as description of the kinetics of quantitative changes in phase proportions in the course of sintering. It has been found that the structure varies widely depending on sintering parameters and the composition of the sinter. Measurements of $Fe–Fe_2B$ cermet hardness and measurements of wear during dry friction by the pin-on-disc method have shown distinct advantages of the cermets under investigation as modern constructional materials. The hardness of $Fe–Fe_2B$ cermets, depending on their chemical composition and sintering parameters, ranges widely from $HV = 150$ to 1500, and their resistance to wear is comparable to that of diffusively boronized steels.

1. Introduction

In modern technology, ceramic materials and cermets play an increasingly important role as constructional materials. Sintered aluminium oxide, Al_2O_3, silicon nitride, Si_3N_4 and silicon carbide, SiC and sinters of the Si–Al–O–N type are the most common among the ceramic materials, while sinters of tungsten carbide with cobalt, WC–Co, possibly with an addition of carbides of other high-melting metals as well as Al_2O_3–Cr and Al_2O_3–Cr–Mo sinters are the most popular of the cermetals. They are used as fast-cutting tool materials or high-temperature constructional materials, e.g. for gas turbine blades and slide bearings. Relatively little attention has been paid so far to iron boride sinters as a constructional material of high hardness and resistance to abrasion. The properties of iron borides mentioned are well known for their numerous uses for cases boronized on carbon and alloy steels. On the other hand, there are no attempts at producing machine elements of sintered iron borides. Cases boronized on steels are usually composed of iron boride, Fe_2B, hence their properties are approximately determined by the properties of this boride. The hardness of Fe_2B, both in the layer and in the form of free crystals, is $HV = 1800–2000$, and the elastic modulus $E = 2.9$ GPa [1]. This boride is characterized by very high resistance to wear under conditions of dry friction and mitigated solid friction and by chemical resistance in many aggressive media, e.g. sulphuric and hydrochloric acid [2–6].

Sinters of iron boride, Fe_2B, constitute a relatively cheap constructional material containing over 90% of iron. The authors see the possibilities of producing $Fe–Fe_2B$ cermets of boron mass concentration 3.8–8.8% w/v, in which a solid solution of boron in iron constitutes a metallic matrix, like the solid solution of tungsten carbide in cobalt in WC–Co sinters, while iron boride, Fe_2B, constitutes the reinforcement. Since a volumetric proportion of the reinforcement phase in the cermet discussed can vary widely, there are many possibilities of altering its properties. The proportion of the metallic matrix is decisive for cermet ductility, while the proportion of the reinforcement is decisive for its hardness and resistance to wear. Machine elements made of $Fe–Fe_2B$ sinters, apart from better ductility compared to cases boronized on steels, have another valuable advantage – owing to the constant hardness in the cross-section they can carry considerable surface stresses. Finally, there is a possibility of making porous $Fe–Fe_2B$ sinters of self-lubricating properties, after having saturated them with oils or polymers.

In the Fe–B system in the range of mass concentrations no greater than 8.83% B there are three components: a solid solution of boron in iron of boron solubility limit 0.0028%; the $Fe–Fe_2B$ eutectic of mass concentration of boron 3.8%; and an intermetallic phase Fe_2B of mass concentration of 8.83% (Fig. 1). Each of these phases has different properties and their volumetric proportions in the cermet are in strict relation to the boron concentration. Thus, changes in the boron concentration in the $Fe–Fe_2B$ cermet result in changes in its microstructure and hence in its properties.

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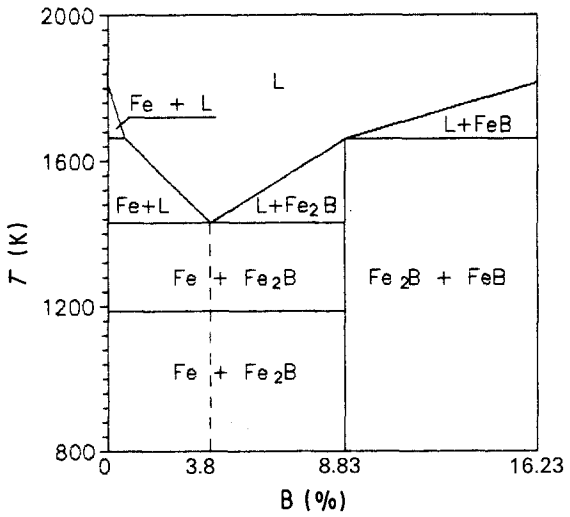

Figure 1 System of equilibrium of Fe–B phases [7].

