Cermet Formation during Mechanical Activation of TiB$_2$ − Fe SHS Powder in Benzine

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Abstract

Phase composition and structure studies have been performed using metallography, X-ray diffraction, and X-ray microstructural analysis for TiB$_2$ − Fe SHS powders mechanically activated in benzine and for sintered alloys of mechanically activated powders. Mechanical activation (MA) in benzine changes the phase composition of titanium diboride in an iron matrix, forming Ti$_{1.87}$B$_{50}$, TiB, Fe$_2$B, and Fe$_3$B. After the sintering, the alloy has the following phases: TiB$_2$, α-Fe, Fe$_2$B, and TiC. Formation of titanium carbide is due to the interaction of benzine with TiB$_2$ − Fe SHS powder in the course of MA.

INTRODUCTION

Modern development in the field of technology owes much of its progress to the creation of new materials capable of operating under conditions of high temperatures and rates, as well as mechanical stress and aggressive media. Acid-free high-melting compounds have recently attracted the attention of metallographers in connection with these developments.

The most promising materials from this class are titanium borides, in particular, titanium diboride possessing hardness, wear resistance, high melting point, resistance to the action of metal melts, and some other useful properties. With all these properties, however, titanium borides have not yet received wide use in technology. Synthesis of borides, and especially those with low porosity has encountered significant technological difficulties. Brittleness of titanium diboride is another obstacle to its wide use.

Developing materials of cermet type from titanium borides seems to be an optimal solution to this problem.

Self-propagating high-temperature synthesis (SHS) is one of effective methods for the preparation of such materials.

The composite material based on titanium diboride with an iron matrix and prepared by the SHS technique had residual porosity 10–15 % and was therefore inapplicable as a material for machine elements and tools [1]. For the preparation of a dense, high-performance material, porous SHS product is powdered and sintered at 1400-1500 °C for 60 and 40 min, respectively, the conditions depending on powder dispersity [2]. These sintering temperatures are high enough, although they are well below the temperatures required for the preparation of a dense material from the TiB$_2$ and Fe components (T_{sint} ~100 °C) [3].

One of the methods to activate the sintering process is vigorously grinding the starting powders in high-energy-strain apparatuses [4]. Using preliminary mechanical activation (MA) for TiB$_2$ − Fe SHS powder permits one to reduce the sintering temperature and the isothermal storage time [5].

The samples obtained by sintering SHS powder after MA in benzine contained a phase

which was not observed in the samples obtained by sintering the starting nonactivated material. In the samples obtained after MA in an argon atmosphere, this phase was not observed either [6]. The appearance of the new phase was explained by the addition of Mo and Cr as dopants to increase ductility of the TiB_2 − Fe composite. Reasons for the appearance of the new phase were not clarified in detail.

The purpose of the present work is to study the product of MA of TiB_2 − Fe SHS powders in benzine and the materials obtained by sintering these products.

EXPERIMENTAL

Mechanical activation was applied to SH-synthesized TiB_2 − Fe composite powder (69 vol. % TiB_2 and 31 vol. % Fe) with dispersity of less than 100 μm. The TiB_2 − Fe SHS material was obtained by burning a mixture of FeB (21.6 mass % B) with titanium. Conditions of SH synthesis are given in [1].

Mechanical activation was conducted in an MPV planetary mill with a water cooling system in benzine (ungraded 2−80/120).

The steel drums were 100 cm^3 in capacity; the steel balls were 0.4−0.5 cm in diameter; mass ratio of powder to balls was 1 : 20. Energy strain factor was 60 *g* for MPV; activation time was 15, 30, and 60 min.

The sintering of the starting powder and activated samples was conducted in a vacuum furnace at 1300 °C for 60 min.

Basic methods of analysis for the starting powder and activated SHS samples were as follows: chemical analysis, X-ray study (DRON-2, CoK_α radiation), metallography (MIM-8), X-ray microstructural analysis (Camebax), and transmission electron microscopy (TEM, EM-125 instrument). For phase analysis, coal replicas with "extraction" were prepared in the sintered samples.

RESULTS AND DISCUSSION

Figure 1 shows the diffraction patterns of the starting sample of the TiB_2 − Fe SHS composite powder and of the sample mechanically activated in benzine. The diffractograms show reflections of TiB_2 and α-Fe. Moreover, a TEM study showed that the sample had small amounts (less than 3 mass %) of TiB, FeB, Fe_2B, and Fe_3B in a ratio of TiB : Fe_xB = 1 : 3.

Mechanical activation changes the intensities of all reflections, and after the sample had been activated for 60 min, the weak reflections vanished. At the same time, the fundamental reflections of titanium diboride broadened, and the background increased. These changes in the diffraction spectra may be due to the small size of crystallites or to microdeformations.

TEM analysis has also revealed the following phases in the activated powders: $Ti_{1.87}B_{50}$, TiB, Fe_2B, Fe_3B, and Fe_4B_2; *i. e.*, two new phases, $Ti_{1.87}B_{50}$ and Fe_4B_2, have appeared, their total mass fraction being less than 5 %.

