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Combustion Synthesis of Titanium Diboride and Zirconia Composite Powders. Part I

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A new method of synthesizing titanium diboride-zirconium oxide composite powders under the combustion mode was investigated. *In situ* stabilization of formed or added unstabilized zirconia by magnesia and/or yttria, control of TiB$_2$ particle size, as well as the formation of TiB$_2$-ZrO$_2$ composites in a wide range of concentrations was investigated. Two different synthesis routes were explored, namely: i) from elemental titanium and, boron powders with addition of zirconia or ii) from zirconium, boron, and titania with or without addition of zirconia. Yttrium oxide and/or magnesium present in boron reactant powder were used for zirconia product stabilization. The effect of initial mixture composition, dilution with stabilized or unstabilized zirconia, and other operating conditions, such as inert gas pressure during the combustion and initial mixture density on combustion front propagation velocity and maximum combustion temperature as well as product microstructure and its phase composition was investigated. Products morphology and compositions were examined using XRD, EDX, and SEM analyses.

I. Introduction

ADVANCED ceramic materials such as silicon nitride (Si$_3$N$_4$), silicon carbide (SiC), zirconia (ZrO$_2$), and titanium diboride (TiB$_2$) offer ideal solutions for many different applications where wear, abrasion, and impact corrosion resistances at high temperatures are important.[1–2] For many years, titanium diboride was the material of interest for lightweight armor.[3] This compound has found wide commercial applications in nozzles, seals, cutting tools, dies, and wear-resistant articles.[4] TiB$_2$ has also found potential application as a material for making electrodes in the manufacture of aluminum due to its excellent wettability and corrosion resistance to molten aluminum.[5]

Pure zirconia may exist in several polymorphic phases depending on the temperature range. It is monoclinic at temperatures below 1000°C, tetragonal between 1000° and 2370°C, and cubic above 2370°C until its melting point (2700°C). The tetragonal form is denser than the monoclinic form, and, during phase transformation (about 1000°C), a considerable change in volume takes place, which is accompanied by the formation of cracks within its structures. Therefore, the use of pure zirconia articles is limited in many high-temperature applications.[6] However, zirconia can be partially or fully stabilized and therefore has been used successfully in many applications. Zirconia-based structural ceramics may be divided into three groups: (a) transformation-toughened (or zirconia-toughened) ceramics; (b) partially stabilized zirconia (PSZ); and (c) tetragonal zirconia polycrystals (TZP). At high temperatures, several oxides (e.g., MgO, CaO, Y$_2$O$_3$) form solid solutions with zirconia, which makes it possible to stabilize the high-temperature cubic phase at a lower temperature.[5] PSZ is a mixture of zirconia modifications (cubic and tetragonal) and it is formed when insufficient cubic phase-forming dopants (stabilizer) are added. Fully stabilized zirconia can be produced by doping zirconia with a stabilizer (e.g., MgO, Y$_2$O$_3$, and CaO) in proper quantities. In this case, a solid solution is obtained with a cubic structure.[6] Two fundamentally different microstructures are formed depending on the type of stabilizer. The addition of MgO leads to the formation of relatively coarse grains, while the addition of yttria (Y$_2$O$_3$) results in a relatively fine microstructure.[7]

Since the discovery of transformation toughening in zirconia ceramics, extensive investigations have been carried out to understand the mechanism. Several efforts have also been made to incorporate the transformable tetragonal zirconia phase into various brittle matrices like TiB$_2$ to develop high-toughness materials.[8–11]

Yttria-stabilized tetragonal zirconia polycrystals are well recognized for their excellent combination of bending strength and fracture toughness (8–12 MPa·m$^{-1/2}$). However, the relatively low hardness (HV-20°C 1120 kg/mm^2)[12] restricts their use in tribological applications. Since the discovery of transformation toughening three decades ago, research efforts have been made to incorporate nonoxide hard phases such as borides, carbides, nitrides, and carbonitrides into a zirconia matrix in order to increase the hardness of Y-TZP monoliths. Titanium diboride (TiB$_2$), for example, has an excellent hardness (1800–2700 kg/mm^2) but not very high fracture toughness (5–7 MPa·m$^{1/2}$),[13] and a moderate bending strength. Therefore, TZP–TiB$_2$ composites are considered to be promising composite materials for tribological applications.[14] Another advantage of a TiB$_2$–ZrO$_2$ composite is associated with a relatively small thermal expansion coefficient mismatch of TiB$_2$ and ZrO$_2$, especially in the cubic phase. At room temperature, thermal expansion coefficients for TiB$_2$ and cubic zirconia are 7.19×10^{-6} and 8.0×10^{-6} K^{-1}, respectively.[15,16]

