Reactions in a Metal Matrix: Synthesis and Properties of TiB$_2$ − Cu Nanocomposites

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Abstract

Synthesis of the hardening phase in a metal matrix by combined mechanical activation and self-propagating high-temperature synthesis (SHS) has been investigated using the TiB$_2$ − Cu system as an example. It is demonstrated that performing the reaction inside the matrix allows the product dispersity to be significantly increased. Mechanical activation of a powder mixture of reagents and SHS reaction product is of critical importance for the production of a composite containing nanosized particles of titanium diboride sized 30−50 μm in a copper matrix. Nanocomposites contain titanium diboride particles sized 30−50 nm and distributed in the copper matrix. The volumetric content of titanium diboride in nanocomposites can vary within a wide range (10−60 %). Evolution of the nanostructure of the resulting composites during compaction has been investigated; conditions necessary for obtaining bulk nanostructural materials have been found. Compact nanocomposites with high strength properties and materials with increased resistance to electric erosion have been synthesized from the TiB$_2$ − Cu system. The potential of and prospects for new nanocomposite-forming synthetic procedure are discussed.

INTRODUCTION

A promising method for synthesizing composite materials is performing reactions in metal matrices [1, 2]. The advantages of synthesis in a matrix are high dispersity and uniformity of distribution of phase particles in the matrix, generally unattainable by the use of simple mixing of previously synthesized compounds. Despite the widespread use of this approach, few works are available on the effect of reaction conditions, on the product microstructure and its further evolution induced by thermal or mechanical action. Particle size control is often limited to variation of only one parameter, namely, the matrix concentration in the system [3, 4].

Synthesis of nanocomposite materials calls for more efficient methods of control over the microstructure of the reaction products. Reactions in metal matrices can be conducted in different ways. When reagents are introduced into a melted metal, they are wetted with the molten metal [5]; high diffusion coefficients in the liquid phase lead to growth of particles. Favorable conditions for the formation of finely disperse particles are realized when reactions are performed in a matrix in mixtures of powders [6].

We have developed a method for the preparation of nanocomposite materials, namely, mechanical activation of powder mixtures combined with self-propagating high-temperature synthesis (SHS); factors governing the microstructure of the resulting product for the given method of synthesis have been determined. From the resulting nanocomposite powders we have synthesized compact materials with preserved nanostructure in the bulk of the substance and studied their properties.
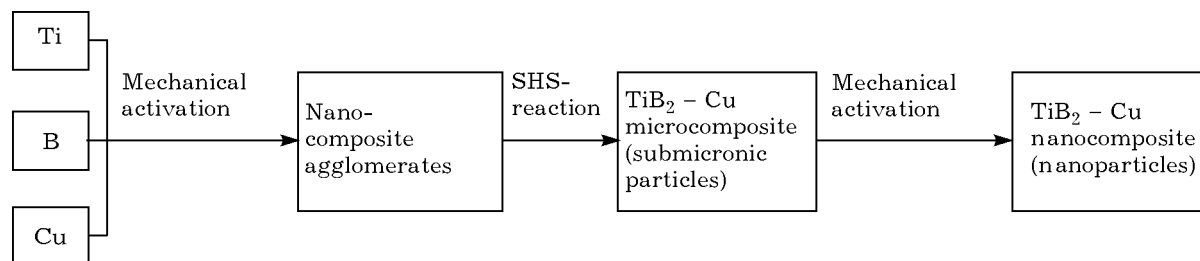
Fig. 1. Sequence of operations and transformations in the course of synthesis of TiB_2 – Cu nanocomposites by reaction in a matrix.

SYNTHESIS OF TITANIUM DIBORIDE IN A COPPER MATRIX BY COMBINED MECHANICAL ACTIVATION AND SHS METHODS. SYNTHESIS OF NANOCOMPOSITES

TiB_2 – Cu may be considered as a model system for studying the reaction in a metal matrix, since titanium diboride is the most thermodynamically stable phase in the system. Interest in the TiB_2 – Cu system from the viewpoint of materials science is dictated by the successful combination of the properties of the components. Copper is a plastic material with high thermal and electric conductivities. Titanium diboride has a high melting point, hardness, and abrasive capacity, as well as fairly high (for ceramics) values of thermal and electric conductivity, which enable one to create high-strength conductors.