Moreover, chemical analysis of the activated samples showed that the carbon content increased. While the starting powder had 0.5 % carbon, the activated powders had from 2 to 3.3 % carbon depending on the activation time.

At the same time, the content of iron increased by 5 % in the activated samples due to the wear of balls and drum walls.
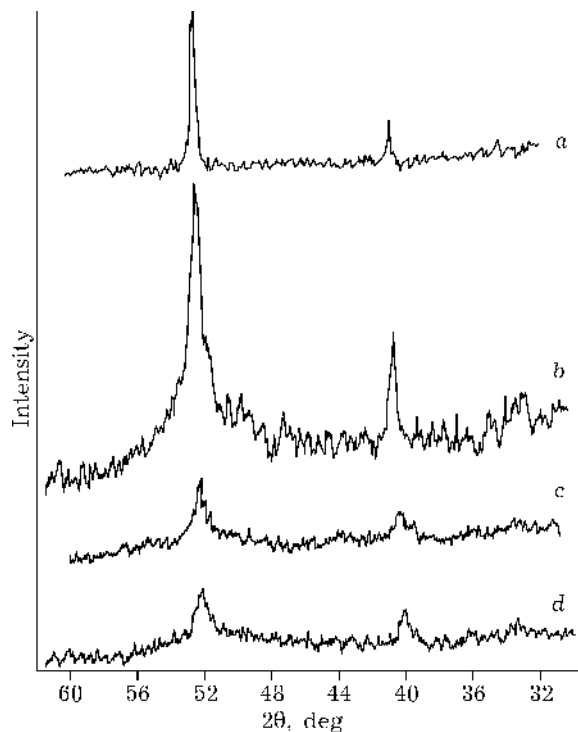

Fig. 1. Diffractograms of the samples of TiB_2 − Fe SHS powders: starting sample (*a*) and the samples mechanically activated in benzine for 15 (*b*), 30, (*c*), and 60 min (*d*).
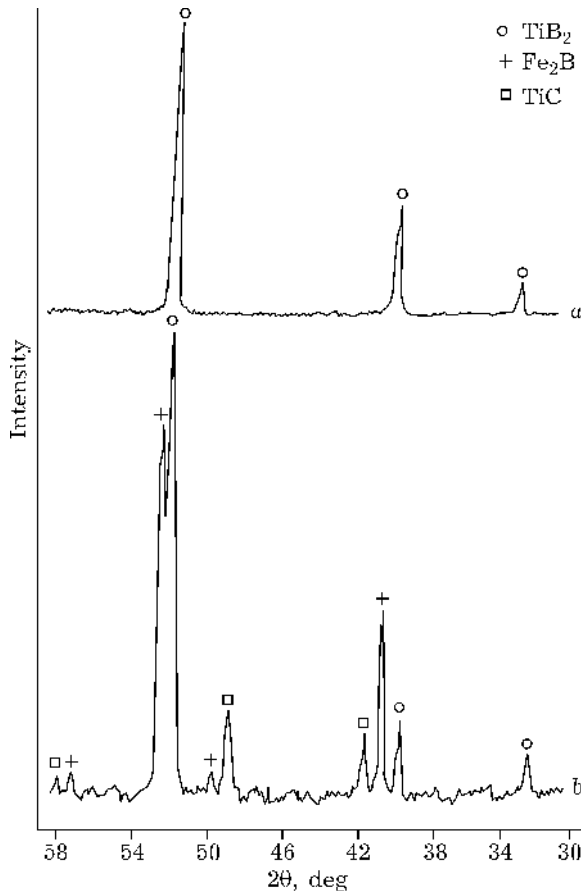
Fig. 2. Diffractograms of TiB$_2$ – Fe SHS powders sintered from the starting sample (*a*) and from the sample activated for 30 min in benzine (*b*).

The starting and activated powders were then sintered. Figure 2 shows fragments of the diffraction patterns of the cakes obtained from the starting and activated TiB$_2$ – Fe SHS powders. Analysis of the diffractograms given in Figs. 1, *a* and 2, *a* indicated that the starting powder and the cake product had the same phase composition. The diffractograms show reflections belonging only to TiB$_2$ and α-Fe.

For the sample sintered from powder after mechanical activation for 30 min in benzine, the diffraction pattern contained new reflections. Identification of reflections using the ICPDS database showed that they belong to titanium carbide TiC and iron boride Fe$_2$B. This set of reflections is present on all diffractograms of samples sintered from powders mechanically activated in benzine for 15, 30, and 60 min.

A TEM study of samples sintered from powders activated in benzine additionally revealed Fe$_{20}$C$_9$, Fe$_3$C, and Fe$_2$C phases, whose total mass fraction was < 5 %.

