SHS in the Ta–Zr–Si–B system and properties of the produced ceramics

S Vorotilo* and E A Levashov

National University of Science and Technology “MISIS”, Leninskii 4, Moscow, 119049 Russia

*E-mail: s.vorotilo@misis.com

Abstract. In this work, we investigated the macrokinetic parameters of combustion of the Ta–Zr–Si–B mixtures, the mechanisms of phase and structure formation in the combustion wave, and the structure and properties of the consolidated combustion products. During the combustion, primary grains of ZrB$_2$ and TaB$_2$ are formed in the preheating zone due to the gas-phase mass transfer mechanism, which involves the evaporation of boron oxide and chemisorption of boron onto the surface of metals. Upon reaching the combustion zone, the Si–B eutectic and Zr particles melt, and crystals of ZrB$_2$, TaB$_2$, TaSi$_2$ and ZrSi$_2$ precipitate from the melt. In the secondary structure formation zone, unreacted boron interacts with the ZrSi$_2$ and produces ZrB$_2$. TaB$_2$ and ZrB$_2$ partially interact and form solid solution (Ta,Zr)B$_2$. Ceramics, produced by hot pressing of SHS, possess relative density 95–98% and a specific microgradient grain structure.

1. Introduction

Transitional metals borides (TMB) are prospective for the development of advanced ultra-high temperature ceramics (UHTCs) for aerospace applications. Metallic bonding in the TM layers provides a high electrical and thermal conductivity, whereas the strong covalent bonding in the B layers is responsible for the high hardness, elastic modulus and relatively low coefficient of thermal expansion of TMBs. This combination of mechanical and thermophysical properties provides the high thermal shock resistance of zirconium diboride [1–4].

Oxidation resistance of TMBs is governed by the formation of a protective B$_2$O$_3$ layer, which hinders the diffusion of oxygen in the material [1, 2, 5–7]. However, at $T \geq 1100$ °C, B$_2$O$_3$ becomes volatile and evaporates, leading to the destruction of the protective oxide layer. Decomposition of the protective layer can be inhibited by alloying of ZrB$_2$ with silicon-containing compounds, such as SiC, MoSi$_2$, ZrSi$_2$, and TaSi$_2$ [2, 5, 6, 8]. During the oxidation, silicon yields either a SiO$_2$ layer or a borosilicate glass layer, which remains stable up to 1600°C [1, 4, 5]. Alloying of ZrB$_2$ with TaB$_2$ to produce (Zr,Ta)B$_2$ solid solution is another viable way to increase its oxidation resistance. [9, 10]. Another approach is adding TaSi$_2$ to the ZrB$_2$-based ceramics [11–20]. In previous works, TaSi$_2$ was introduced into the ceramic mixtures as a powder.

Meanwhile, the simultaneous in situ co-synthesis of both refractory boride and disilicide is of a great interest. Phase and structure formation mechanisms during the combustion of Ta–Zr–Si–B mixture were
investigated in the previous work [20]. The aim of this work was to investigate the influence of TaSi$_2$ addition on the microstructure of the ZrB$_2$–TaB$_2$ ceramics, produced by elemental SHS.

2. Materials and Methods
TaPM grade Ta, PTsrK-1 grade Zr, KEF-4.5 grade Si and B-99A boron powders were used in this work. The reaction mixtures were mixed in a 3 L ball mill for 4 h using hard-alloy balls at a 1:8 mixture to ball weight ratio. The mixing duration was optimized to achieve homogeneous distribution of the reagents in the reaction charge mixture. The SHS was carried out in a sand mold. The combustion products were ground in a ball mill for 6 h until the micron-sized ZrB$_2$–TaB$_2$–TaSi$_2$ composite powder was obtained. Ceramic powders were hot-pressed (HP) on a DSP-515 SA Direct Hot Pressing apparatus (Dr. Fritsch Sondermaschinen GmbH) under the following conditions: temperature 1700°C, pressure 30 MPa, exposure time 10 min. The density of consolidated samples was determined by hydrostatic weighing on an AND1 GR-202 analytical balance (A&D, Japan); true density was measured using an AccuPyc 1340 helium pycnometer (Micromeritics, USA). The hardness of the dense ceramics after hot pressing was measured using a Vickers hardness testing machine under a load of 10 N. The SEM and EDS of the sintered samples were conducted using an S-3400N scanning electron microscope (Hitachi) equipped with a NORAN energy-dispersive X-ray spectrometer.

3. Results and Discussion
Figure 1 demonstrates the microstructure of the ZrB$_2$–20%TaB$_2$ and ZrB$_2$–20%TaB$_2$–35%TaSi$_2$ samples, produced by the hot pressing of SHS products.

