STRUCTURAL CHARACTERISTICS AND MECHANICAL
PROPERTIES OF SINTERED Fe−B₄C MATERIALS

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At present, sintered constructional materials are extensively used in industry. Investigations into methods of producing such materials involve studying the transformations occurring in them during sintering, the character of the resultant structure, and its effect on their mechanical properties. One such investigation is described below.

Sintered materials produced from iron powder possess comparatively poor mechanical properties, which, however, can be substantially improved by adding to the powder an interstitial-phase type compound. A possible addition is boron carbide, which dissociates in contact with iron at high temperatures [1, 2]. The addition of B_4C to an iron powder would be expected to result during sintering in the formation of iron carbides and borides, whose amount and morphology would determine the properties of the resultant sintered material. Now B_4C is a compound of comparatively low carbon content, and consequently one could expect the carbides to become fairly evenly distributed throughout the material [3], but the boron−iron compounds might form concentrations near the diffusion sources or, because of the positive adsorption activity of boron, nuclei on structural defects. This points to a possible way of controlling the structure of such materials.

In our work a mixture of PZh4M (a fine reduced iron powder of 96.0% minimum purity) and a B_4C powder of 40- to 60-μ particle size was pressed to a given porosity into compacts, which were then sintered for 2 h in a hydrogen stream at temperatures of 1050-1200°C. The amount of boron carbide in the mixture was varied from 0.5 to 2.0 wt.%. Measurements were made of the shrinkage, hardness, transverse rupture strength, and pycnometric density of compacts. The data yielded by the density measurements together with information on phase composition enabled the porosity of the specimens to be calculated. Structure and phase composition were investigated by optical and electron microscopy, x-ray structural analysis, and electron probe microanalysis.

Structure and Transformations during Sintering

Metallographic examinations revealed that the sintered materials had a heterogeneous ferritic−pearlitic structure, depending on the amount of boron carbide in the mixture. After sintering at 1050°C a light-colored, hard (1400 kgf/mm²) phase concentrated in the vicinity of incompletely decomposed boron carbide particles was found in the structure (Fig. 1a). The same phase was observed also after sintering at 1100-1200°C, but in this case its morphology was different: It was distributed along boundaries, forming a more or less developed skeleton (depending on the amount of B_4C and sintering temperature) (Fig. 1b). This skeleton must have formed in the presence of a liquid phase, which appeared at temperatures above 1100°C as a result of eutectic contact melting. Direct evidence for the formation of a liquid phase during sintering was provided by crystallization structures. These structures contained eutectic areas (Fig. 1b), whose morphology is shown in Fig. 2b, and lamellas (Fig. 2a) forming a characteristic cellular structure appearing during crystallization under conditions of slight concentration supercooling [4], and hence in this case at the sintering temperature. Such lamellas were frequently detected in a white phase located at grain boundaries (although on the whole its structure was fairly varied), and it can therefore be concluded that, like the pearlite (Fig. 1b), this phase had formed by a mechanism of recrystallization of material through a liquid phase.

To discover the nature of the white phase, sintered specimens were dissolved electrolytically, and the insoluble residue was examined by x-ray diffraction. Values of interplanar spacings calculated with the aid of diffraction photographs and data on the reflection intensities and symmetry of anticipated phases enabled the phase composition of the residue to be determined. From Table 1 it follows that the sintered materials contained cementite and the borides Fe_2B and FeB, apparently with dissolved carbon (carboborides). Electron probe microanalyses demonstrated that the white phase at grain boundaries corresponded in composition to the
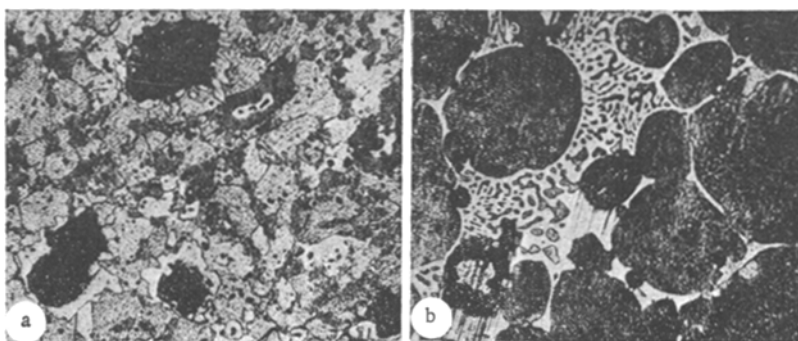
Fig. 1. Structures of materials sintered at 1050 (a) and 1150°C (b), ×300.

