Pulsed electric current sintering of TiB₂-based ceramics using nitride additives

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ABSTRACT

In this research, various types of nitride additives were incorporated into titanium diboride attaining dense TiB₂-based ceramics by field-assisted sintering technique. The addition of different types of nitride additives, namely Si₃N₄, BN, AlN, and TiN, significantly improved the sinterability of TiB₂, achieving near fully dense ceramics. The X-ray diffraction analysis and microstructural evaluation confirmed the presence of the h-BN compound in all specimens. In the TiB₂-Si₃N₄ ceramic, Si₃N₄ additive reacted with B₂O₃ oxide, in-situ generating h-BN, and SiO₂ phases. Although the h-BN phase was produced in the TiB₂-AlN specimen, the main proportion of AlN remained in the sample as an unreacted ex-situ phase. In terms of the TiB₂-TiN ceramic, some of the nitrogen and boron atoms could leave the TiN and TiB₂ crystalline structures, contributing to the in-situ formation of h-BN.

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KEYWORDS

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Field assisted sintering technique

1. Introduction

As an ultra-high-temperature ceramic (UHTC), TiB₂ possesses many magnificent advantages, such as high melting point, great hardness, good wear resistance, good thermal conductivity, high Young’s modulus, and relatively low coefficient of thermal expansion [1–5]. Having such diverse features has made TiB₂ an appropriate candidate for several applications, including armors, cutting tools, turbine blades, Hall-Heroult cells’ cathodes, abrasion, and corrosion resistance compounds, etc. [6,7]. However, this notable substance had some demerits, e.g. low self-diffusion coefficient, surface oxide layers (TiO₂, B₂O₃), and strong covalent bonding, which make its sinterability problematic [8–10].

According to the previous studies, reaching a near fully dense TiB₂ material needs both a high sintering temperature and a very high external pressure (~3 GPa). However, implementing a high sintering temperature results in grain coarsening, which deteriorates both fracture toughness and flexural strength [11–13]. Accordingly, quite a few researches have been carried out to elevate the sinterability of TiB₂ substances by incorporating different additives [14–22]. Although the addition of a metallic additive boosts the sinterability of TiB₂, the high-temperature qualities of the resulted material may be adversely affected thanks to the low melting temperature of the metallic ingredient [23,24]. However, a suitable ceramic secondary phase not only can improve the sintering behavior but also can have positive impacts on the mechanical features [25–27]. On the other hand, utilizing an
advanced sintering technique like spark plasma sintering (SPS) can significantly remove obstacles against the production of high-quality ceramics owing to the unique merits of such a process, namely short dwelling time, high applied external pressure, and relatively low sintering temperature [28–32].

Several papers have been published on the TiB₂-based composites incorporated by various nitrides as sintering aids/reinforcements. Júnior et al. [20] studied the impact of sintering temperature on the sinterability of TiB₂-30 vol% AlN. According to their results, the best relative density value of almost 95% was attained for the sample sintered at 1900 °C, which was around 20% higher than that at 1500 °C. Moreover, some in-situ compounds, i.e., h-BN, Al₂O₃, TiN, and AlB₂, were produced over the sintering process. The incorporation of low content of AlN additive (5 wt%) on the relative density of TiB₂-based ceramics was also investigated by Nguyen et al. [30]. The composite sample reached its near fully dense density, manifesting the beneficial role of AlN as a sintering aid. Besides, both microstructural observations and XRD patterns verified the in-situ formation of the h-BN ingredient owing to a chemical reaction between the introduced AlN and the surface oxide of B₂O₃. The TiB₂–h-BN system was also studied by Nguyen et al. [7]. It was reported that the nucleation and growth of nano-sized BN platelets had a significant effect on the sinterability of such a system, reaching a near fully dense composite. The same phenomenon occurred when 5 wt% TiN was added to TiB₂ as an additive, leading to a sample with a relative density of more than 99% [33]. The influence of various weight percentages of Si₃N₄ on the relative density of TiB₂-based ceramics was assessed by Park et al. [34]. The hot-pressing technique at 1800 °C was used to fabricate specimens in this research. A low content of Si₃N₄ (2.5 wt%) significantly improved the sinterability of TiB₂ thanks to the elimination of TiO₂ surface oxide as well as the in-situ formation of h-BN, TiN, and SiO₂ compounds. However, the addition of more Si₃N₄ resulted in a reduction in the relative density of samples. Finally, Mahaseni et al. [35] also produced a fully dense TiB₂–5 wt% Si₃N₄ composite using the SPS route at 1900 °C. The in-situ formation of the h-BN, TiN, and SiO₂ phases were verified in this study, too.

