

## Synthesis and Characterization of Dense $Ti_{0.5}Zr_{0.5}B_2$ Solid Solutions by Electrically-Stimulated Combustion

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(Received September 23, 1998)

Solid solutions of  $Ti_{0.5}Zr_{0.5}B_2$  were successfully synthesized and densified simultaneously from elemental reactants by the use of a field-activated, pressure-assisted synthesis method. The method involves the application of an electric current and mechanical pressure across reactant compacts to achieve combustion synthesis. Dense solid solutions with relative densities of up to 99% were produced and characterized by XRD, SEM, and EPMA methods. With a maximum measured temperature of 1450°C under a load of 86 MPa for 30 min, the desired dense solid solution was synthesized.

**Key words:**  $Ti_{0.5}Zr_{0.5}B_2$ , Solid solution, Electrically-stimulated combustion, Combustion synthesis, Borides

### I. Introduction

The potential use of refractory borides and carbides in such applications as armor, cutting tools, and electrode materials has generated considerable interest in such materials as  $TiB_2$ ,  $TiC$ , and their composites. Their utilization in these and other applications is prompted by such attractive properties as high melting temperatures, superior strength, high hardness, and relatively high chemical and thermal stabilities.<sup>1-3)</sup> Additionally, many of the borides, such as  $TiB_2$  and  $ZrB_2$ , have attractive electrical and magnetic properties and thus are potentially useful as electronic materials.<sup>4)</sup>

A large number of these refractory borides have been prepared by the self-propagating high-temperature synthesis (SHS) method<sup>5)</sup> and some have been consolidated by hot-pressing in monolithic or composite forms.<sup>6,7)</sup> Many of the borides have been shown to exhibit considerable or complete mutual solubilities. For example, the system  $NbB_2$ - $CrB_2$  was reported to form a complete solid solution after heat treatment at 2500°C<sup>8)</sup> and at 1800°C<sup>9)</sup> and a limited solid solution when heated at 1400°C for 50 hours.<sup>10)</sup> In the system  $TiB_2$ - $WB_2$ , the limited solid solubility of  $WB_2$  in  $TiB_2$  was investigated by Telle, *et al.* and Mitra and Telle<sup>11,12)</sup> who found that the addition of  $CrB_2$  extended this limit. For example, the addition of 10 mol%  $CrB_2$  extended the solubility of  $WB_2$  in  $TiB_2$  at 2000°C from 30 to 40 mol%. Other investigations have also reported significant or extensive solid solubilities in the boride systems  $WB$ - $CrB$  and  $WB$ - $MoB$ <sup>13)</sup> and in one investigation the formation of compounds of  $NbTiB_2$  and  $WTiB_2$  was reported after heating elemental powders at temperatures in the range 1800-2600°C.<sup>14)</sup>

In general, solid solutions of borides are synthesized by

direct reactions between the elemental powders, between mixtures of the boride phases, or by carbothermal and borothermal reduction of oxide raw materials.<sup>15-17)</sup> The powder mixtures are heated to temperatures near or beyond the melting point of the boride end members to form the solid solution,<sup>15,16)</sup> and in the reduction method the oxides are reduced at temperatures in the range 1975-2025°C.<sup>17)</sup> Complete solid solution formation, however, does not occur in all cases, depending on differences in the atomic radii of the metal atoms. The physical, chemical, and electrical properties of some of these solid solutions have been shown to exhibit a non-linear or parabolic relationship between the end-member compositions and the solid solutions.<sup>18)</sup>

In this paper we report on the results of the simultaneous synthesis and densification of  $Ti_{0.5}Zr_{0.5}B_2$  from elemental reactants by the field-activated, pressure-assisted synthesis method.<sup>19)</sup> Details of this method have been reported in a previous publication.<sup>20)</sup>

### II. Experimental Materials and Methods

The materials used in this work were powders of 99% pure Ti, >95% pure Zr (both with a particle size classification of -325 mesh) and 90% pure amorphous B. The latter had an average particle size of 2-3  $\mu m$ . All powders were obtained from Alfa Co. (Ward Hill, MA, USA). A schematic diagram of the field-activated and pressure-assisted synthesis apparatus (FAPASA) is shown in Fig. 1. The mixed-powders sample is placed inside a graphite die and is then heated by the passage of a high AC current up to temperatures at which it simultaneously combusts and densifies by the imposed pressure.