It is well known that many inorganic refractory materials can be obtained using the self-propagating high-temperature synthesis (SHS) method, also called combustion synthesis (CS), which is one of the most economical synthesis methods.[17–19] Particularly, SHS can be used effectively for synthesizing TiB$_2$ and a number of composites on its basis.[20–25]

The objective of this paper was twofold: (i) to determine the possibility of one-step CS[25–27] of TiB$_2$ with different contents and phase compositions of zirconia and ii) *in situ* stabilization of zirconia during the one-step formation of a TiB$_2$–ZrO$_2$ composite by utilization of magnesium present in boron powder as well as added yttria powder.

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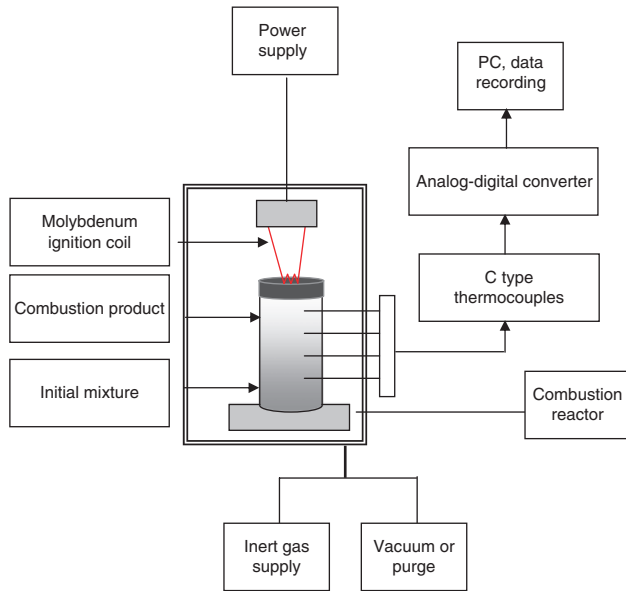[†]Author to whom correspondence should be addressed. e-mail: jan.puszynski@sdsmt.edu

Fig. 1. Setup for combustion synthesis (CS) experiments.

II. Experimental Procedure

CS experiments were performed in a constant pressure reactor in an argon atmosphere (99.8% purity) (see Fig. 1). The powders used in this research are presented in Table 1.

Reactants and additives were dry mixed for 1 h. Subsequently, cylindrical pellets 19 mm in diameter and 18–25 mm in height were prepared by uniaxial pressing of the reactant mixture. The pellets were placed into the high-pressure reactor, which was evacuated, purged, and pressurized with argon to a desired operating pressure (0.1–0.5 MPa). The combustion process was initiated using a resistively heated molybdenum coil. The maximum combustion temperature (T_c) was measured using tungsten–rhenium thermocouples (tungsten–5% rhenium versus. tungsten–26% rhenium). The thermocouples were placed at different axial positions inside the pellet and an average combustion front velocity (U_c) was calculated based on dynamic responses from individual thermocouples. After the combustion process was completed, the pellet was crushed with a mortar and pestle. The resulting powder was further dry milled in a ball mill filled with 1/2 in. alumina grinding media for 2 h. Later, the powder was wet milled in an attritor (Union Process, Szegvari Attritor System, Union Process Co., Akron, OH, Reeves) using zirconia 1 mm grinding media and distilled water as a liquid

