



Synthesis of Ti/TiB Composites via Hydrogen-Assisted Blended Elemental Powder Metallurgy

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Titanium–titanium boride (Ti/TiB) metal matrix composites have been widely identified as promising materials for various applications. The traditional ingot metallurgy processing strategies used to fabricate these materials are energy intensive and have fallen short of their perceived mass production potentials. Powder metallurgy processing, especially that aimed at *in-situ* synthesis of Ti/TiB composites from titanium and TiB₂ powder blends, is currently widely used for the cost-efficient production of such composites. However, this approach usually results in excessive sintered porosities and associated mechanical property degradation. Therefore, further thermomechanical or hot isostatic pressing steps are required for porosity reduction. In the present study, low-porosity Ti/TiB composites were synthesized using TiH₂ and TiB₂ powders via a simple press-and-sinter hydrogen-assisted blended elemental powder metallurgy route. The manufacturing route included two stages. Compaction and vacuum sintering of the noted blended powders was followed by hydrogenation and ball milling of the pre-sintered product to produce a hydrogenated, pre-alloyed powder. This was followed by compaction and final sintering. X-ray diffraction, light microscope, and scanning electron microscope were employed to investigate the powder morphology and material microstructures after various processing steps. The role of temporary alloying with hydrogen was established in tailoring the microstructure. When an optimized particle size distribution that was carefully controlled using a Malvern Mastersizer laser analyzer was combined with optimized hydrogenated pre-alloyed Ti/TiB powder compaction and sintering parameters, a nearly dense, uniform composite was formed. The above approach can be considered a promising solution for economical manufacturing of Ti/TiB parts with improved properties, such as a high performance-to-cost ratios.

Keywords: titanium matrix composite, titanium boride, blended elemental powder metallurgy, hydrogenation, densification, microstructure

INTRODUCTION

Titanium alloys have been thoroughly investigated and are used in intensive aerospace, military, biomedicine, and automotive materials applications because of their superior intrinsic properties, such as high specific strengths, excellent corrosion resistance, and high-temperature characteristics. Nevertheless, inferior hardness, poor wear resistance, and unaffordable final-product prices have limited the commercial success of these materials. Ceramic-reinforced titanium matrix composites

may offset the physical property shortcomings of conventional titanium alloys (Abkowitz et al., 2004; Morsi and Patel, 2007; Hayat et al., 2019).

Of the various hard reinforcement materials available, such as TiB₂, Al₂O₃, SiC, and TiC, in-situ-formed titanium boride (TiB) is considered the most compatible because it offers a chemically stable composition and its density is similar to that of the titanium matrix. It also exhibits distinctive metallurgical bonding with the titanium matrix (Hu et al., 2017). In addition, since the thermal expansion coefficients of TiB and the matrix are similar, little residual stress forms at their interface. This further enhances the mechanical properties of the material (Yamamoto et al., 1997; Huang et al., 2015).

TiB-reinforced, titanium-based metal matrix composites can be produced via a traditional ingot metallurgy (IM) approach (Chandravanshi et al., 2011; Prasad et al., 2011; Sarkar et al., 2013). A mixture of titanium and boron sources in titanium diboride (TiB₂) or elemental forms dissolves and transforms into a titanium-boron alloy during the melt heating cycle. The *in-situ* TiB phase precipitates in the matrix during solidification via a eutectic reaction at elevated temperatures. Usually, secondary thermal work, such as rolling or extrusion, is introduced to help modify the inevitable as-cast defects in the cast products and convert coarse as-cast grains into finer microstructures.

Powder technologies are effective alternative manufacturing methods. However, pre-alloyed (PA) powder technology involves a melting stage during powder fabrication and subsequent complex powder consolidation operations. Thus, this processing route is relatively complicated. For example, the Ti-B alloy melt can be fast-cooled to obtain PA Ti-B powders via inert gas atomization (Tamirisakandala et al., 2004). Thus, the TiB phase forms and is evenly distributed among the particles. After outgassing to remove volatile impurities, the PA powders can be pressed into green parts and subjected to the abovementioned thermo-mechanical processes to produce wrought products. Advanced alloy production technologies could also be candidates in the fabrication of Ti/TiB composites with enhanced mechanical properties. Selective laser melting (SLM) is proven to be able to fabricate biomedical materials with a superb anti-corrosion ability, while spark plasma sintering (SPS) is time-saving, taking advantage of combining sintering and post treatment with the assistance of current and pressure (Zhang and Chen, 2019). With melt filling into clearance in between the reinforcements and the matrix, semi-solid sintering (SSS) can be adopted to tailor the composite densification (Yang et al., 2017).