The aim of this work is to investigate the effect of chemical composition and sintering parameters of the Fe–Fe_2B cermet on its structure and properties.

2. Experimental procedure

Fe–Fe_2B sinters were made from sprayed iron powder with a particle size of 0.07–0.15 mm and amorphous boron of particle size 0.005–0.010 mm. The use of iron particles of a considerable size allowed a decrease in the contact surface and the reaction rate between the components, which facilitated observation of the diffusion effects at the first stage of sintering. The investigations were carried out on sinters of three boron concentrations: eutectic with 3.8% w/v of B, hypereutectic with 6.3% B, and one corresponding approximately to the composition of iron boride (Fe_2B) with 8.8% B.

Profiles pressed under a pressure of 600 MPa were subjected to reaction sintering in a partial vacuum of $p = 1 \times 10^{-2}$ Pa at two temperatures; 1373 and 1433 K, for 0.25, 3, 15, 30, 121.5 and 240 min. The first temperature of sintering is lower than the temperature of formation of the Fe–Fe_2B eutectic (Fig. 1), while the other is higher. Such selection of temperatures allowed us to carry out the sintering of profiles in two variants: in the solid phase and with the participation of the liquid phase. The Fe–Fe_2B eutectic formed during sintering constituted the latter phase.

The sinters prepared served to carry out the following:

(i) metallographic studies by a qualitative method and quantitative linear analysis [8, 9],

(ii) X-ray analysis by the structural qualitative and quantitative method of direct comparison of intensities of selected diffraction lines [10],

(iii) observation of fractures in the scanning electron microscope,

(iv) qualitative measurements of boron distribution by the X-ray microanalysis method,

(v) measurements of the microhardness of phase components and of the average hardness of the sinter as a function of boron concentration,

(vi) measurements of wear during dry friction by the pin-on-disc method using a pin of diameter 3 mm made of the sinter and a disc of diameter of 100 mm made of steel with 0.4% C, 1% Cr, toughened to a hardness of $HRC = 58$.

3. Results

Sintering in the solid phase at a temperature of 1373 K led to the formation of porous structures with a slight proportion of the Fe_2B phase on the surface of iron particles (Figs 2 and 3). As the time of sintering increased, an increase in the concentration of the Fe_2B phase and a decrease in porosity showed unsatisfactory intensity (Table I). Part of the boron was

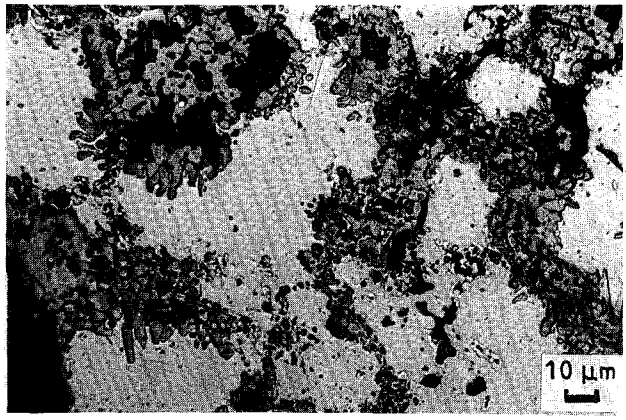

Figure 2 Microstructure of Fe–Fe_2B cermet of boron concentration 8.8% w/v sintered at 1373 K for 1 min, not etched.