Table I. Producers and Powders Used in this Research

| Reagent name	Producer	Average particle size
Titanium powder	Atlantic Equipment Engineers Co., Bergenfield, NJ	5 μm
Amorphous SB-95 boron (95–97% purity)	SB Boron Co., Bellwood, IL	~1 μm
Amorphous boron (99+% purity)	STREM Chemicals Co., Newburyport, MA	~1 μm
Stabilized zirconia	Zircar Co., Florida, NY	15 μm
Unstabilized zirconia	Zirconia Sales Co., Kennesaw, GA	15 μm
Yttria Y_2O_3 (99.99% purity)	Unocal Molycorp Co., Englewood, CO	200 nm
Titania (TiO_2) (99.9% purity)	Millennium Tiona Co., Ashtabula, OH	~1 μm
Zirconium (Zr)	Teledyne Co., Thousand Oaks, CA	(−325 mesh)
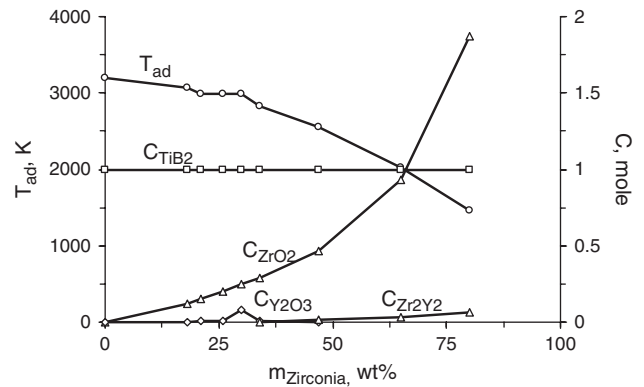
Fig. 2. Adiabatic combustion temperature and equilibrium concentrations for the stoichiometric Ti+2B reaction as the function of the added zirconia and yttria at the constant mass ratio $m_{yttia}/m_{zirconia} = 0.14$.

medium. The constant rotational speed of the shaft was 3200 rpm and the milling time was 40 min. The ratio of the grinding media to milled powder was 10:1 by weight. Combustion-synthesized products were examined using scanning electron microscopy (SEM), X-ray diffraction (XRD), Energy-dispersive X-ray spectrometer (EDX), and particle size analysis.

III. Results and Discussion

(1) Thermodynamic Analysis

In order to estimate values of adiabatic combustion temperatures (T_{ad}) and equilibrium compositions of combustion-synthesized products, thermodynamic analyses of the Ti–$2B–nZrO_2$, Ti–$2B–nZrO_2–mY_2O_3$, Zr–$TiO_2–2B–nZrO_2$, and Zr–$TiO_2–2B–nZrO_2–mY_2O_3$ systems were performed using HSC and ISMAN Thermo software packages. Results generated by both software packages have shown that there is no chemical interaction between TiB_2 and ZrO_2 over a wide temperature interval (298–3000 K). Calculated heat of reactions between Ti and B as well as Zr and TiO_2 indicate that both reactions are highly exothermic and their adiabatic temperatures without any diluents are 3200 and 2900 K, respectively. In order to form a desired solid solution between yttria and zirconia, temperatures below 2700 K are preferred. Therefore, a thermal dilution technique with zirconia was applied. Figure 2 shows the effect of dilution with zirconia and yttria on the adiabatic temperature and equilibrium product composition in a Ti+2B system. It can be concluded that dilution with zirconia as high as 50 wt% is needed to reduce the adiabatic combustion temperature below 2700 K in the Ti+2B reacting system.
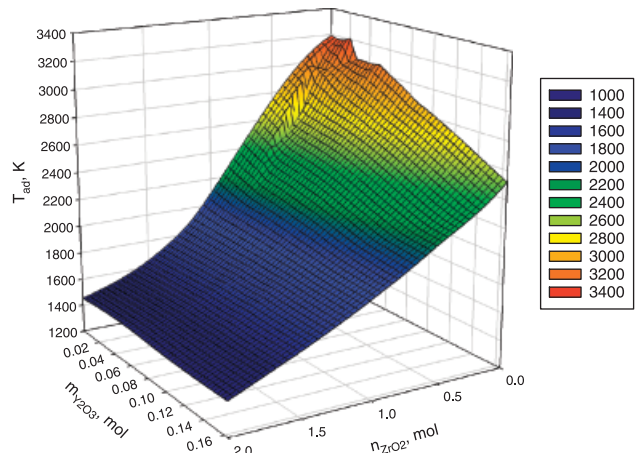