Although the impact of various nitride additives on the properties of TiB₂ was scrutinized in different studies, this investigation has tried to assess the microstructural development and sinterability of various TiB₂-nitride (Si₃N₄, h-BN, AlN, and TiN) composites in a single research work. The SPS process was implemented to fabricate the targeted specimens, and subsequently, the SPSed samples were characterized using XRD and FESEM.

2. Experimental procedure

Table 1 presents the initial materials used in this investigation and their relevant characteristics. Table 2 also exhibits the composition of five different specimens designed to compare the role of various nitrides on the characteristics of TiB₂-based ceramics. Initially, a digital scale was implemented to weigh the required ingredients for any sample. Next, the powder mixtures were scattered using an ultrasonic facility for 0.5 h in ethanol. After that, a hot-plate agitator was used (3 h, 120 °C) for both extra mixing and removing the ethanol medium. Subsequently, the prepared slurries were put into a Universal oven for complete dehumidification at 110 °C for 24 h. Next, in order to reach homogeneous powder mixtures, as well as refining the powder particles, each powder sample was separately wet-mixed using a ball-mill device. Regarding ball-milling parameters, each mixture, together with 50 cc ethanol, was poured into a zirconia cup. The ratio of balls/powder was 10:1, and the ball-milling was carried out at 200 rpm for 5 h. Next, powder mixtures were dehumidified for 24 h at 100 °C using an oven. After that, the dried slurries were smashed and passed through a 100-mesh sieve. A graphite die was used for loading the powder mixtures in it, which was lined by a graphite foil, too. Ultimately, a spark plasma sintering machine was utilized to sinter the specimens at 1850 °C for 8 min under 35 MPa. The final ceramics were disk-shaped with 30 mm diameter and 7 mm in height. The fraction of bulk to the theoretical density of each ceramic was recorded as the relative density. The bulk density was estimated using the Archimedes principle, while the theoretical one was calculated using the rule of mixture. An X-ray diffractometer (XRD) was used for phase analysis, whereas the elemental evaluation was carried out using energy-dispersive X-ray spectroscopy (EDS). The latter device was coupled with a field emission scanning electron microscopy (FESEM), which was utilized for microstructural investigation on polished and fracture surfaces. Moreover, an X-ray fluorescence device (XRF) was employed to analyze the exact composition of the initial TiB₂ powder. Finally, the thermodynamic study was fulfilled using another computer program named HSC chemical package.

3. Results and discussion

3.1. Thermodynamic assessment and sinterability

Based on the SEM images and XRD patterns (not presented here) of the raw substances used in this investigation, the morphology and particle size of the powders were in agreement with those claimed by the manufacturer in Table 1. In addition, identifying no peak except the base materials in all XRD patterns indicates the high-purity of the as-purchased powders (see Table 3 for XRF analysis of the TiB₂ powder). However, it is a recognized fact that all these raw materials are covered by some oxide phases, namely TiO₂ and B₂O₃ (for TiB₂), SiO₂ (for Si₃N₄), Al₂O₃ (for BN), Al₂O₃ (for AlN), and TiO₂ (for TiN). The
presence of such oxides, especially on the matrix powder, may lead to partial densification. In short, surface oxides negatively affect consolidation behavior in two different ways. On the one hand, they hinder proper bonding among the particles during the sintering process, and on the other hand, they promote grain coarsening. Subsequently, the most important role of an additive in these kinds of sintering systems could be the annihilation of the surface oxides [36–38]. The influence of various nitride additives on this phenomenon will be discussed in the following section.