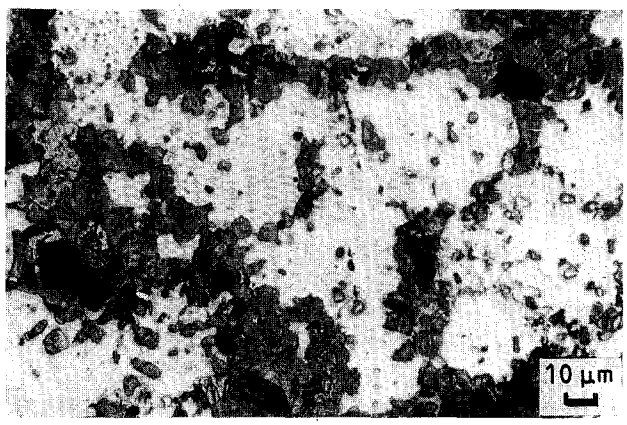

Figure 3 Microstructure of Fe–Fe_2B cermet of boron concentration 8.8% w/v sintered at 1373 K for 120 min, not etched.

TABLE I Proportion of Fe_2B in Fe–Fe_2B cermet for selected boron concentrations and sintering times at 1373 K

Boron concentration (% w/v)	Sintering time (min)	Proportion of Fe_2B (vol %)	Porosity (%)
3.8	0.25	8.2	11.8
4.8	120	12.3	7.6
6.3	0.25	11.1	14.8
6.3	120	24.7	11.5
8.8	0.25	15.1	18.4
8.8	120	26.4	14.1

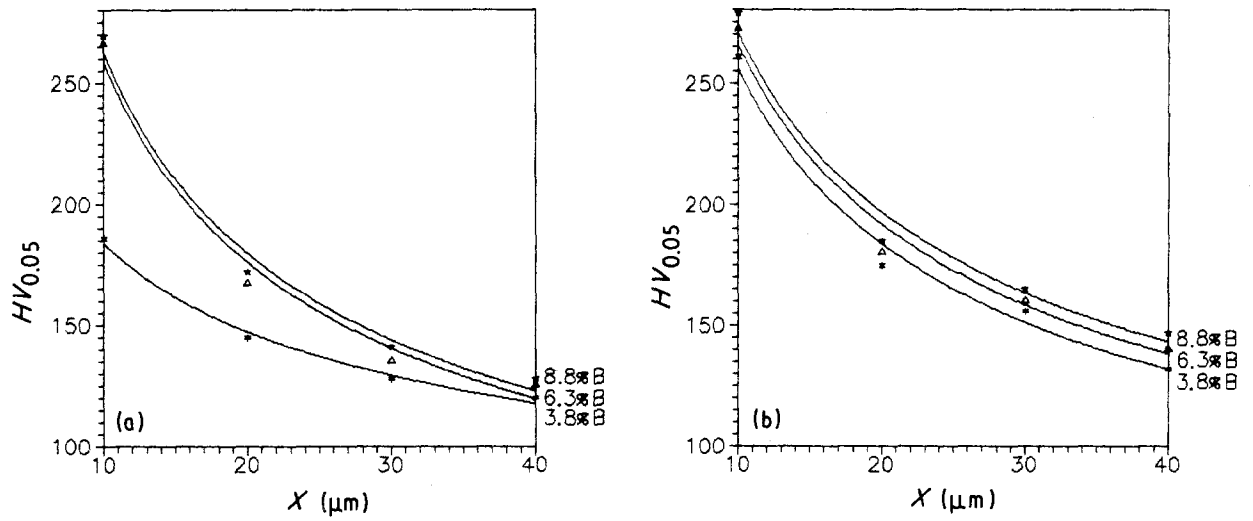

Figure 4 Hardness distribution of iron, $HV_{0.05}$, in Fe–Fe_2B cermet as a function of boron concentration (%B) for sintering times (t) of (a) 0.25 min and (b) 120 min at 1373 K; X = distance from surface of the particle of iron.

dissolved in the surface of iron particles, causing an increase in its hardness (Fig. 4).

Diffusion processes during the sintering of boron and iron in the solid phase are limited to the surface of separation between these elements, and boron in the pores did not participate in the reactions. As a result, increments of the concentration of the Fe_2B phase are slight. Therefore, further investigations concentrated on sintering with the participation of the liquid phase. The liquid phase should intensify the mobility of boron atoms found in pores and devoid of direct contact with iron.