Synthesis of titanium diboride from elements by the SHS method results in particles sized from 5 to 40–60 µm depending on the coarseness of the starting reagents [7, 8]. When a diluent is added to the system, the particle size of titanium diboride decreases to 1–5 µm [7, 9]. Obviously, mutual dispersion of reagents to the nanosized level is essential to obtain nanocomposite reaction products. This state of the system is achieved by mechanical activation of the powder mixture [10].

The sequence of operations and transformations in the course of nanocomposite synthesis is presented in Fig. 1. Titanium diboride fails to form in the activated mixtures when the selected modes of mechanical activation and selected compositions of reaction mixtures are used [11, 12]. Composite particles (agglomerates sized 50–100 µm) with a complex structure are formed from the starting element powders in the course of mechanical activation [11]. Transmission electron microscopy (Fig. 2) shows that conditions are created in the me-

chanically activated mixture for a reaction between titanium and boron to proceed in the system made up from well agitated particles with a large interface between the initial components.

Preliminary mechanical activation increases the maximum possible copper content in mixtures capable of reacting in the SHS mode and decreases the combustion temperature (to temperatures not exceeding the melting point of copper, Fig. 3) and the temperature of the reaction initiation compared to nonactivated mixtures [12]. The lower combustion temperature is due to the peculiarities of heat emission in mechanically activated mixtures, which starts at low temperatures (100 °C) and devel-
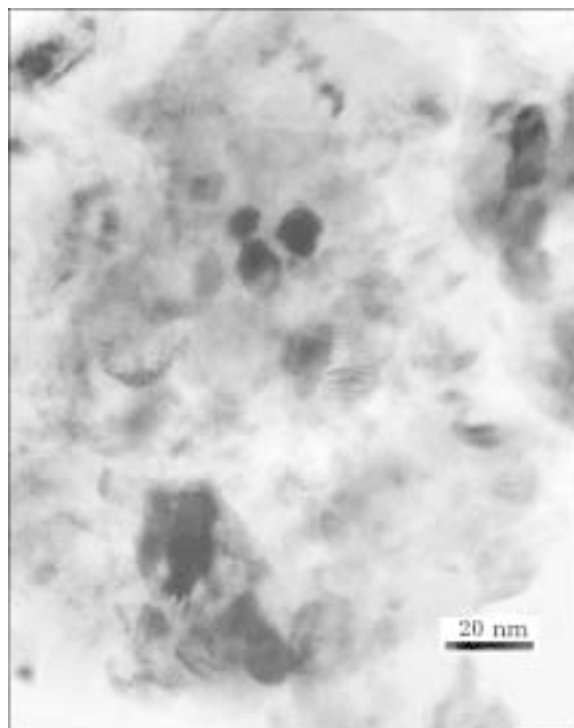

Fig. 2. Structure of composite agglomerates (Ti-2.1B) – 60 mass % Cu (TEM image).

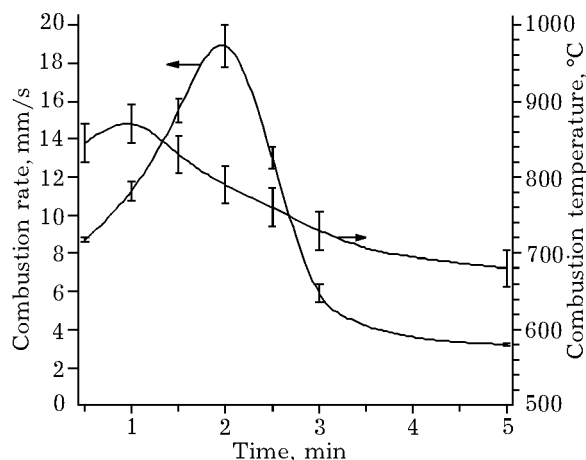Fig. 3. Dependence of the combustion rate and temperature on the mechanical activation time for a (Ti-2.1B) – 60 % Cu mixture.

