Features of the structure of a TiB$_2$-based powder material obtained under self-propagating high-temperature synthesis and shear deformation

P M Bazhin$^1$, A M Stolin$^1$, A S Konstantinov$^1$, N I Mukhina$^1$ and A Pazniak$^2$

$^1$ Merzhanov Institute of Structural Macrokinetics and Materials Science Academician Osipyan str. 8, Chernogolovka, Moscow Region, 142432, Russia

$^2$ National university of science and technology «MISiS», Leninskii ave. 4, Moscow, 119049, Russia

olimp@ism.ac.ru

Abstract. The results of an experimental study of TiB$_2$-based powder material obtained under the combination of SHS processes with shear deformation are presented. The effects of the rotor velocity and the delay time before shear deformation application upon the structure of the synthesized powder are studied. The grain structure of titanium diboride is shown to become predominantly round with particles size of 1-5 μm with increasing the rotor velocity from 120 to 600 rpm. At the same time, particles of 200-400 nm size can be observed on the surface of the agglomerates.

1. Introduction

Self-propagating high-temperature synthesis (SHS) is one of the most promising areas of modern materials science [1-3]. Products synthesized by this method are characterized by a complex of effective properties that are achieved by presence in the product structure phases with complementary physicochemical, mechanical and other characteristics. The main goal of SHS is traditionally to produce powder composite materials for manufacturing products of various functional purposes in powder metallurgy [4-6], such as protective coatings using methods of plasma, arc or detonation spraying, and others [7-9].

The wide range of possibilities to create new composite materials is opened by the use of the SHS process in combination with shear high-temperature deformation of the initial components and the resulting combustion products during the synthesis [10]. These conditions are realized in the SHS-grinding method. The essence of the method consists in grinding of the material obtained in a combustion wave under conditions of shear high-temperature deformation and application of external pressure. The implementation of the method is based on the ability of the hot mass of the synthesized product to macroscopic deformation.

It is shown that the deformation parameters, in particular the deformation rate, strongly influence both the size and morphology of the synthesized particles and powder phase composition [11]. This paper demonstrates that the intensity of shear deformation and time delay before deformation influence the structure of the synthesized material.
2. Objects and methods of research
Materials based on TiB₂ are chosen as the objects of research. The choice stemmed from well-known properties of titanium diboride such as high melting point, hardness, thermal conductivity, resistance to abrasion and aggressive media [12, 13]. Titanium diboride is widely used in modern technology, chemical equipment, and as a part of cermets for nuclear power engineering [14, 15]. Commercial powders of 68.6 wt% PTM titanium (>99.1%, 45 μm) and 31.4 wt% amorphous black B-99B boron (99%, 5 μm) are used by authors. The mixture is premixed in ball mill and dried in drying cabin at a temperature of 100 °C for 6 hours.

The experiments are carried out in a closed reactor without rotation of the rotor and at rotational velocities of 120, 240 and 600 rpm [11]. The rotor has conic form with the apex angle of 140°. After the combustion wave propagation in the SHS mode, the rotor with a specified frequency of rotation is dropped to the bottom base of the graphite beaker for 40-60 s until the structure transformations in the synthesized charge are complete.

For the structure studies of synthesized powder materials the equipment of the Distributed Center for Collective Use of ISMAN is used: the high-resolution field-scanning electron microscope Carl Zeiss Ultraplus (Germany), the powder X-ray diffractometer ARL XTRA, and other certified equipment, methods and techniques.

3. Discussion
The results of scanning electron microscopy showed that the particles obtained by the SHS method without shear deformation are agglomerates of 1-3 mm size. The presence of this agglomerates of 1-3 mm in size require more time for the subsequent grinding process. The agglomerates contain titanium diboride fragments sintered together (figure 1). Most of the titanium diboride particles are crystallites from 1-3 μm to 9-30 μm. Rounded particles ranging from 1-3 μm to 25 μm were also found. The surface of the agglomerated particles is coated with a thin oxide film (figure 1b). The presence of oxide inclusions in the material, even in the amount that does not exceed 5% (since oxides are not observed on XRD), will adversely influence on further use of the material in powder metallurgy to produce nonporous products.

![Figure 1. SEM of TiB₂ particles, obtained by SHS without shear deformation](image)

The macrostructure of the material synthesized during SHS and shear deformation, regardless of the rotational velocity of the rotor, is analogous, and presented by agglomerated sintered titanium diboride particles. Material obtained at the rotor rotational velocities of 120 and 240 rpm is characterized by particles with comminuted structure (figure 2). The particle sizes are predominantly 5-10 μm. The particles of 200-400 nm can also be observed on the surface of the agglomerates, but the oxide films were not detected.

For the material obtained by SHS with shear deformation at rotational velocity of 600 rpm (figure 3), the grain structure is predominantly round. The grain sizes are approximately the same (1-5 microns), compared with the powder material obtained at low rotational frequencies of 120-240 rpm. The presence of carbon in the synthesized powder is associated with sample preparation procedure.
Figure 2. Microstructure and energy dispersive analysis of TiB$_2$ particles obtained by SHS method with shear deformation at 120 rpm

Figure 3. Microstructure and energy dispersive analysis of TiB$_2$ particles obtained by SHS method with shear deformation at 600 rpm

The influence of the time delay before the shear deformation implementation on the synthesized material microstructure at a rotor velocity of 240 rpm is studied (figure 4). The time delay is varied between 0 and 15 s with 5 s step. The countdown begins at the moment of the combustion wave passage and ends at the start of shear deformation. It is found that applying of shear deformation immediately after the combustion wave passage results in the formation of rounded particles with size up to 5-10 μm. With an increase of time delay, transformation of the titanium diboride grains occurs during cooling. At the 10 s time delay, the TiB$_2$ grains are characterized by comminuted structure, and at 15 s delay the grain form of the titanium diboride particles becomes predominantly parallelepiped. At long time delays before external effects implementation the grains grow dominantly in one direction and become mostly parallelepiped.

Shear deformation in SHS and subsequent cooling of material prevents the agglomeration of the formed particles with each other, and also leads to the destruction of the sintered titanium diboride particles. Intensive shear deformation of the powder prevents the enlargement of TiB$_2$ particles during cooling of the synthesized material.

Figure 4. The microstructure of TiB$_2$ particles obtained by the SHS method with mechanical influences at a rotor rotation velocity of 240 rpm with time delay: a-c 5, 10, 15 s respectively.
4. Conclusion
The structure of a powder material based on titanium diboride obtained under SHS conditions and shear deformation in a closed type reactor depends on the intensity and time delay before deformation. For the material obtained by the SHS method without deformation, titanium diboride particles are crystallites with sizes from 1-3 μm to 9-30 μm. With increase of the rotor rotation velocity from 120 to 600 rpm, the grain structure becomes predominantly round with a size of 1-5 μm. At low rotational velocities (120-240 rpm) particles have a comminuted structure with particle dominant size of 5-10 μm. At the same time, particles of 200-400 nm can also be observed on the surface of the agglomerates.

It is found that the shear deformation application immediately after the passage of the combustion wave leads to the formation of rounded particles with sizes up to 5-10 μm. With the increase in the delay time, transformation of the titanium diboride grains occurs in the process of cooling with onset of parallelepiped grain shape. At long delay times before implementation of external load, the grains grow in one direction and become predominantly parallelepiped.

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