The results of investigation confirmed this thesis. Using the methods of quantitative metallography and X-ray structural quantitative analysis, a great intensity of reaction between boron and iron during sintering with the participation of the liquid phase was shown, the effects of which are large increments of concentration of iron boride (Figs 5 and 6). The proportion of Fe_2B increases in the system as the concentration of B and sintering time increase. As a result of sintering a mixture composed of 91.2% Fe (w/v) and 8.8% B at a temperature of 1433 K for 240 min, a sinter was obtained with a composition of 82.9 vol % iron boride, Fe_2B, in the matrix of the Fe–Fe_2B eutectic.

Since the method of X-ray structural quantitative analysis was used to determine the total proportion of the Fe_2B phase in grains and the eutectic, and the metallographic method of linear analysis to determine the boron only of Fe_2B occurring in the form of free grains, the results of these two methods differ. The total volumetric proportion of the Fe_2B phases, V_{Fe_2B}%, in the sinter, which depends on the percentage concentration of boron, b, and the process duration in minutes, t, determined by the method of X-ray structural quantitative analysis, is described by Equation 1 below, while the volumetric proportion of Fe_2B in the form of free grains, v_{Fe_2B}%, determined by metallographic linear analysis is described by

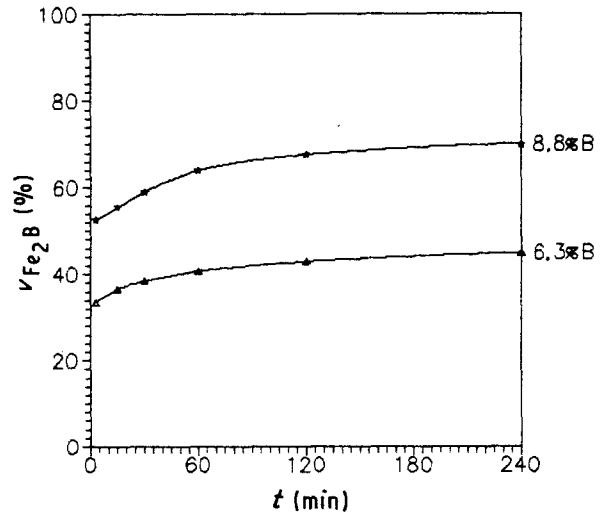

Figure 5 Dependence of volumetric proportion of free Fe_2B (v_{Fe_2B}) in Fe–Fe_2B cermet on boron concentration (%B) and sintering time (t) at 1373 K, determined by the method of microscopic linear analysis.

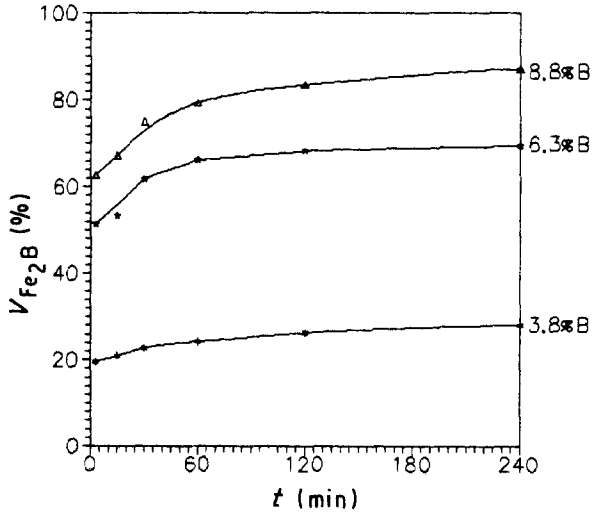

Figure 6 Dependence of the total proportion of Fe_2B (V_{Fe_2B}) in Fe–Fe_2B cermet on boron concentration (%B) and sintering time (t) at 1433 K, determined by the method of X-ray structural quantitative analysis.