Fig. 3. 3D plot of adiabatic temperature for the Ti–$2B–nZrO_2–mY_2O_3$ system as the function of molar coefficients n and m.
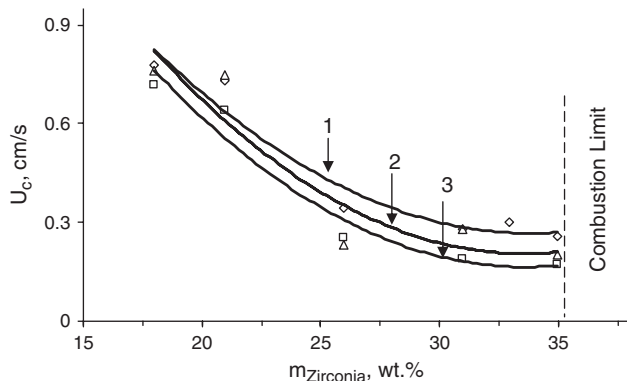
Fig. 4. Combustion front velocity in Ti+2B (95 SB Boron) reacting system as the function of stabilized or unstabilized concentration of ZrO_2 used as a diluent: (1) only stabilized zirconia; (2) unstabilized zirconia with the addition of yttria, $m_{yttria}/m_{zirconia} = 0.06$; (3) unstabilized zirconia with the addition of yttria, $m_{yttria}/m_{zirconia} = 0.14$.

Figure 3 shows a 3D plot of the adiabatic temperature as a function of zirconia and yttria concentrations. It should be noted that the concentration range for yttria in this graph was chosen in order to satisfy the formation of partially or fully stabilized zirconia.

The data presented in Fig. 3 are very useful for the selection of initial compositions in CS experiments.

(2) Ti–2B–nZrO₂–mY₂O₃ System

In CS of TiB₂ with the addition of yttria and zirconia, both stabilized and unstablized zirconia were used as an inert thermal diluent. It should be emphasized here that the boron powder SB-95 used contains up to 4 wt% magnesium, which could also influence the stabilization of zirconia. This effect will be discussed later.

Experimental results have shown, as expected, that increased concentration of zirconia in the initial mixture causes a decrease of combustion front propagation velocity. It was determined that this effect was identical when stabilized or unstabilized zirconia powders were used as a thermal diluent. However, when unstabilized zirconia was used as a diluent, an additional amount of yttria was also added in order to obtain fully or PSZ in the final combustion product. When yttria was added, the decrease in combustion velocities was even more pronounced because of a higher degree of dilution of the reactant mixture (see Fig. 4).

SEM micrographs of combustion-synthesized TiB₂ with zirconia and yttria are shown in Fig. 5. The product microstructure shown in Fig. 5(a) was obtained when the Ti and B reactants were diluted with stabilized zirconia, while the microstructure presented in Fig. 5(b) was formed when unstabilized zirconia was *in situ* stabilized by yttria during the combustion reaction. In both cases, well-developed TiB₂ crystals were formed and they were well bonded to the zirconia phase.

The experimental results have clearly indicated that inert gas pressure in the range between 0.1 and 1.5 MPa and green compact density between 1800 and 2200 kg/m³ affected neither the combustion front velocity nor the maximum combustion temperature.

EDX elemental mapping showed that the dark gray crystals shown in Fig. 5 are TiB₂ whereas the light gray region is ZrO_2. Elemental mapping showed the presence of yttrium mainly in the zirconia phase. EDX spectra corresponding to both regions are shown in Fig. 6. It is interesting to note that magnesium, which was initially present in the boron powder, was distributed
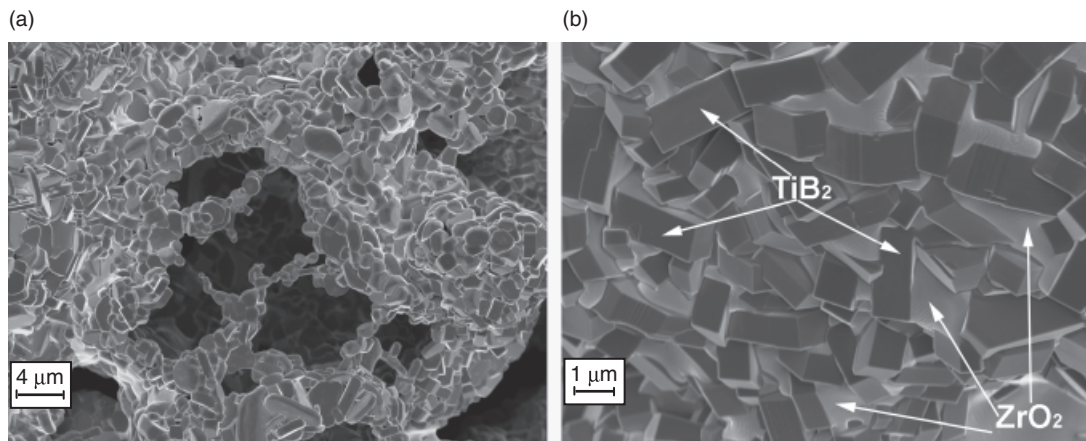