Fig. 4. Microstructure of the SHS reaction product of TiB$_2$ – 43 vol. % Cu composition under the scanning electron microscope.

ops through several stages, reducing thereby the total rate of heat emission and hence the combustion temperature. The lower temperature of reaction initiation is attributable to the decreased temperature of titanium diboride formation in mechanically activated mixtures and to additional heat emission related to defect annealing in plastically distorted metals.

Hence, the lower synthesis temperature and the occurrence of the reaction in a nanocomposite system of mutually dispersed reagents create conditions for submicronic 0.1–0.5 μm sized particles of titanium diboride to be formed (Fig. 4).

In the course of synthesis, it is important that the relationship between the burning rate of the mixture and the activation time for mechanically activated mixtures is described by a curve with a maximum (Fig. 3). The increased burning rate at small times of mechanical treatment is explained by the increased phase boundary of the components and higher defect concentrations. The decreased burning rate after the maximum is associated with the formation of the reaction product even in the course of mechanical treatment and «poisoning» of the reaction mixture with it [13]. In our case, titanium diboride does not form during activation, but «poisoning» may arise from the formation of other fixed forms of the starting elements, for example, supersaturated Ti – Cu solid solutions.

Mechanical treatment of the SHS reaction product allows the particles of titanium diboride
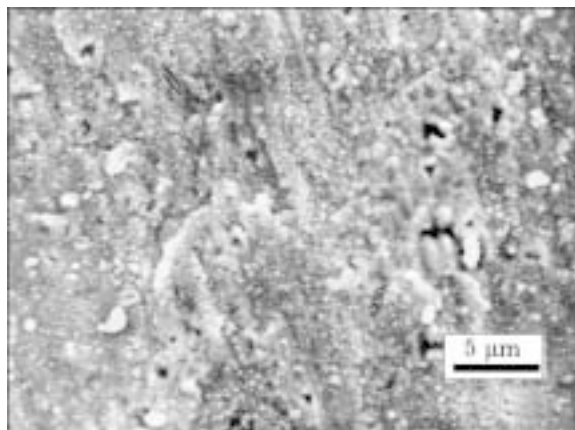
to be additionally dispersed in the matrix. Transmission electron microscopy data (Fig. 5) demonstrate that the particle size of titanium diboride in the SHS reaction product is 30–50 nm after 5 min of treatment and is practically constant at increased activation times. The size of the crystallites estimated from the broadening of titanium diboride lines on the X-ray diffraction patterns is in satisfactory agreement with electron microscopy data. The resulting nanocomposite has an unusual structure with nanosized particles distributed in the matrix, in which they occupy a significant volume.
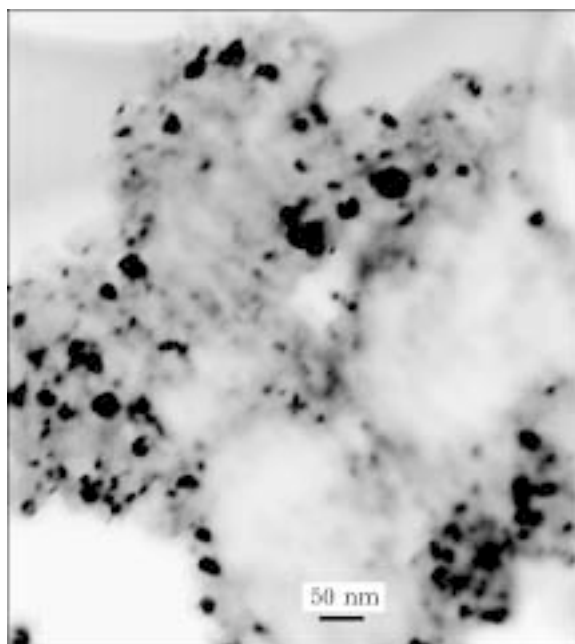

Fig. 5. Microstructure of the TiB$_2$ – 43 vol. % Cu nanocomposite (TEM image).