Equation 2.

$$V_{Fe_2B} = -80.4348 + 33.0104b + 0.09703t - 1.90402b^2 - 0.0004t^2 + 0.01333bt \quad (1)$$

$$v_{Fe_2B} = -80.9084 + 28.5210b + 0.0057t - 1.3989b^2 - 0.0002t^2 + 0.0147bt \quad (2)$$

As a result of the experiments performed, cermets of two kinds of microstructure were produced:

(i) grains of the solid solution of boron in iron (Fe–B) in the matrix of the Fe–Fe_2B eutectic (Fig. 7), and

(ii) Fe_2B grains in the matrix of the Fe–Fe_2B eutectic (Fig. 8).

The proportions of the structural components of the cermet mentioned change as a function of the boron concentration and sintering time. In the case of sinters with the structure of grains of Fe–B solution in a matrix of Fe_2B eutectic, the proportion of the eutectic, V_E, increases as the sintering time increases, while in sinters with the structure of Fe_2B grains in a matrix of Fe–Fe_2B eutectic this proportion decreases (Equation 3 below and Fig. 9).

In both cases the proportion of Fe_2B phase in the sinter increases as the sintering time increases. As the sintering time increases, the porosity V_p of the sinter decreases and the Fe_2B grain size increases. The porosity of the sinters under investigation decreases rapidly at the initial stage of sintering and more and more slowly as the process proceeds according to Equation 4, presented graphically in Fig. 10

$$V_E = -3.8758 + 17.6674b + 0.2147t - 1.6352b^2 - 0.0004t^2 - 0.0104bt \quad (3)$$

$$V_p = 2.3010 - 0.4031b - 0.0075t + 0.0573b^2 + 0.00003t^2 - 0.0005bt \quad (4)$$

The minimum porosity of the sinters produced range from 0.66% at a boron concentration of 3.8% w/v to 1.72% at a concentration of 8.8% w/v. The Fe_2B grain size increases from 0.025 mm to about 0.080 mm as the sintering time increases (Fig. 11). The geometry of the surface of a fracture (Fig. 12) points to the possibility of inhibiting the development of fractures of fragile grains of iron boride, Fe_2B, by more plastic grains of the Fe_2B eutectic.

The hardness of Fe–Fe_2B cermets changes depending on their microstructure, which is determined by

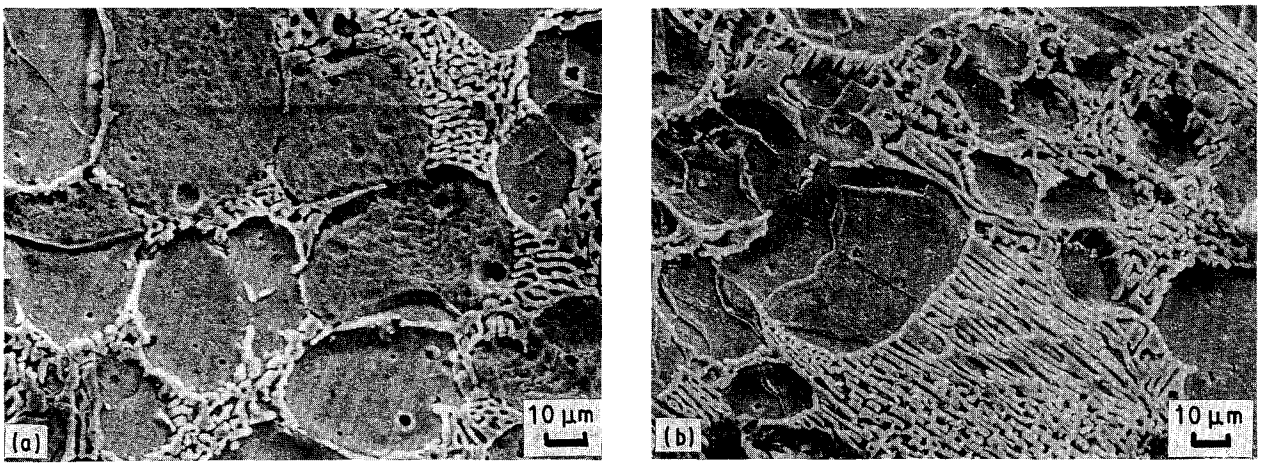

Figure 7 Microstructure of Fe–Fe_2B cermet of boron concentration 3.8% w/v sintered at 1433 K for (a) 3 min, (b) 120 min; etched with 3% HNO_3 in alcohol.