Fig. 5. Micrographs of the combustion product formed from: (a) Ti–2B (95 SB Boron) with the addition of 25 wt% ZrO2 and (b) Ti+2B (95 SB Boron) with the addition of 25 wt% ZrO_2 calculated based on Ti+2B and ZrO2 components only, and 14 wt% Y₂O₃ based on zirconia.
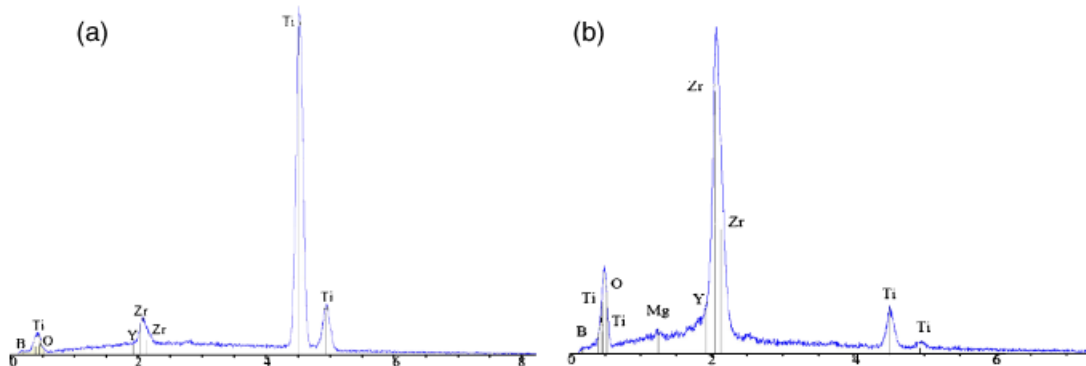

Fig. 6. Energy-dispersive X-ray (EDX) spectra of combustion synthesized product from Ti+2B (95 SB Boron) with the addition of 25 wt% ZrO2 calculated based on Ti+2B and ZrO2 components only, and 14 wt% Y₂O₃ based on zirconia: a) dark gray region and b) light gray region in Fig. 5(b).
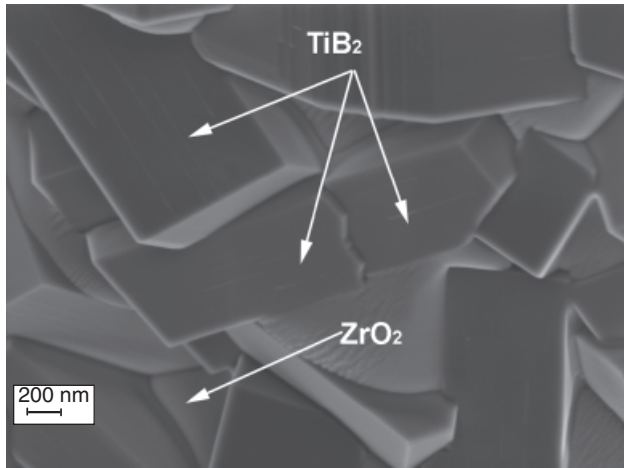
Fig. 7. Fractured TiB2 grain in the product obtained from Ti+2B (95 SB Boron) with the addition of with the addition of 25 wt% ZrO2 calculated based on Ti+2B and ZrO2 components only, and 14 wt% Y_2O_3 based on zirconia.

Fig. 9. X-ray diffraction (XRD) patterns of the combustion product formed from: Ti+2B (high purity boron) with the addition of 25 wt% ZrO2 calculated based on Ti+2B and ZrO2 components only, and 14 wt% Y_2O_3 based on zirconia.

into the zirconia phase. This transfer of magnesium has had an additional effect on stabilization of zirconia during the combustion process.