However, the abovementioned technologies all face the same dilemma between property and cost efficiency, resulting in the limitation of industrial acceptance. Moreover, there are problematic metallurgical issues. The application of hot deformation is a key problem in ingot metallurgy (IM) processing. The growth of coarse primary TiB phases in hypereutectic compounds is the main obstacle that restricts both the IM and PA approaches (Tamirisakandala et al., 2010).

Unlike conventional IM and PA powder routes for Ti/TiB composite fabrication, blended elemental powder metallurgy

(BEPM) is well known to provide a large processing “window” for microstructure control, improved TiB particle distribution uniformity in the metallic matrix, and better cost efficiency because of the lack of melting operations.

To produce composites via the BEPM route, TiB₂, boron, and boron carbide (B₄C) (Gorsse and Miracle, 2003; Saito, 2004; Tamirisakandala et al., 2004; Tjong and Mai, 2008; Tamirisakandala et al., 2010; Kumar et al., 2012; Huang et al., 2015; Li et al., 2016; Baglyuk et al., 2017; Ivasishin et al., 2017; Ivasishin et al., 2019) powders are used as starting materials. They are blended with either titanium or titanium hydride (Saito, 2004; Baglyuk et al., 2017; Ivasishin et al., 2017; Ivasishin et al., 2019) powders to form monoboride TiB particles via a high-temperature reaction between titanium and the abovementioned powders (Tjong and Mai, 2008). However, solid-state reactive sintering of such blends with the *in-situ* formation of Titanium–titanium boride (Ti/TiB) composites generally leads to excessive porosity, which is detrimental to mechanical behavior. Thus, BEPM processing routes always include complex hot deformation operations designed to reduce porosity and produce nearly dense Ti/TiB materials with an improved set of properties. Abkowitz et al. (2004) included hot isostatic pressing (HIP), forging, or extrusion of sintered products in the processing scheme, while Saito (2004) extruded, forged, and annealed sintered semi products to produce materials with properties sufficient for practical application. Li used hot extrusion to eliminate the massive pores that formed during sintering between the Ti matrix and boron powder at the expense of reinforcement aggregation (Li et al., 2016). Kumar compared HIP, spark plasma sintering, and vacuum sintering when making high-density Ti/TiB composites. The denser sintered compacts were acquired by following the first two expensive fabrication techniques; however they could not meet application requirements (Kumar et al., 2012). In the study by Gorsse and Miracle (2003), heat treatment after HIP was conducted for up to 100 h to improve the microstructure and reinforcement distribution of Ti/TiB composites.

The state-of-the-art strategies designed to reduce Ti/TiB composite porosity in most published papers typically required tedious post-thermal mechanical work or long-term heat treatment. These processes are not ideal with respect to economic factors and actual engineering demands. Only studies by Abkowitz et al. (2004) and Saito (2004) were directly aimed at the practical application of titanium-based composites.

Undoubtedly, if residual porosity can be abated, simple compaction and sintering of elemental powder blends could be one of the most fundamental and industrially viable approaches to cost-efficient fabrication of near-net-shape Ti/TiB composites. Such a process could overcome the financial obstacles driven by high material waste and the complex, expensive thermomechanical procedures that other methods require (Geng et al., 2004).

Titanium hydride TiH₂ powders have been demonstrated to be substantial substitutes for conventional CP-Ti powders that do not suffer from the abovementioned severe problems associated

with press-and-sinter BEPM fabrication of titanium alloys (Ivasishin and Moxson, 2015). Because of the temporary presence of hydrogen in titanium powder, residual pores can be reduced up to 1%–2% and the contents of interstitials, such as oxygen and chlorine, can be decreased to acceptable levels via dehydrogenation and sintering (Savvakin et al., 2012). However, unlike with titanium alloys, the titanium hydride approach is less effective in producing *in-situ* Ti/TiB and Ti-6Al-4V/TiB composites via the BEPM route (Baglyuk et al., 2017; Ivasishin et al., 2017). Better densification of TiH₂-based blends than Ti-based blends has been observed only at low TiB-phase contents. However, because of the significant porosity induced by the Ti + TiB₂ → 2TiB reaction, its overall value increases by 7%–9%, as observed in Ti powder-based blends with reasonable TiB contents. Such poor results require that researchers develop a better understanding of factors that affect the densification of BEPM compacts with boride powder additions in order to more effectively use the positive potential of hydrogenated powders.