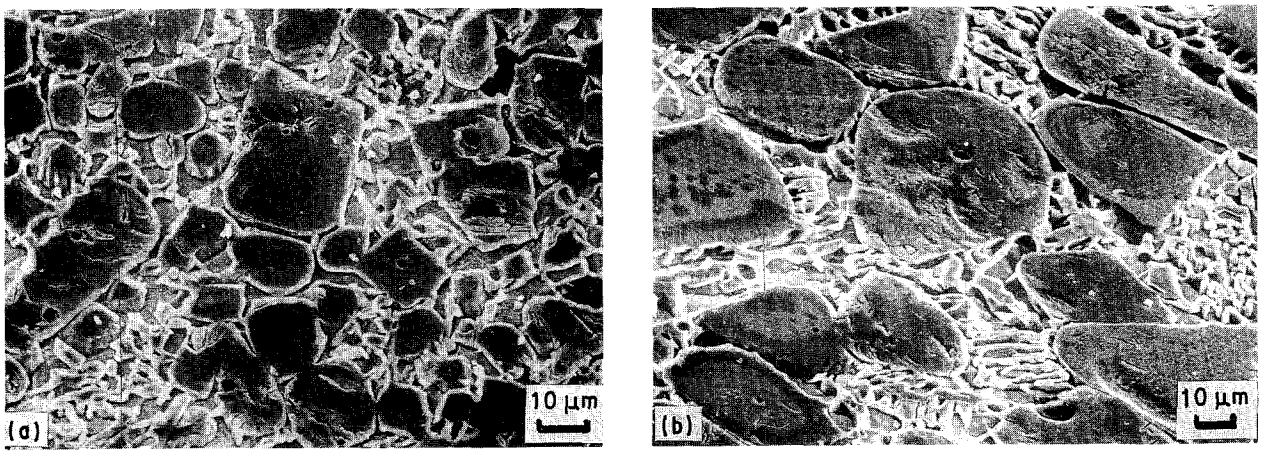

Figure 8 Microstructure of Fe–Fe_2B cermet of boron concentration 8.8% w/v sintered at 1433 K for (a) 3 min, (b) 120 min; etched with 3% HNO_3 in alcohol.

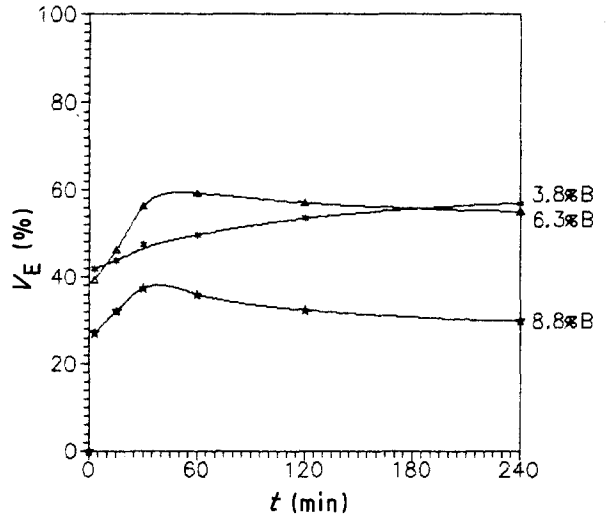

Figure 9 Dependence of volumetric proportion of Fe–Fe_2B eutectic, V_E, in Fe–Fe_2B cermets on boron concentration and sintering time, t, at 1433 K, determined by the method of microscopic quantitative analysis.