Higher magnification SEM images of the combustion-synthesized TiB_2 product with *in situ* stabilized zirconia with yttria are shown in Fig. 7. This micrograph shows that zirconia adheres well to the TiB_2 crystals. One of the TiB_2 crystals is cracked but well adhered to the zirconia phase. It is very likely that this crack occurred during the cooling process of the combustion products.

According to the results of XRD analyses, TiB_2 and zirconium magnesium oxide ($Zr_{0.86}Mg_{0.14}O_{1.86}$) (Fig. 8) were obtained in Ti–2B–0.2ZrO$_2$. Identical XRD peaks were obtained with the addition of yttria. It should be emphasized here that the $Zr_{0.86}Mg_{0.14}O_{1.86}$ peaks and those corresponding to YSZ are superimposed and therefore cannot be distinguished. For reference, please refer to Fig. 9, which presents XRD patterns of the TiB_2–ZrO_2 composite stabilized with yttria only. In this case, high-purity boron was used instead of 95 SB Boron powder. Similar patterns were obtained for annealed YSZ powders by.[28] $Zr_{0.86}Mg_{0.14}O_{1.86}$ has a cubic lattice and is

stable at room temperature. As a result, even a small content of magnesium in commercial boron powder (approximately 3–4 wt%) is sufficient to stabilize zirconia in the TiB_2 composite formed in the combustion regime.

(3)   Zr–TiO₂–2B–nZrO₂–mY₂O₃ System

Based on thermodynamic calculations of Zr–TiO$_2$–2B–nZrO$_2$–mY$_2$O$_3$, two consecutive reactions take place. In the first reaction, zirconium reduces titanium oxide, yielding zirconia and titanium. Titanium reacts further with boron and forms titanium boride. Both reactions are strongly exothermic.

1. $Zr + TiO_2 = ZrO_2 + Ti$ $\Delta H = -155.71$ kJ, $T_{ad} \sim 1650$ K

2. $Ti + 2B = TiB_2$ $\Delta H = -280.36$ kJ, $T_{ad} \sim 3190$ K

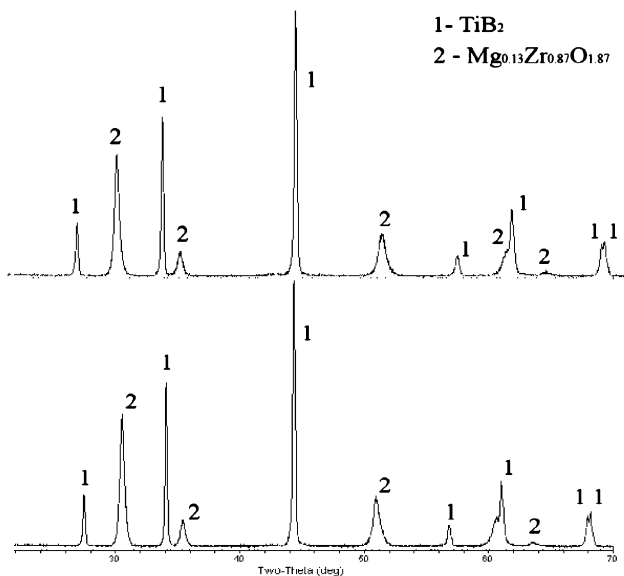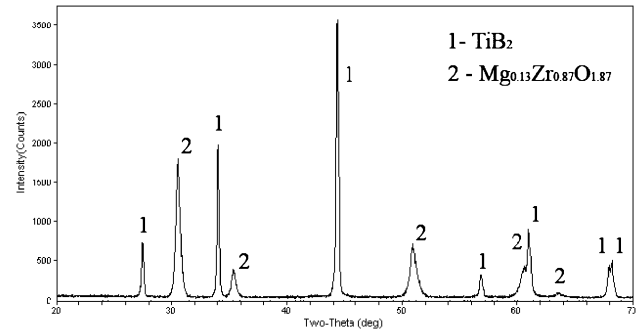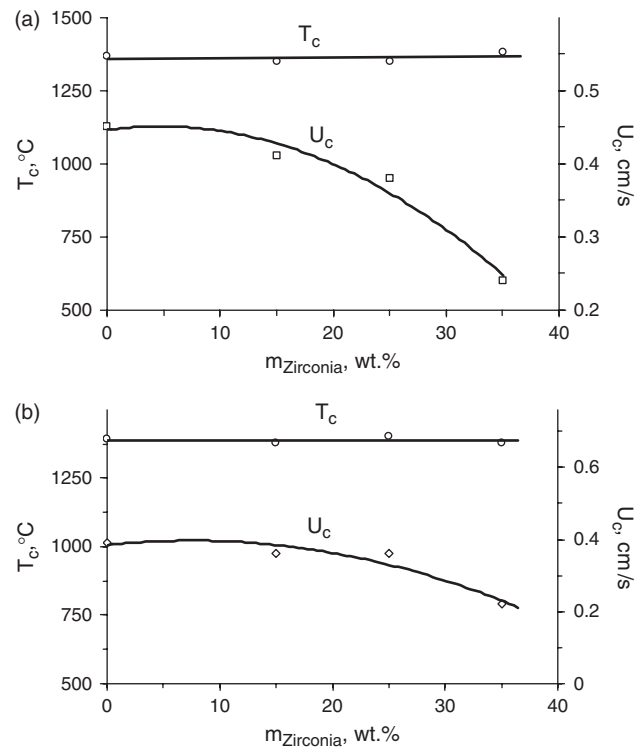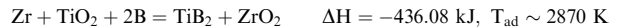$Zr + TiO_2 + 2B = TiB_2 + ZrO_2$ $\Delta H = -436.08$ kJ, $T_{ad} \sim 2870$ K