Synthesis of titanium diboride by this method enables one to combine the advantages of a reaction in a matrix and those of the integrated method of mechanical activation and SHS, giving rise to the $TiB_2 - Cu$ nanocomposite as the end product, in which the volume content of nanoparticles can vary within a wide range (10−60 %). The advantage of the three-stage synthesis of nanocomposites lies in the fact that the composition of the matrix can be varied by adding appropriate amounts of metal powders, and also in the fact that functional additives can be introduced at the stage of mechanical treatment of the SHS reaction product. This operation may be used for synthesis of substances with increased contents of the metal thinner, which are difficult to obtain by direct SHS in a matrix, and also for synthesis of composites with complex matrices.

MICROSTRUCTURE OF THE COMPACT TiB₂ − Cu MATERIAL. RETENTION OF NANOSTRUCTURE ON COMPACTING

Investigation of the evolution of the composite nanostructure on compacting is needed to reveal possible methods of obtaining nanostructured bulk materials. Therefore, we have studied the evolution of the microstructure of the $TiB_2 - Cu$ nanocomposite under conditions which differed drastically in the reaction mode and time: thermal annealing, sintering by the electron-beam powder metallurgy technique (EBPM), sintering with electric current, and explosion compacting.

Of special interest are unique studies of changes in the microstructure of composites with high contents of titanium diboride nanoparticles [14, 15].

Sintering pressed pellets with a composition $TiB_2 - 43$ vol. % Cu at a temperature equal to $0.7T_{melt}$(Cu) (680 °C) leads to the formation of nano- and submicrofibres from titanium diboride nanoparticles; it seems likely that these fibres originated from the movement of nanoparticles as a whole inside the matrix and their agglomeration [15]. In a matrix, particles can be set in motion due to the high mobility of nonequilibrium defects in copper, generated during mechanical treatment of the SHS reaction product.
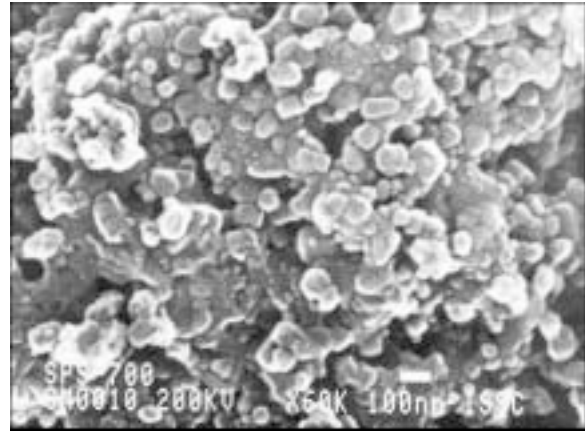

Fig. 6. Microstructure of the titanium diboride framework formed from nanoparticles during SPS sintering of the $TiB_2 - 43$ vol. % Cu composite.

Sintering the pressed pellets using the EBPM method involving the liquid phase leads to growth of titanium diboride crystals with dimensions of more than 1 μm.

Sintering with electric current using the Spark Plasma Sintering (SPS) procedure promotes the formation of high-temperature points in the bulk of the sample and their travel during sintering, as well as fast cooling of the interparticle contact points. Under the nonequilibrium conditions of the SPS procedure, a rigid nanostructured skeleton (Fig. 6) [14] is formed from nanoparticles in the $TiB_2 - 43$ vol. % Cu composite in the SPS temperature range 700−950 °C; the structure of the framework shows up clearly after copper removal by electrochemical etching.

The explosion compacting method yields good results in efforts to preserve the nanosized titanium diboride particles and to produce high-density compacts throughout the whole range of compositions owing to high pressures (3 GPa) [16] developed in the wave and owing to the lack of a fluid phase. Metallographic studies of the microstructure of explosion compacts did not reveal any crystals or agglomerates in the samples where recrystallization and growth of titanium diboride particles took place. The materials obtained by explosion compacting have densities close to theoretical (more than 98 %) and exhibit a homogeneous structure that inherited the structure of the composite agglomerates of the powder. When the titanium diboride content was more

than 50 vol. % in the composite, the compact material retained the nanostructural framework whose structure was similar to that of the framework of the SPS compacts.