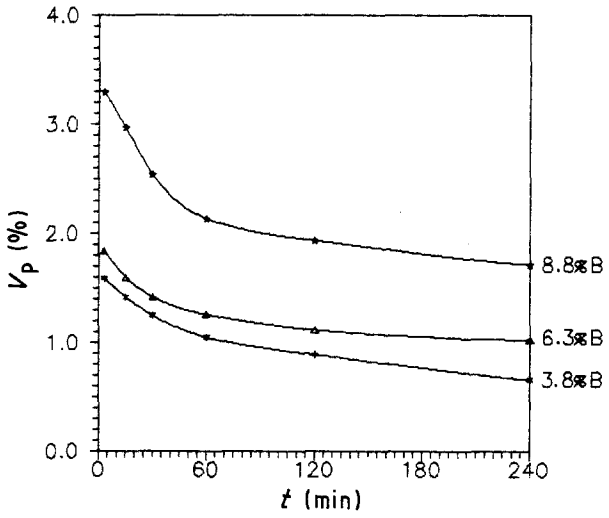

Figure 10 Dependence of porosity of Fe–Fe_2B cermet, V_p, on boron concentration (%B) and sintering time, t, at 1433 K determined by the method of microscopic quantitative analysis.

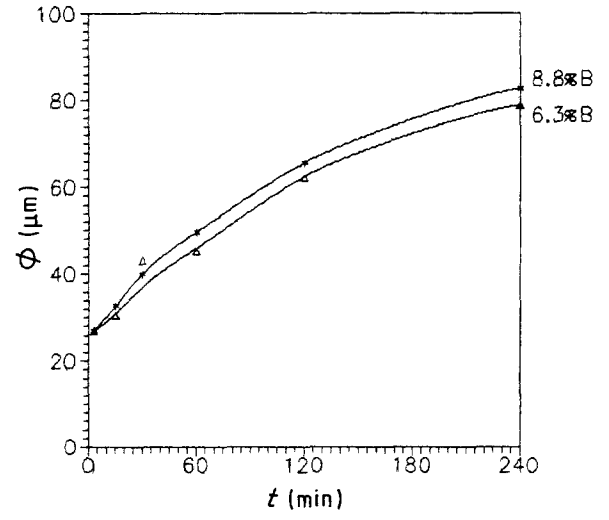

Figure 11 Dependence of Fe_2B grain size in Fe–Fe_2B cermet, Φ, on boron concentration (%B) and sintering time, t, at 1433 K determined by the method of microscopic linear analysis.

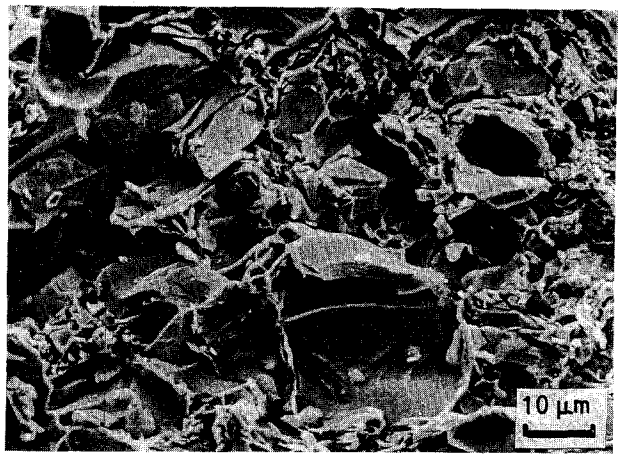

Figure 12 Surface of fracture of Fe–Fe_2B cermet of boron concentration 8.8% w/v sintered at 1433 K for 120 min.

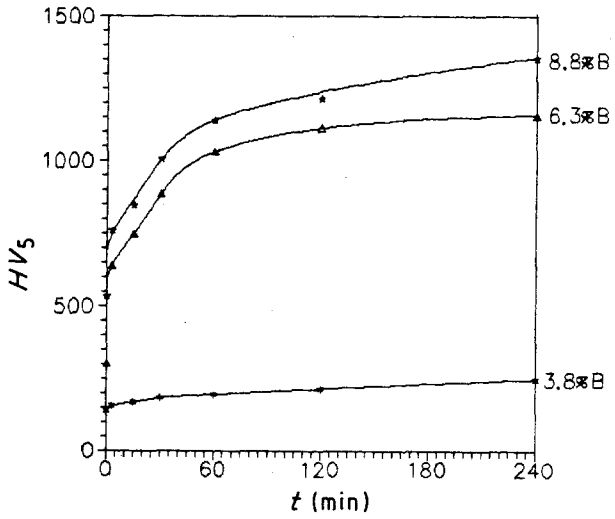

Figure 13 Dependence of hardness HV_5 of Fe–Fe_2B cermet on boron concentration (%B) and sintering time (t) at 1433 K.