Powder mixtures with molar ratios of B : Zr : Ti of 1 : 0.5 :

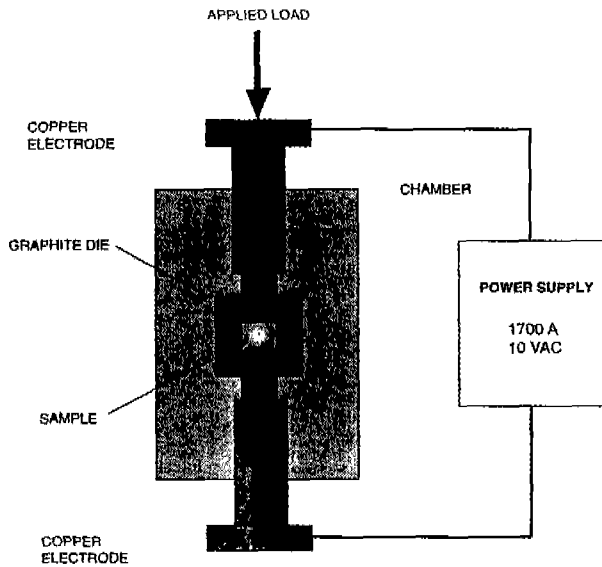


Fig. 1. Schematic diagram of the field-activated and pressure-assisted synthesis apparatus (FAPASA).

0.5 were mixed and ball-milled under an argon atmosphere for 12 hours. The milled powders were then outgassed in a tube furnace at  $600^{\circ}\text{C}$  for 3 hrs under Ar atmosphere. About 6 g of the powders were placed in a BN-sprayed graphite die (outside diameter: 45 mm; inside diameter: 20 mm; height: 40 mm), and cold pre-pressed at 43 MPa. The die with the pre-pressed sample was then loaded into the reaction chamber and subjected to a light pressure of about 5 MPa. The chamber was then evacuated and back-filled with argon gas. This was followed by the application of pressure up to 85 MPa (3 ton) at a rate of about  $10\text{ MPa}\cdot\text{s}^{-1}$ . An AC current of 1000 A (at 30 V) was then applied for a total duration of 30 s to minimize the thermal shock to the graphite die. The current was then increased to 1700 A resulting in the rapid heating of the sample. The temperature of the sample, which was measured by a pyrometer focused on the outside surface of the die, increased from  $1000^{\circ}\text{C}$  to  $1450^{\circ}\text{C}$  in 4 min as shown schematically in Fig. 2. Four holding times of 10, 20, 30, and 40 min were utilized in the synthesis and densification. Following this, the sample was cooled to room temperature at an estimated rate of  $200^{\circ}\text{C}\cdot\text{min}^{-1}$ .

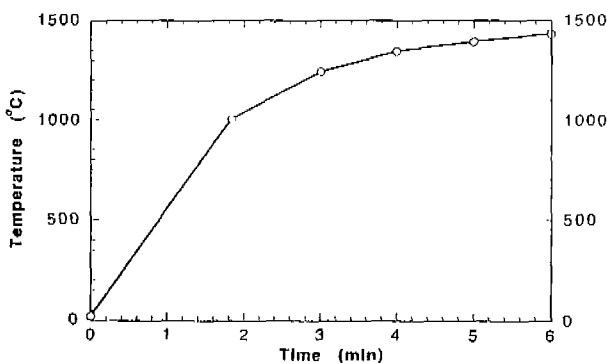


Fig. 2. Typical temperature rise during synthesis with 1700 A.