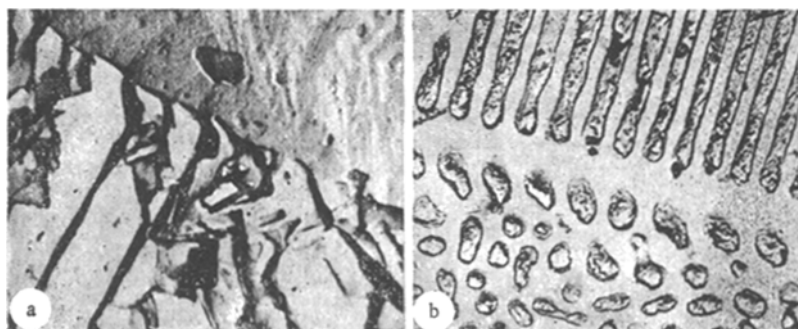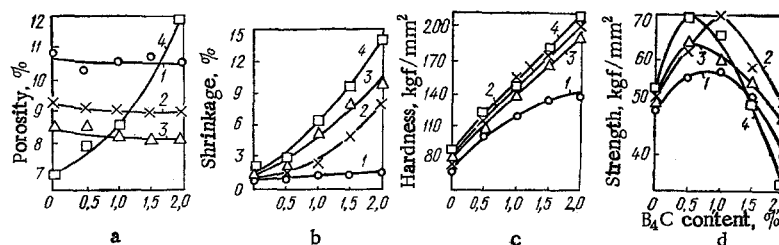Fig. 2. Structure of crystallization products, ×20,000: a) lamellas; b) eutectic.

Fig. 3. Properties of materials produced by sintering iron—boron—carbide powder mixtures at temperatures of 1050 (1), 1100 (2), 1150 (3), and 1200°C (4).

compounds Fe_2B and FeB, and this was confirmed also by the way it was etched by sodium picrate. In special experiments, conducted with a powder mixture containing ferroboron instead of B_4C, an identical phase was observed at grain boundaries after sintering (in this case, of course, there was no cementite).

Preferential formation of borides at boundaries and, at low temperatures, around boron carbide particles was due to the compound B_4C being much richer in boron than in carbon. Apart from this, it is known that $Fe(B, C)$ alloys vary in composition; thus, in [5-7] carbon was found to be "forced out" by boron in the course of boronizing. In Fig. 2b are shown eutectics of two — rod and lamellar — types. Such morphological differences are due to a difference in relative orientation between a "leading" and a "trailing" phase during eutectic transformation, which in turn depends on the symmetry and composition of the phases and the thermal conditions of crystallization. It is reasonable to assume that the structure shown in Fig. 2b reflects a stratification of boron and carbon in the liquid.

As the structure of such a sintered material forms so that the carbides pass mainly into the pearlite and the borides concentrate at grain boundaries, the possibility arises of independently strengthening these two structural constituents with boron and carbon. This means that, by varying the composition of the powder mixture and the sintering temperature, it is possible to obtain materials with different phase compositions and

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TABLE 1. Interplanar Spacings (d, Å) and Reflection Intensities (I) for Fe_3C, FeB, and Fe_2B Residue

Experimental values		Fe_3C		FeB		Fe_2B	
s.	2,4	s.	2,38	s.	2,26	—	—
m.	2,25	m.	2,26	s.	2,33	—	—
m.	2,13	—	—	—	—	m.	2,12
v.s.	2,04	v.s.	2,001	v.s.	2,003	v.s.	2,008
m.	1,99	m.	1,97	—	—	—	—
s.	1,83	—	—	—	—	s.	1,83
m.	1,78	m.	1,76	s.	1,78	—	—
m.	1,70	m.	1,682	—	—	—	—
m.	1,60	m.	1,58	s.	1,58	m.	1,61
w.	1,52	w.	1,51	—	—	—	—
w.	1,45	—	—	m.	1,458	—	—
w.	1,41	—	—	m.	1,418	—	—
m.	1,34	m.	1,33	—	—	w.	1,37
m.	1,26	—	—	m.	1,28	m.	1,27
s.	1,22	m.	1,22	v.s.	1,22	—	—
m.	1,20	m.	1,21	—	—	v.s.	1,20
m.	1,18	—	—	m.	1,18	m.	1,18
m.	1,16	m.s.	1,16	—	—	—	—
s.	1,15	m.	1,15	v.s.	1,15	—	—
s.	1,13	m.s.	1,126	—	—	—	—
v.s.	1,108	m.s.	1,105	—	—	—	—

structures, i.e., with different levels of "volume" (due to carbides) and "skeletal" (due to borides) strengthening. This would enable powder metallurgy materials of this type to be "tailored" to fit their applications [3].

Since the properties of such sintered materials depend also on the structural state of their ferrite component, the latter's fine structure was investigated by x-ray diffraction. It was found that at low sintering temperatures the size of coherent scattering blocks decreased with increasing volume fraction of borides and cementite. At 1150°C intense recrystallization led to a substantial increase in the sizes of the blocks (from 1000-1400 Å at 1100°C to 8000-10,000 Å at 1150°C) and grains.

Properties of Sintered Materials

Sintering at 1050°C was accompanied by slight shrinkage, and the sintered materials had an appreciable porosity, which was virtually independent of the amount of B_4C added to the powder (Fig. 3). The appearance of hard compounds in the structure produced a monotonic increase in the hardness of the material (Fig. 3c, curve 1), while its strength at first rose to a maximum and then fell (Fig. 3d, curve 1). The fall in strength at high B_4C concentrations was apparently linked with the presence of undecomposed boron carbide particles.