Fig. 1 compares the beneficial impact of each nitride additive on the relative density of the SPSed ceramics. As can be seen in this bar chart, the monolithic TiB$_2$ hit a relative density of 94.9%, which implies more than 5% remaining porosity in the undoped ceramic. Nevertheless, the incorporation of all nitride additives, namely Si$_3$N$_4$, h-BN, AlN, and TiN, promotes the sintering behavior of TiB$_2$, resulting in four near fully dense composites. Although the relative density values of the composite specimens were roughly similar, the routes through which these additives could improve the sinterability of TiB$_2$ may be different. Accordingly, the influence of each nitride on the sintering behavior of TiB$_2$ was individually studied and linked to the relevant XRD outcome.

Firstly, understanding the sintering mechanism of the monolithic TiB$_2$ looks advantageous. The XRD pattern of the TiB$_2$ sample (Fig. 2) indicates that just TiB$_2$ peaks were detectable. As noted earlier, initial TiB$_2$ particles contain surface oxides, namely TiO$_2$ and B$_2$O$_3$. These oxide compounds have some harmful impacts on the sintering behavior of TiB$_2$, namely hindering strong bonding between the TiB$_2$ particles, and grain coarsening.

According to the XRD pattern of the TiB$_2$-Si$_3$N$_4$ ceramic, it seems as if the whole content of the additive was consumed over the SPS process, participating in producing the in-situ h-BN phase. Eq. 1 presents the possible chemical reaction through which the in-situ h-BN may be generated. The feasibility of such a reaction was evaluated through the estimation of its $\Delta G^\circ$ at 1850 °C (-281 kJ), and as a result, Eq. 1 can be advanced in the present sintering system. Excluding the produced h-BN compound, an oxide phase, namely SiO$_2$, may also form based on this equilibrium. The presence of the SiO$_2$ peaks in the XRD pattern of the TiB$_2$-Si$_3$N$_4$ sample fortifies the possibility of progressing Eq. 1 over the SPS. By contrast, the in-situ created the SiO$_2$ phase and that, from the surface oxide on the Si$_3$N$_4$ particles can create a low melting point compound with B$_2$O$_3$ [39]. This molten phase can be beneficial in promoting the chemical reaction in Eq. 1 through assisting mass transfer. The remaining liquid phase would fill the unclosed cavities, increasing the relative density of the sample.

The XRD pattern of the TiB$_2$-AlN specimen clearly shows that both AlN and BN phases were available in the sample, along with the TiB$_2$ matrix. Eq. 2 proposes the possible chemical interaction through which the in-situ BN can be produced. This equation is favorable at the current sintering conditions thanks to its highly negative $\Delta G^\circ$ at 1850 °C (-177 kJ). According to Eq. 2, the Al$_2$O$_3$ oxide was also the other product of the reaction, increasing the Al$_2$O$_3$ content of the system, which was available as the surface oxide on the initial AlN particles. It is also worth mentioning that the Al$_2$O$_3$ content can react with B$_2$O$_3$, forming several compounds like Al$_{18}$B$_4$O$_{33}$ and Al$_4$B$_2$O$_9$ [40]. The reason for not detecting Al$_2$O$_3$ in the relevant XRD result could be due

$$\text{Si}_3\text{N}_4 + 2\text{B}_2\text{O}_3(l) = 3\text{SiO}_2 + 4\text{BN} \quad (1)$$

$$\text{TiB}_2 + 2\text{AlN} = 3\text{Al}_2\text{O}_3 + 4\text{BN} \quad (2)$$

| Elements | Ti | B | C | N | H | O |
|----------|----|---|---|---|---|---|
| wt%      | 68.1 | 30.0 | 0.35 | 0.27 | 0.41 | 0.87 |

Table 3. XRF analysis of the initial TiB$_2$ powder.

Fig. 1. The relative density of the as-sintered samples.