The relative density of the synthesized samples was measured using the Archimedes method. For microstructural information, the sintered samples were cut, polished, and etched using a solution of HF (10 vol%),  $\text{HNO}_3$  (20 vol%), and  $\text{H}_2\text{O}$  (70 vol%). phase identification of the products was made through X-ray diffraction (XRD), and microstructural and chemical analyses were done by electron microprobe. Vickers microhardness measurements under 400 g force were made on the synthesized  $Ti_{0.5}Zr_{0.5}B_2$  solid solution samples.

### III. Results and Discussion

The densified product samples were disks of 20 mm in diameter and about 3 to 5 mm in height, depending on holding time. The relative densities of the consolidated specimens were 4.63, 5.08, 5.23 and  $5.20\text{ g}\cdot\text{cm}^{-3}$ , corresponding to holding times of 10, 20, 30 and 40 min, respectively. Assuming a solid solution product (see below) with a theoretical density of  $5.29\text{ g}\cdot\text{cm}^{-3}$ , these values correspond to relative densities of 87, 96, 99, and 98% for the samples which were heated up to  $1350^{\circ}\text{C}$  with a current of 1700 A and subjected simultaneously to a pressure of 85 MPa (3 ton), as shown in Fig. 3.

X-ray diffraction analyses were made on the products syn-

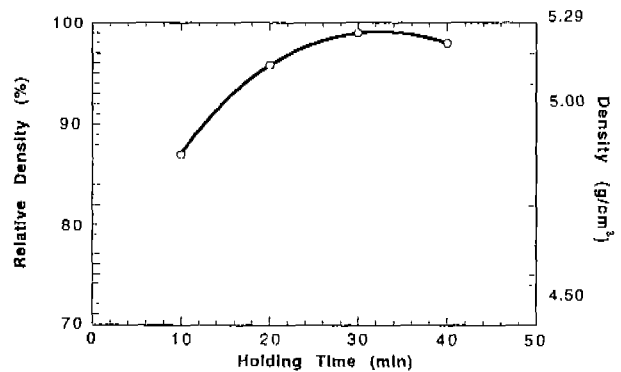


Fig. 3. The dependence of the relative density of  $Ti_{0.5}Zr_{0.5}B_2$  on holding time.

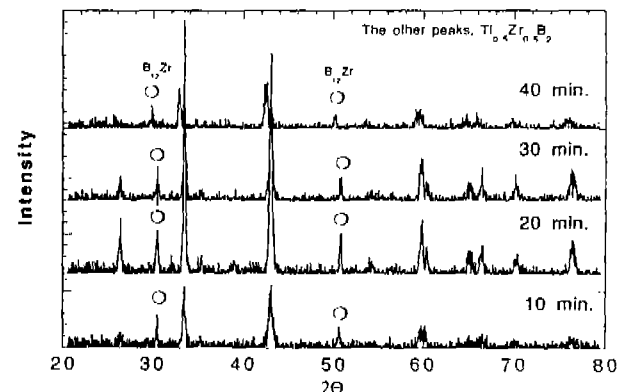


Fig. 4. XRD analysis of the products of synthesis of  $Ti_{0.5}Zr_{0.5}B_2$  for holding times of 10, 20, 30 and 40 min.