PROPERTIES OF TiB$_2$ − Cu NANOCOMPOSITE COMPACTS

Mechanical properties

The mechanical properties of TiB$_2$ − Cu compact materials that differ in density and microstructure are reported in [15]. The high values of toughness, yield limit, and hardness in compacts obtained by the SPS method are due to the rigid nanostructural framework of titanium diboride. The yield limit of the nanocomposite material is 540 MPa; for the microcomposite of the same composition obtained by sintering the mixtures of titanium diboride and copper powders sized 3−5 μm, this value is up to 300 MPa [17].

Based on the synthesized nanocomposites one can obtain materials with a mixed Cu − Ni matrix. Modification of the matrix by adding a metal with a higher melting point decreases the intensity of recrystallization processes and allows titanium diboride particles to retain dispersity after compacting to a greater extent, which was confirmed by comparing the microstructures of TiB$_2$ − Cu and TiB$_2$ − Cu − Ni SPS samples with the same volume content of titanium diboride. Due to nickel addition leading to increased wetting in the system, the TiB$_2$ − Cu − Ni compacts exhibit increased stability.

Resistance to electric erosion under conditions of high-current arc discharge

The problem of increasing the erosion resistance of copper electrodes is generally solved by creating W − Cu and Mo − Cu composites [18, 19]. The role of the high-melting component reduces to formation of a skeleton which favors the retention of the form and dimensions of the electrode and reduces the droplet entrainment of the copper melt in the course of electrode operation. An alternative approach to the creation of erosion-resistant materials is modification of the copper matrix due to the dispersed inclusion particles that constitute a
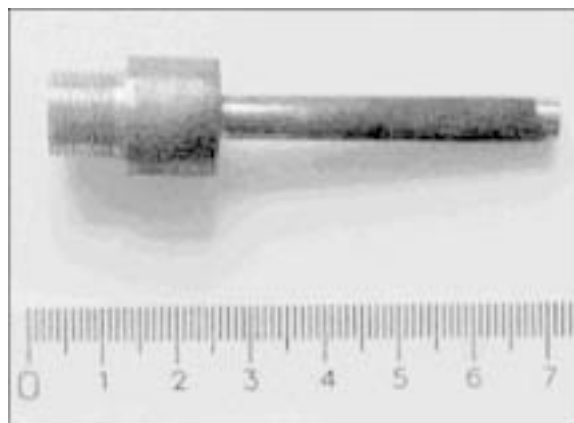

Fig. 7. Overall view of electrodes from the TiB$_2$ − 82 vol. % Cu nanocomposite material obtained by explosion compacting.

small volume fraction of the composite (less than 20 %). Investigation of the behavior of the microspots under conditions of arc discharge suggests that inclusions, particles, grain borders, and surface defects of the material appear to be centres of abnormal emission [20]. In this case, the material turns out to be «active» in relation to arc formation.

The synthesized TiB$_2$ − Cu nanocomposite material is certainly of interest for studies of erosion resistance and degradation processes occurring in this material.

The explosive molding method was used for making electrodes. Compacting was performed in a cylindrical ampule with a copper rod at the center. The ratio between titanium diboride and copper in the material of electrodes was chosen to satisfy the requirements of increased erosion resistance and plasticity required for mechanical treatment of the electrode. The selected composition TiB$_2$ − 82 vol. % Cu meets the specified requirements.

Electroerosion tests of electrodes (Fig. 7) were performed under conditions of high-current arc discharge using a coaxial accelerator as a model with a pulse time of 50 μs and a maximum current of 180 kA [18]. It was found that the weight loss of the nanocomposite material during erosion is 10 times smaller than the corresponding values for electrodes from compact copper. Chemical analysis of the entrainment products showed that titanium was present in trace amounts, which is indicative of the predominant removal of copper in the course of erosion entrainment. Copper evaporation re-
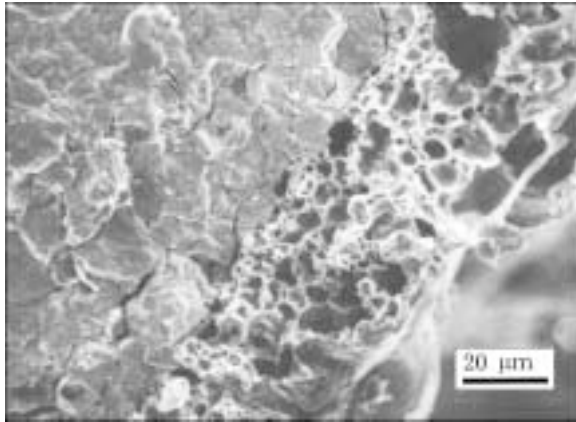
Fig. 8. Porous layer enriched with titanium diboride and formed on the surface of the TiB$_2$ − 82 vol. % Cu electrode as a result of electroerosion.