The objective of this study was to develop a manufacturing approach for *in-situ* production of nearly dense Ti/TiB composites via hydrogen-assisted BEPM using an economically friendly cold compaction and sintering approach. Sintering of TiH₂ and TiB₂ blends was investigated to establish a better understanding of the role of hydrogen in microstructure evolution during the formation of a nearly dense Ti/TiB composite.

Peculiarities of Densification of TiH₂ + TiB₂ Blends and the Microstructures of the Resulting Ti/TiB Composites

Powder blends of TiH₂ with 5 and 10 wt% TiB₂ corresponding to Ti/8.4 vol% TiB and Ti/16.8 vol% TiB composites, respectively, were used in the present investigation to elucidate the general peculiarities of *in-situ* formation of Ti/TiB materials via BEPM. TiB inclusions were expected during the sintering process due to the reaction TiB₂ + Ti → 2TiB.

As the dominant starting component, single-phase titanium hydride TiH₂ (3.5 wt% H) powder was sieved to less than 100 μm and blended with corresponding amounts of fine TiB₂ powder less than 25 μm in size. **Figure 1** shows the particle size distributions of the initial powders, as determined using a Malvern Mastersizer 3,000 laser analyzer. The maximum size of titanium hydride particles sieved through an 100 μm cell sieve is approximately 120 μm because the particles are not spherical. The peak of the TiH₂ powder size distribution curve appears at approximately 40 μm. The average TiB₂ particle is approximately 8 μm in size. The powders were blended in a drum container for 6 h. Once the elemental blends were prepared, cold pressing (600 MPa) was used to fabricate cylindrical (10 mm in diameter, 10 mm long) and prismatic (60 × 9 × 9 mm) preforms. Sintering was performed in vacuum at 1,250°C (heating rate 10°C/min), followed by 4 h of isothermal exposure. Vacuum heating up to sintering temperature resulted in hydrogen emission from TiH₂ and formation of

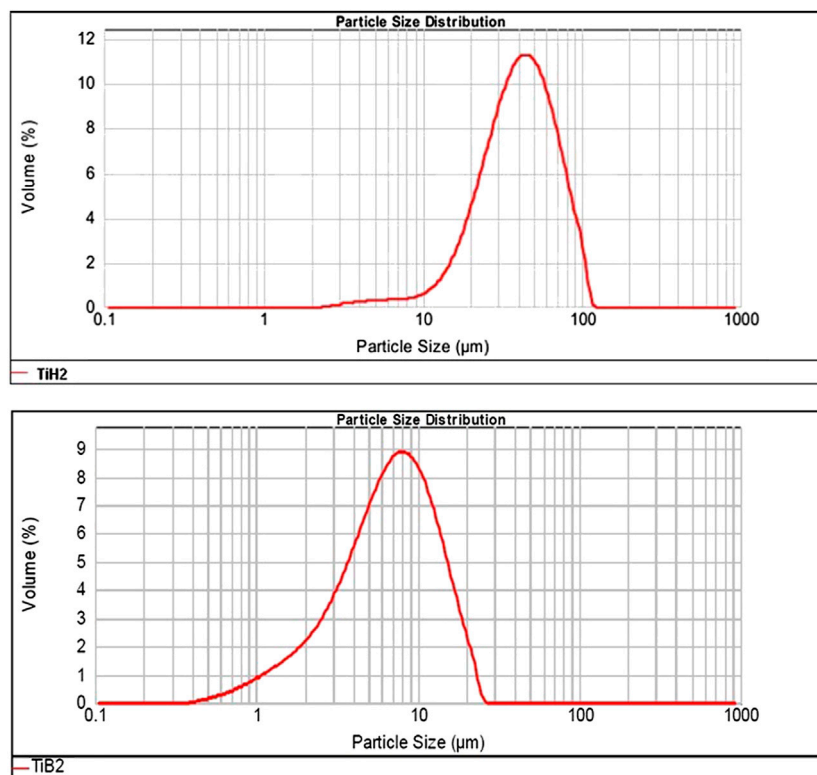


FIGURE 1 | Particle size distributions of starting powders: (A) TiH₂ and (B) TiB₂.

dehydrogenated titanium powder particles. The negative Gibbs free energy ensures that the TiB formation reaction occurs with the development of boron diffusion into the Ti matrix (Singh et al., 2019).