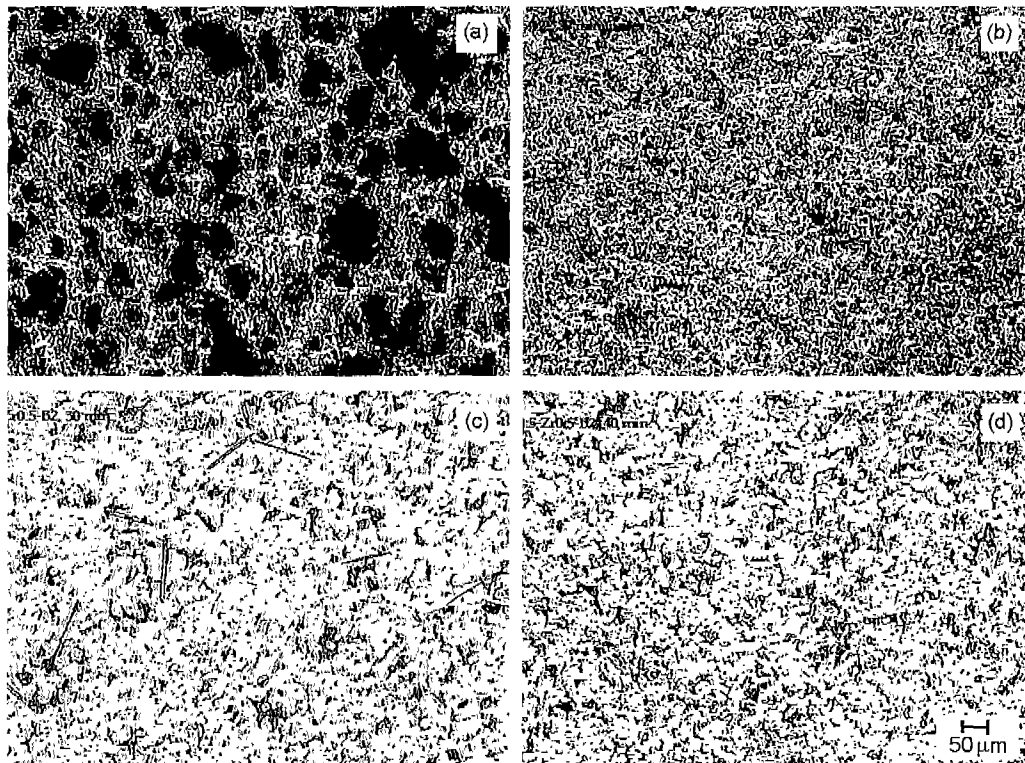


Fig. 5. SEM microstructures of  $Ti_{0.5}Zr_{0.5}B_2$  synthesized at  $1450^{\circ}C$  (1700 A) for (a) 10, (b) 20, (c) 30 and (d) 40 min holding time.

thesized by this method. A typical diffraction pattern which covered the  $2\theta$  range of  $20-80^{\circ}$  is shown in Fig. 4. In each sample, peaks around  $2\theta$  values of  $26, 33, 43^{\circ}$  are observed and are situated between the main peaks of the pure phases  $TiB_2$  and  $ZrB_2$ , indicating the formation of solid solutions on the basis of peak shift relative to the pure boride phases. Because of the absence of published data for the solid solution, these peaks were compared to results provided by Mroz<sup>21)</sup> from her reported study on these solid solutions.<sup>17)</sup> The present x-ray results are also in agreement with XRD peaks of a product synthesized by SHS by H. B. Lee *et al.*<sup>22)</sup> In this study, however, small peaks identified with the symbol (○) in Fig. 4 were also observed at  $2\theta$  values near  $30^{\circ}$  and  $50^{\circ}$ . These are believed to represent the phase  $B_{12}Zr$  which was formed near the surface of the sample during the rapid cooling to room temperature. Using a higher current ( $>1700$  A) or adding an annealing stage of a slow or furnace cooling may be adopted to avoid the formation of  $B_{12}Zr$ , and thus effect the formation of a pure solid solution.<sup>17,20)</sup>

Microstructural evaluations on the prepared solid solutions are shown in Figs. 5(a-d). The 10 min hold sample which was 87% dense shows numerous pores. In the sample of 20 min hold time two different regions are observed, with different apparent densities. It is believed that this is caused by an inadequate holding time and a possible attendant temperature gradient. The region near surface is relatively dense while the region inside the sample contains porosity equivalent to that in the 10 min hold sample. The 30 and 40 min hold time samples are nearly fully-

dense with 99 and 98% relative densities, respectively. The difference in grain size between these two samples is not significant, as shown in Figs. 5 (c) and (d), respectively. The average grain size of these latter samples is about  $15 \mu m$ .