Fig. 8. X-ray diffraction (XRD) patterns of the combustion product formed from: (a) Ti–2B (95 SB Boron) with the addition of 25 wt% ZrO$_2$ and (b) Ti+2B (95 SB Boron) with the addition of 25 wt% ZrO$_2$ calculated based on Ti+2B and ZrO2 components only, and 14 wt% Y_2O_3 based on zirconia.

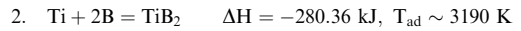**Fig. 10.** Combustion parameters against to amount of ZrO$_2$ for the a) Zr+TiO$_2$+2B (SB Boron) with the addition of ZrO$_2$ and b) Zr+TiO$_2$+2B (SB Boron) with the addition of ZrO$_2$ and Y_2O_3 where $m_{yttria}/m_{zirconia} = 0.14$.
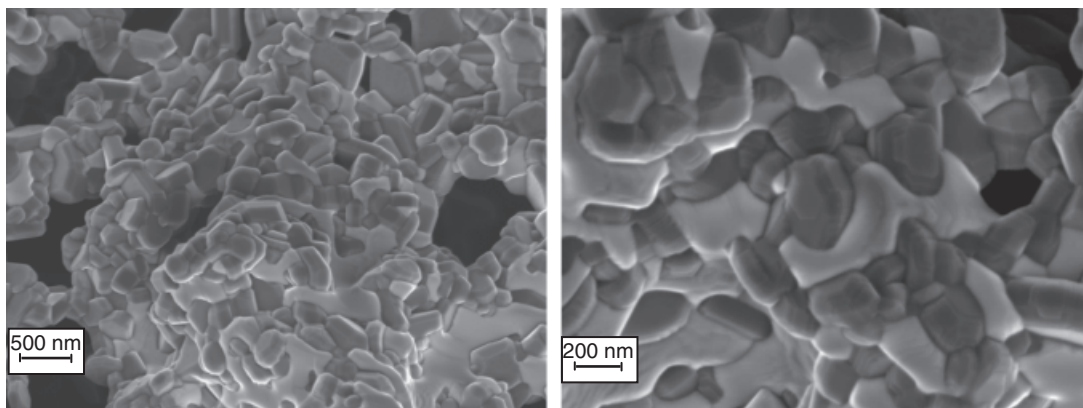
Fig. 11. Micrographs of combustion products obtained from the Zr–TiO$_2$–2B (95 SB Boron) reacting system.