The microstructure of sintered Ti/8.4% TiB material is shown in **Figure 2** (TESCAN VEGA3). Images of the sintered samples indicate the presence of local microstructural inhomogeneity and substantial residual porosity. The porosity level was determined to be 7.5% via analysis of polished cross sections of the material. This is similar to early residual porosity values obtained in Ivasishin et al. (2017). The density of the sintered compact as determined via Archimedes's technique is 4.16 g/cm^3 . The phase composition of the powder blends and sintered materials (**Figures 3A,B**) was analyzed using an "Ultima IV" diffractometer (Rigaku, Japan) that used monochromatic $\text{CuK}\alpha$ radiation. The sintered material consists of completely dehydrogenated α titanium matrix with orthorhombic TiB as the main boride phase and trace amounts of unreacted TiB_2 phase (**Figure 3B**). **Figure 2** clearly reveals that the reaction of TiB_2

particles with titanium and the diffusion of boron inside the matrix during high-temperature sintering forms boride crystals with various morphologies. The *in-situ* nucleated TiB phase exhibits coarse needle-like or lamellar crystals that are located mainly between and inside large titanium grains. Some irregularly-shaped gatherings of disperse boride particles exist locally, as shown in **Figure 2B**. Relatively large equiaxed boride particles, like those presented in **Figure 2C**, are identified as intermediate reaction products consisting of a mixture of TiB_2 and TiB phases (Ivasishin et al., 2019). Inhomogeneous boride redistribution within the titanium matrix produces relatively large areas (up to $60\text{--}80 \mu\text{m}$ in size) that are free of boride precipitation. The sizes of such areas correlate with that of the initial titanium hydride powder. This implies that finer starting titanium hydride powder might achieve better sintered composite microstructural homogeneity. Considerable porosity appears near boride crystals. Most pores form and aggregate directly alongside large boride clusters at the locations of initial TiB_2 particles and intermediate Ti-B reaction products.