their chemical composition and sintering conditions. As the proportion of iron boride, Fe_2B, the hardness of which is $HV_{0.1} = 1800$ increases, the total hardness of the sinter increases.

As the proportion of the Fe–Fe_2B eutectic of hardness $HV_{0.1} = 350$–500 increases, the total hardness of the sinter decreases. As a result, depending on the chemical composition and sintering conditions, the hardness of the sinters produced changes in a very wide range ($HV_5 = 150$–1500), according to Equation 5 presented graphically in Fig. 13

$$HV_5 = -2081.646 + 759.004b + 1.210t - 50.008b^2 - 0.009t^2 + 0.427bt \quad (5)$$

Fe–Fe_2B sinters show slight wear in the process of dry friction, comparable to the wear of diffusion layers boronized on low-alloyed steels, and considerably smaller than the wear of toughened steels.

The magnitude of wear of the sinters under investigation is related to their microstructure and decreases as the volumetric proportion of iron boride, Fe_2B, increases (Fig. 14).

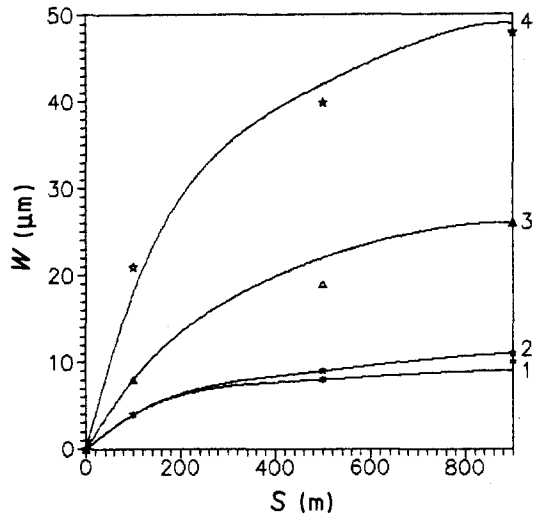

Figure 14 Dependence of wear (W) on path of friction (S) of (1) Fe–Fe_2B cermet of boron concentration 8.8% w/v sintered at 1433 K for 240 min, (2) diffusion layer boronized on iron, (3) Fe–Fe_2B cermet of boron concentration 3.8% w/v sintered at 1433 K for 240 min, (4) 0.6% C steel toughened to $HRC = 60$.

4. Conclusions

The results of the investigations carried out show that there is a possibility of producing Fe–Fe_2B cermets with a boron concentration of 3.8–8.8% w/v, with two kinds of microstructure:

(i) $(Fe–B)_p\,(Fe–Fe_2B)_q$ $\quad 0.40 \leqslant p \leqslant 0.45;\ 0.60 \leqslant q \leqslant 0.55,$

(ii) $(Fe_2B)_r\,(Fe–Fe_2B)_s$ $\quad 0.59 \leqslant r \leqslant 0.70;\ 0.41 \leqslant s \leqslant 0.30.$

In the first case, grains of the solid solution of boron in α-iron (Fe–B) of a hardness $HV_{0.1} = 120–230$ are settled in the eutectic (Fe–Fe_2B) of a hardness of $HV_{0.1} = 350–500$. In the second case, in the eutectic (Fe–Fe_2B) grains of iron boride (Fe_2B) of a hardness $HV_{0.1} = 1800$ are settled. The qualitative and quantitative phase composition of the cermet resulting from its chemical composition and sintering conditions is decisive for its mechanical properties. The high hardness and resistance to wear as well as the residual porosity of the sinters produced point to further research aimed at using them as constructional materials for high-loaded elements of slide bearings.

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