Wavelength dispersive spectroscopy (WDS) and back-scattered electron (BSE) image analyses for the samples synthesized with holding times of 10 and 30 min were made to confirm the formation of a solid solution. The results are shown in Figs. 6(a) and (b), respectively. Although XRD analysis suggested the formation of a solid solution, the WDS results show that the solution is not homogeneous. For both holding times, the product contains three regions: a dark gray region (arrow A) which is Ti-rich, a lighter gray region (arrow B) which is the homogeneous solid solution, and a bright (nearly white) region (arrow C) which is a Zr-rich phase. As the holding time increased, the elemental distribution became more homogeneous, as seen in Fig. 6 (b) for the 30 min hold time sample. Here the Ti distribution is reasonably uniform but that of Zr is less so, with distinct regions showing high Zr concentrations (the nearly white regions in Fig. 6(b)).

The homogeneity of the solid solution improved with longer holding time, but even for a 40 min holding time, the product is not completely homogeneous. The proportion of phases of Ti and Zr-rich phases by wt.% in three regions of 10 and 30 min is presented in Fig. 7 from the WDS results.

The microhardness of the synthesized samples was deter-

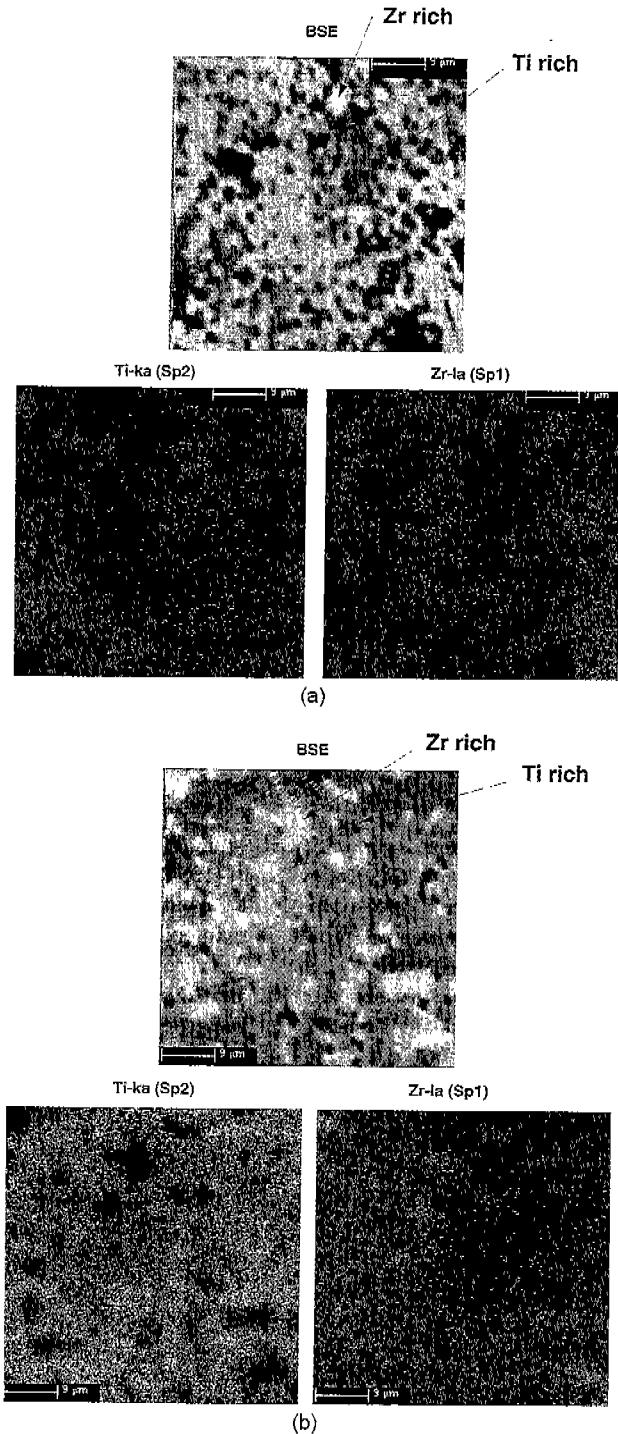


Fig. 6. Back-scattered electron images and X-ray dot maps of products synthesized at 1450°C with holding times of: (a) 10 min, (b) 30 min.