At 1100 and 1150°C a slight decrease in porosity and an increase in shrinkage occurred (Fig. 3a and b) as a result of transition to liquid-phase sintering. In this case the shrinkage substantially grew with rise in the amount of B_4C in the mixture, whereas the porosity showed very little change, which must have been due to loss of material linked with the formation of gaseous oxides and escape of liquid from compacts. These phenomena were particularly pronounced during sintering at 1200°C. With rise in boron carbide concentration in the mixture the hardness of the material grew owing to the appearance of borides and pearlite in its structure. A slight fall in hardness recorded when the sintering temperature was changed from 1100 to 1150°C (Fig. 3c, curves 2 and 3) was accompanied by an increase in the size of coherent scattering blocks at 1150°C, as determined by x-ray diffraction.

The strength vs composition curves obtained (Fig. 3d) reflect a strengthening of the sintered materials through the formation of hard phases and a simultaneous change in their relaxation properties. At high B_4C concentrations the strength appreciably decreased, although the porosity remained practically unchanged. From the results of the structural investigation it follows that this phenomenon could have been due only to a decrease in the relaxation ability of the material, brought about by the development of a boride skeleton along grain boundaries. At any given composition the formation of the skeleton was influenced, as was established by direct observations, by the sintering temperature.

Because of this, materials sintered at high temperatures exhibited a fall in strength at lower boron carbide contents (Fig. 3d, curves 2-4). The level of strength, like that of hardness, depended also on the structural
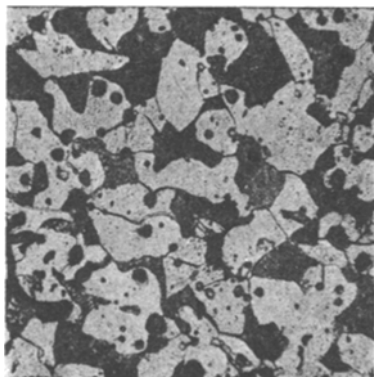
Fig. 4. Structure of material sintered from iron— 0.5% B_4C mixture at 1200°C, ×300.

state of the ferrite. A sharp decrease in the physical broadening of the diffraction lines in the α phase observed after sintering at 1150°C was in good accord with the shape of curves 2 and 3 in Fig. 3d; the maximum attainable strength was always less after sintering at 1150°C than after sintering at 1100°C, although the porosities of the materials at these two sintering temperatures were approximately equal.

Sintering at 1200°C produced a coarsening of structure and a strong development of the boride skeleton, resulting in a sharp fall in strength. At low B_4C addition contents, however, materials sintered at 1200°C exhibited high strength, which, judging from the results of structural investigations, was due to completeness of phase transformations and a favorable phase morphology. In this case a rise in B_4C content led to a marked increase in both porosity and shrinkage (Fig. 3a and b, curves 4); these changes were indicative of loss of material through vaporization and escape of liquid. Direct observations provided evidence for the occurrence of this phenomenon, which was accompanied by the development of a coarse macroscopical porosity, and undoubtedly it was this effect that was responsible for the fall in strength. Nevertheless, the hardness, being dependent mainly on the amount of carbide particles and of the boride phase, steadily grew (Fig. 3c, curve 4).

Optimum Processing Conditions

From the results cited above, it follows that the best combinations of service properties were exhibited by materials from iron + 1.0% B_4C and iron + 0.5% B_4C powder mixtures sintered at 1100 and 1200°C, respectively. They had a strength of 70 kgf/mm², and were characterized by comparatively small shrinkage and a fairly fine-grained hypoeutectoid matrix structure with boride inclusions forming no skeletons.

Materials of the first type had a structure which was similar to that shown in Fig. 1a except that it contained a very small quantity of eutectic fields. Materials of the second type had a ferritic—pearlitic structure (Fig. 4). In this structure the eutectic and the boride skeleton were almost completely absent, because in a powder mixture of low B_4C content the amount of liquid forming during heating is small and all of it is expended during recrystallization at the sintering temperature. Use of a 1% B_4C addition is appropriate in those cases where parts are to operate under wear conditions, without having to meet severe bulk strength requirements. A mixture containing 0.5% B_4C can be recommended for the manufacture of parts carrying substantial static loads, because of the strength of material made from it is less sensitive to composition and sintering temperature deviations. Measurements of permanent bending deflections and percentage elongations to rupture have shown that such material is more ductile than material sintered from a mixture with 1% B_4C, although the latter is harder and better able to resist wear.

A variety of small-sized components widely used in engineering (supports, catches, stops, Maltese crosses, segments, keys, gibs, pawls, hooks, etc.) have been produced under these conditions. They have all passed industrial tests in accordance with existing technical specifications. The method proposed is now being used for the production of such machine components at an instrument factory, giving appreciable savings.

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