sulted in the formation of a porous layer (30−50 μm thick) enriched with titanium diboride (Fig. 8) on the electrode surface. The structure of this surface (Fig. 9) testifies that melted spots do not form in the course of erosion; therefore, the surface is free from the drop-shaped ridges, usually arising on electrodes of pure copper and causing fast reduction of the operation life [21]. It is important that the size of the arc spot increases by one order of magnitude in the case of composite electrodes, thus reducing the local densities of erosion currents. It may be assumed that the presence of inclusion nanoparticles creates high density of defects on the electrode surface, which are centres of abnormal emission of electrons. As a consequence, the greater part of the electrode surface appears to be involved in the process of arc formation.
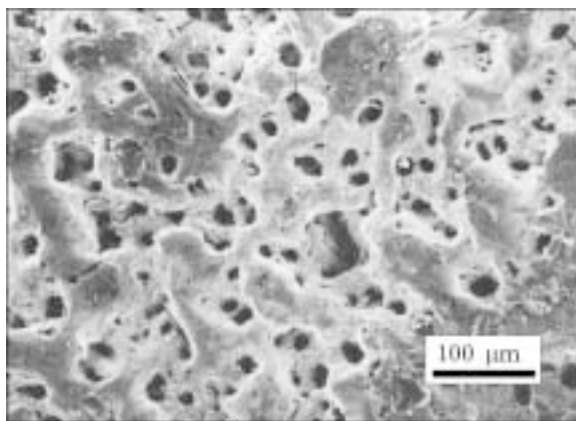

Fig. 9. Surface of the TiB$_2$ − 82 vol. % Cu electrode after electroerosion tests.

Thus passing from copper to nanocomposite electrodes brings about cardinal changes in the mechanism of degradation of electrodes. Electrodes of the TiB$_2$ − Cu nanocomposite material exhibit minor losses of weight during erosion, and they also retain the form under conditions of arc discharge and have increased operation lives. Practical application of these materials may appear to be advantageous in manufacturing switches, sliding contacts, and rails for electromagnetic accelerators of solids.

CONCLUSIONS

The results presented in this work demonstrate the efficiency of our approach to synthesis of composites with a metal matrix for the production of nanocomposites. Synthesis in a matrix using combined SHS and mechanical activation offers wide possibilities of controlling the reaction parameters: combustion temperature and rate; composition and size of the particles of the hardening phase. The suggested scheme of synthesis may be used for obtaining nanocomposites with metal and intermetallic matrices. For the hardening phase, one can employ various high-melting compounds possessing high values of formation heat necessary for effecting SHS reactions.

Synthesis of nanocomposites with unique microstructures offers good opportunities for investigating growth and agglomeration of nanoparticles in matrices with high volume contents of the latter. Using the TiB$_2$ − Cu system as an example, we have demonstrated that evolution of the nanostructure of the composites during compaction may lead to a variety of microstructures in bulk materials depending on the method of treatment. Using nonequilibrium methods of compacting and sintering, one can minimize growth of particles and obtain bulk materials containing nanosized inclusions or nanostructural skeleton and showing high-strength properties.

The behavior of the TiB$_2$ − Cu nanocomposite material under conditions of electric erosion during high-current arc discharge suggests that a new class of erosion-resistant materials can be created, which differ strongly in the mechanism of degradation and show in-

creased operation lives. Nanocomposite electrodes may be an alternative to the traditional electrode materials – copper and copper-based composites – obtained by compacting mixtures of micron powders.

Acknowledgements

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