Figure 3 presents the microstructures of the sintered samples obtained from TiB$_2$ – Fe powder and from the powder resulting from MA in benzine. The sample sintered from the starting specimen with dispersity less than 100 μm is a porous cake consisting of the starting particles sintered onto contact sites. Each particle consists of clearly faceted TiB$_2$ crystals positioned in a metallic matrix. The samples sintered from powders activated in benzine are very dense. Thus for the sample sintered from the powder activated for 30 min in benzine, volume shrinkage was over 20 %. In the microstructure of these samples, one can identify a gray phase
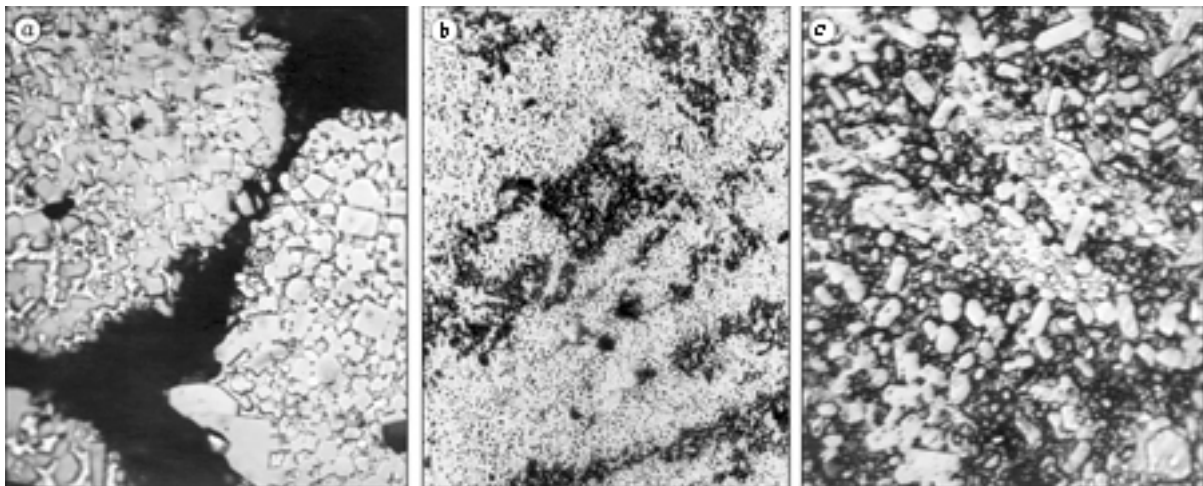

Fig. 3. Microstructures of the samples sintered from the starting sample of SHS powder (*a*) and from the sample mechanically activated in benzine (*b*, *c*): *a*, *c* − ×500; *b* − ×400.

No products

having dimensions of less than 2 μm and uniformly distributed over the section (see Fig. 3, b, c). According to X-ray and X-ray microstructural analysis data, the gray phase is titanium carbide TiC.

The presence of titanium carbide among the products of sintering may be explained by the interaction of benzine with $TiB_2 -$ Fe SHS powder leading to benzine decomposition in the course of MA or by adsorption of a thin benzine film on the surface of the powder.

It is noteworthy that SHS powder mechanically activated in benzine is in an active state, which accounts for the increased sintering ability of this powder. Sintering occurs at 1300 °C and proceeds to a density of more than 99 %. For comparison, nonactivated SHS powder is sintered at a temperature of 1450 °C at which residual porosity reaches ~5 % (density 99 %).

The high density of the powder, as well as the peculiarities of microstructure and phase composition, ensure high hardness of the cake material obtained after mechanical activation of powder in benzine (HRA = 90−95 %).

CONCLUSIONS

1. Mechanical activation of $TiB_2 -$ Fe SHS powder in benzine changes the chemical and phase compositions of the starting product.

2. Sintering the $TiB_2 -$ Fe SHS powder activated in benzine forms a new cermet whose structure and composition are such that TiB_2, TiC, Fe_2B, and α-Fe are dominant phases. The phase composition and the morphological peculiarities of this material ensure high density and hardness of the sintered material.

REFERENCES

1 Yu. M. Maksimov, M. Kh. Ziatdinov, A. T. Pak *et al.*, Pat. 938629 USSR, 1982.
2 L. G. Raskolenko, O. K. Lepakova, Yu. M. Maksimov, in: Samorasprostranyayushchiysya vysokotemperaturny sintez, Tomsk, 1991, p. 110.
3 V. F. Funke, S. I. Yudkovskiy, G. V. Samsonov, *Zhurn. prikl. khimii*, 5 (1961) 1013.
4 E. G. Avvakumov, Mekhanicheskiye metody aktivatsii khimicheskikh protsessov, Nauka, Novosibirsk, 1986.
5 O. G. Terekhova, O. K. Lepakova, *Neorgan. materialy*, 3 (1998) 309.
6 O. G. Terekhova, O. K. Lepakova, *Khimiya v interesakh ustoichivogo razvitiya*, 6 (1998) 195.