Fig. 2. XRD patterns of the as-sintered samples.
to the advancement of such reactions. As a result, the content of each Al-based compound has been below the limit that the XRD device was able to detect.

\[2\text{AlN} + \text{B}_2\text{O}_3(l) = 2\text{BN} + \text{Al}_2\text{O}_3\]  

Fig. 2 also illustrates the XRD pattern of the TiB\(_2\)-TiN sample. Although identifying no peak related to the TiN phase implies its full consumption over the SPS process, the thermodynamic assessment revealed that such a thing could not be possible. However, a partial interaction between the introduced TiN and the TiB\(_2\) matrix could happen, leading to the in-situ formation of h-BN. According to the literature [41], when TiB\(_2\) and TiN coexist under the SPS circumstances at high temperatures, TiN can lose nitrogen, and TiB\(_2\) can lose boron. In this way, the free nitrogen and boron can form a BN ingredient, which is in harmony with the corresponding XRD result. On the other hand, Kitiwan et al. [42] reported that in a TiB\(_2\)-TiN system, the exited boron atom from the TiB\(_2\) crystalline structure could dissolve into the TiN phase, forming a solid solution. In other words, TiN not only can lose N but also can absorb B atoms. This phenomenon can roughly justify why no peak associated with TiN was identified in the attributing pattern. Comparing the XRD pattern of the TiB\(_2\)-TiN sample with the other TiB\(_2\)-based ceramics in this investigation shows that some TiB\(_2\) peaks were shifted to the higher degrees (around 0.5°), fortifying the above-mentioned assumption. However, it sounds that the formation of the in-situ h-BN compound has had a significant influence on improving the relative density of this composite. Indeed, other factors such as grain refining, adding a finer secondary phase, etc. were also effective in promoting the sintering behavior of these TiB\(_2\)-based materials.

3.2. Microstructural study

Figs. 3-6 compare the corresponding micrographs from the polished surfaces of the SPSed samples. As can be seen, all micrographs comprise a bright-colored TiB\(_2\) matrix in which a grey-colored secondary phase is distributed. The relevant EDS point analysis was fulfilled from these phases, and the results were attached to the attributing FESEM images. According to these EDS outcomes, the dominant secondary phase was BN in the samples incorporated with Si\(_3\)N\(_4\), BN, and TiN, while the dark phase in the TiB\(_2\)-AlN specimen was associated with the remaining AlN. As shown clearly, the source of the BN phase was different in the TiB\(_2\)-BN composite, compared to TiB\(_2\)-Si\(_3\)N\(_4\) and TiB\(_2\)-TiN. Briefly, the TiB\(_2\)-BN sample contained the ex-situ BN, while such a phase was formed as an in-situ compound in the others. In addition, no apparent pore can be seen in the micrographs of the composite samples, confirming the relative density results. However, the cavities related to the pulled-out secondary phase(s) over the polishing may be mistaken for the pores that should be taken into account.
The FESEM fractograph of the TiB₂-Si₃N₄ is also illustrated in Fig. 7. Looking at this image, some solidified glassy phase can be seen. According to the explanation in the “thermodynamic assessment and sinterability” section, this glassy phase mainly consists of the TiO₂ oxide in the monolithic sample. The other oxide compound, namely B₂O₃, was possibly evaporated and left the system owing to the high applied vacuum. However, as explained earlier, more liquid phase can be formed in the sample containing Si₃N₄, compared to the monolithic TiB₂ (shiny surfaces and round edges in Fig. 7 proves the formation of liquid phase in this composite over sintering). This observation is in agreement with the contribution of the SiO₂ oxide in creating a limited content of the liquid phase. The formation of h-BN platelets in this fractograph is utterly apparent.

4. Conclusions

The incorporation of several nitrides, namely Si₃N₄, BN, AlN, and TiN, into the microstructural features and sinterability of TiB₂-based composites was studied. All these additives had a remarked influence on the relative density of TiB₂, obtaining four near fully dense samples. The XRD results, along with the microstructural evaluation, confirmed the presence of the h-BN phase in the microstructure of all SPSed specimens. However, the main proportion of the AlN additive remained in the TiB₂-AlN sample as an unreacted phase. In terms of the TiN additive, some of the N atoms left the crystalline structure of TiN, forming the BN compound through interacting with the exited B from TiB₂.

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