As is evident from the figure 1, the ZrB$_2$–20%TaB$_2$ and ZrB$_2$–20%TaB$_2$–35%TaSi$_2$ samples have drastically different microstructures. Single-phase solid solution ZrB$_2$–20%TaB$_2$ is comprised of equiaxial grains 4–20 µm in diameter, with no noticeable compositional gradients between or within the grains. In the case of ZrB$_2$–20%TaB$_2$–35%TaSi$_2$ ceramic, the diboride matrix had a microgradient structure. Tantalum content was maximal in the center of grains and decreases towards the grain boundaries; vice versa, zirconium content increased from the center of grain towards the grain boundaries. To better estimate the grain size, a fracture of ZrB$_2$–20%TaB$_2$–35%TaSi$_2$ was investigated (figure 2).
As can be seen at figure 2, relatively large TaSi2 particles (3–5 µm) are surrounded by submicron boride grains (0.2–0.7 µm), embedded in the disilicide matrix. Apparently, such structure is the result of the formation and decomposition of the solid solutions (Zr,Ta,Si)B2 during the SHS and hot pressing of the ceramics. This effect provides the opportunity for optimization of the microstructure of boride-silicide ceramics, including the production of nanostructured materials.

The fabrication scheme and microstructure of ZrB2–TaB2–TaSi2 composite are summarized in the figure 3.

**Figure 2.** SEM of the fracture of ZrB2–20%TaB2–35%TaSi2

**Figure 3.** Fabrication scheme and microstructure of ZrB2–TaB2–TaSi2 composite

**Acknowledgment**

This work was conducted with the financial support from the Ministry of Science and Higher Education of Russian Federation in the framework of state assignment № 11.1207.2017/ПЧ.

**References**

[1] Low I M, Sakka H and Hu Ch 2013 MAX phases and ultra-high temperature ceramics for extreme environments ed J Gamon (Hershey: IGI Global) p. 649
[2] Opeka M M, Talmy I G and Zaykoski J A 2004 J. Mater. Sci. 39 5887–5904
[3] Zhang Z, Nan C W, Xu J J, Gao Z H, Li M and Wang J 2014 J. Mater. Sci. Tech. 30 1223–29
[4] Guo S Q 2009 J. Eur. Ceram. Soc. 29 995–1011
[5] Fahrenholtz W G, Hilmas G E, Talmy I G and Zaykoski J A 2007 J. Am. Ceram. Soc. 90 1347–64
[6] Wuchina E, Opila E, Opeka M, Fahrenholtz W and Talmy I 2007 Interface 16 30–36
[7] Silvestroni L, Kleebe H J, Lauterbach S, Muller M and Sciti D 2010 J. Mater. Res. 25 828–834
[8] Rodríguez-Sánchez J, Sánchez-González E, Guiberteau F and Ortiz A L 2015 J. Eur. Ceram. Soc. 35 3179–85
[9] Opila E and Levine S 2004 J. Mater. Sci. 39 5969–77
[10] Levine S R and Opila E J 2003 Tantalum Addition to Zirconium Diboride for Improved Oxidation Resistance, NASA/TM-2003-212483
[11] Sciti D, Silvestroni L, Guicciardi S, Fabbriche D D and Bellosi A 2009 J. Mater. Res. 24 2056–65
[12] Talmy I G, Zaykoski J A and Opek M M 2008 J. Am. Ceram. Soc. 91 2250–57
[13] Ghaffari S A, Faghihi-Sani M A, Golestani-Fard F and Mandal H 2013 J. Am. Ceram. Soc. 33 1479–84
[14] Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications 2014 ed W G Fahrenholtz, E J Wuchina, B Lee and Y Zhou (Wiley) p. 465
[15] Silvestroni L and Sciti D 2011 J. Am. Ceram. Soc. 94 1920–30
[16] Silvestroni L and Sciti D 2101 Characterization of Ultra High Temperature Ceramics via Transmission Electron Microscopy. Part II: UHTCs sintered with addition of TaSi2 (technical report) ISTEC-CNR (Institute for Science and Technology for Ceramics)
[17] Justin J F and Jankowiak A 2011 AerospaceLab 1–11.
[18] Opila E J, Smith J, Levine S R, Lorincz J and Reigel M 2010 Open Aero Eng J 3 41–51
[19] Wang S, Xu C, Ding Y and Zhang X 2013 Int. J. Refract. Met. H. 41 507–516
[20] Vorotilo S, Levashov E A, Petrzhyh M I and Kovalev D Yu 2018 Ceram. Int. doi:10.1016/j.ceramint.2018.10.020