mined by a Vickers indentation technique using a 400 g load. The relationship of holding time with hardness is shown in Fig. 8. The hardness of the products ranged from 2000 to 2200  $kg \cdot mm^{-2}$ , showing little dependence on holding time when the latter exceeded 20 min. Attempts to determine the fracture toughness of the products by crack size

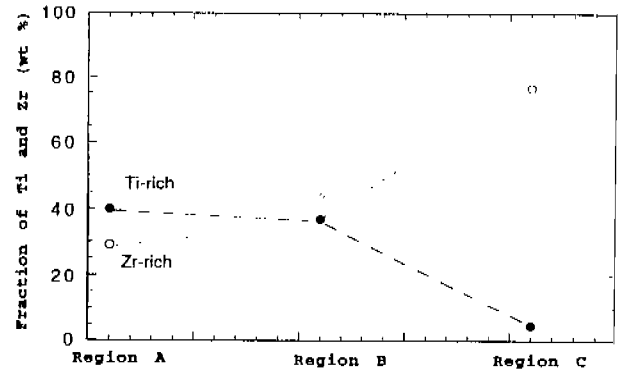


Fig. 7. Compositional analysis of regions A, B and C of Fig. 6(b).

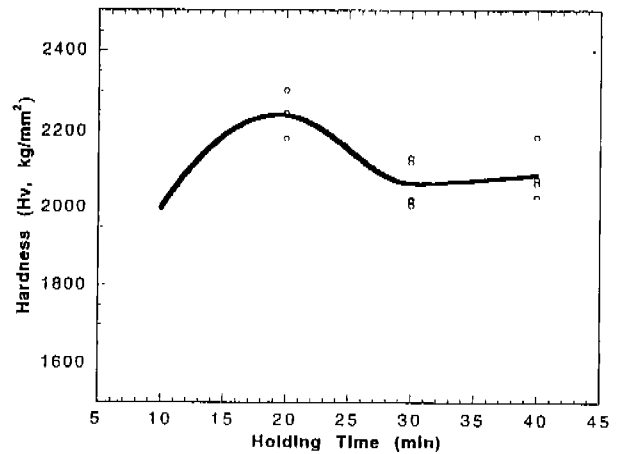


Fig. 8. The dependence of the microhardness of products the holding time.

measurements were not successful due to the brittleness of the material of the observed inhomogeneity in its elemental distribution.

#### IV. Conclusions

Using elemental powders as reactants, the feasibility of the simultaneous synthesis and densification of  $Ti_{0.5}Zr_{0.5}B_2$  solid solutions was investigated. The process of field-activated, pressure-assisted synthesis involves the simultaneous imposition of a high AC current (1700 A) and a uniaxial pressure of 85 MPa on the reactants. The total holding time, which includes the heat-up period, was changed from 10 to 40 min. X-ray diffraction analyses on the products showed the formation of solid solutions on the basis of peak shift relative to the pure boride phases. The absence of standard XRD data for the solid solutions rendered the XRD results inconclusive. However, back-scattered electron image and x-ray dot-map analyses showed the formation of a solid solution, albeit not entirely homogeneous. The homogeneity of the solid solution improved with longer holding time, but even for a 40 min holding time, the product is not completely homogeneous. The relative density of the products showed a dependence on holding time,

changing from about 87 to 98% as the time was increased from 10 to 40 min.

Vickers microhardness measurements showed little dependence on holding time when the latter exceeded 20 min. The values ranged from 2000 to 2200 kg·mm<sup>-2</sup>.

Higher reaction temperatures and, to a lesser extent, longer holding times are believed to provide homogeneous solid solutions of Ti<sub>0.5</sub>Zr<sub>0.5</sub>B<sub>2</sub>. Investigations are underway to synthesize these and similar solid solutions.

### Acknowledgments

The partial support of this work by the Army research Office (ARO) is gratefully acknowledged. Our sincere thanks to Dr. Cathleen Mroz for providing us with the XRD patterns of her previously reported study.

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