In order to obtain composite powders with a small average particle size, it is necessary to reduce the maximum combustion temperature. In this case, various amounts of zirconia were added, resulting in products with different compositions of zirconia. Surprisingly, the experiments showed that the combustion temperature and the average particle size of the TiB$_2$ crystals formed were not affected by the addition of zirconia in a relatively wide composition range of ZrO$_2$ (up to 35 wt%). However, the dilution affected the combustion front velocity. Figure 10(a) presents combustion front velocity and maximum combustion temperature as a function of the amount of zirconia diluent. Figure 10(b) shows the dependence of the combustion front velocity and the maximum combustion temperature in the same reacting system modified by the addition of 14 wt% of yttria based on combined amount of zirconia initially added and formed during the combustion process.

SEM micrographs of the combustion products generated from the Zr–TiO$_2$–2B (95 SB Boron) reacting system without any addition of zirconia and yttria are shown in Fig. 11. In this case, the combustion-synthesized product also consists of TiB$_2$ and ZrO$_2$ compounds. However, much finer grain sizes of the product were obtained in comparison with those formed during direct synthesis from Ti and B in the presence of ZrO$_2$ (see Fig. 5 for reference).

XRD analysis of the products obtained from the Zr–TiO$_2$–2B (95 SB Boron) reacting system contained TiB$_2$, unstabilized monoclinic zirconia, and some amount of magnesia-stabilized zirconia Mg$_{0.13}$Zr$_{0.87}$O$_{0.187}$ (see Fig. 12).

The zirconia product was not fully stabilized because of the insufficient amount of magnesium provided by the boron powder. In order to fully stabilize zirconia, sufficient quantity of yttria was added to the reacting mixture. It was found that zirconia formed in the presence of yttria and small quantity of magnesium was successfully stabilized during the combustion process. Depending on the amount of yttria added, tetragonal ((ZrO_2)$_{0.91}$(Y_2O_3)$_{0.09}$)$_{0.917}$ or cubic oxides ((ZrO_2)$_{0.88}$(Y_2O_3)$_{0.12}$)$_{0.893}$) were obtained (see Fig. 13). Some of the ZrO$_2$ was stabilized in the form of ZrO$_{0.904}$Mg$_{0.096}$O$_{1.904}$.
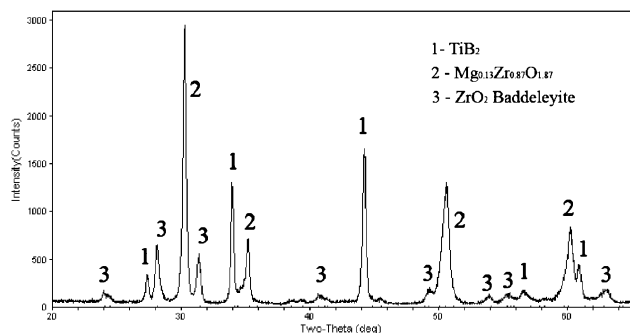

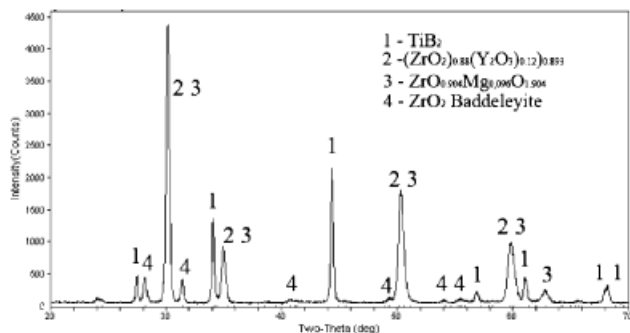**Fig. 12.** X-ray diffraction (XRD) patterns for combustion product of Zr-TiO$_2$-2B (95 SB Boron) system.

Fig. 13. X-ray diffraction (XRD) patterns for the combustion product formed from Zr–TiO$_2$–2B (95 SB Boron) with the addition of 4.3 wt% Y$_2$O$_3$.

IV. Conclusions

It was demonstrated that TiB$_2$ and zirconia composite powders can be synthesized using the CS technique using two different approaches, namely: (i) direct synthesis from elemental titanium and boron powders with the addition of zirconia or (ii) from the formation of zirconium, boron, and titania with or without addition of zirconia. In the second synthesis route, TiB$_2$ crystals are much finer than in the former route.

It was also found that magnesium present in a boron reactant plays a very important role in the stabilization of zirconia. Depending on the total concentration of zirconia in the product, it is necessary to add yttria in order to obtain fully or PSZ.

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