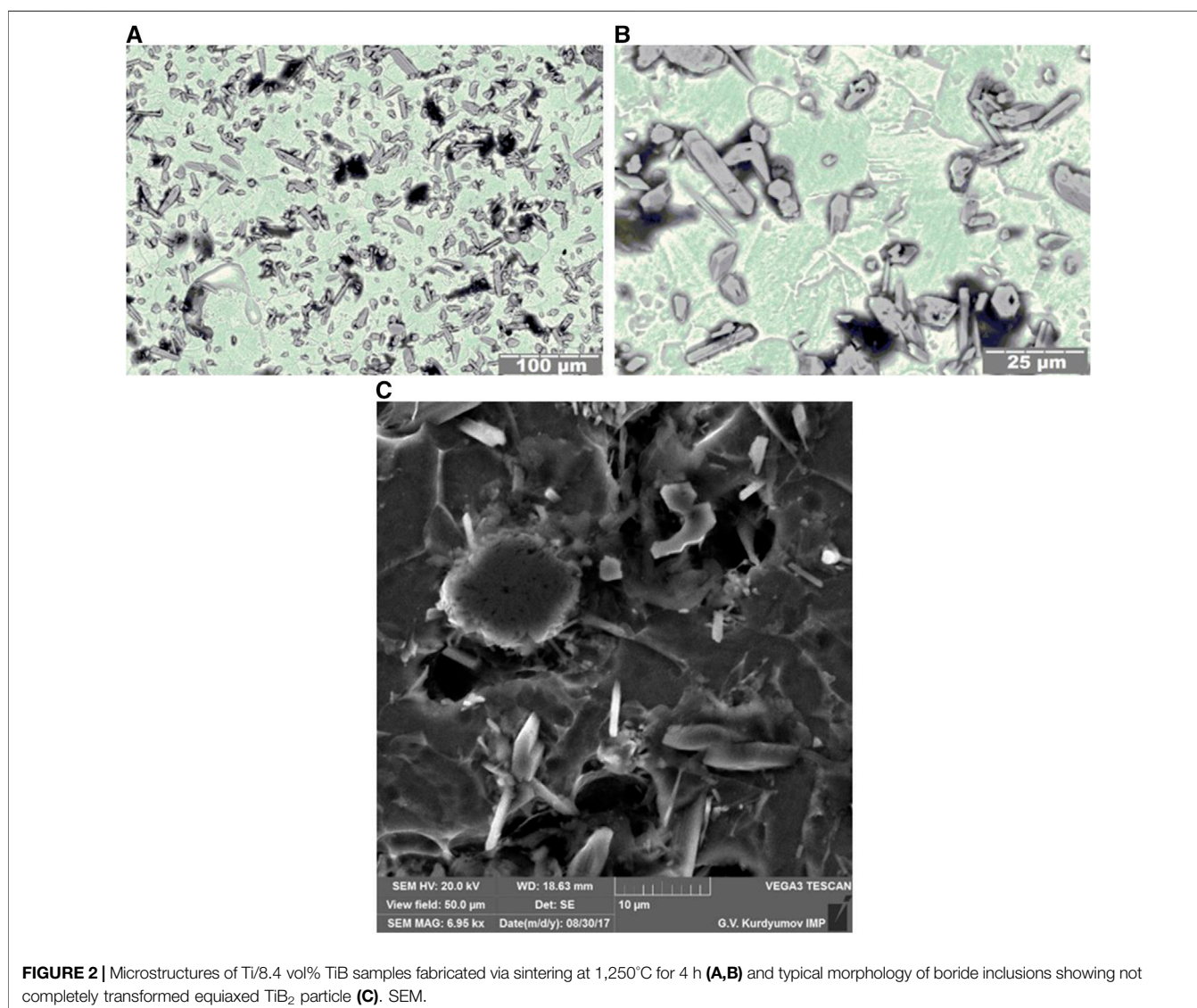
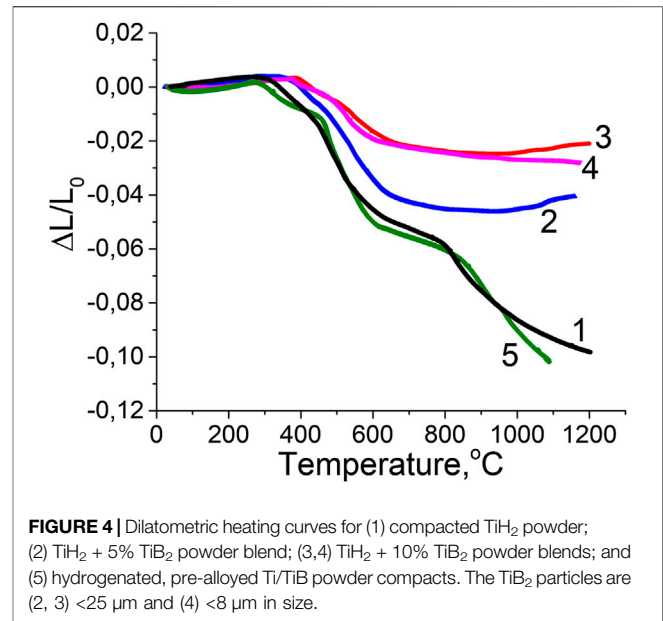
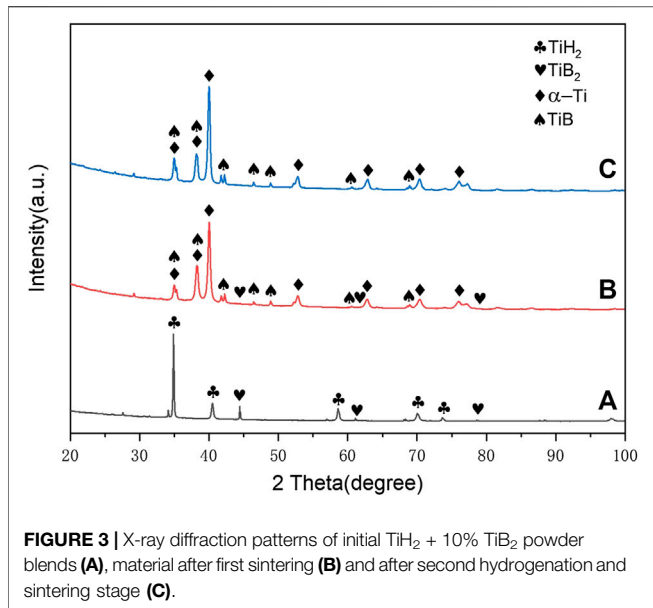


FIGURE 2 | Microstructures of Ti/8.4 vol% TiB samples fabricated via sintering at $1,250^\circ\text{C}$ for 4 h (**A,B**) and typical morphology of boride inclusions showing not completely transformed equiaxed TiB_2 particle (**C**). SEM.



To investigate the sintering kinetics and to understand the reasons for increased Ti/TiB composite porosities, *in-situ* shrinkage curves (Figure 4) were measured during vacuum heating (rate of $10^\circ\text{C}/\text{min}$) of powder compacts using a special dilatometric complex (Ivasishin et al., 2010). It is clearly seen (Figure 4) that the densification kinetics of the TiH_2 + 5% TiB_2 (curve 2) blend are worse than those of a pure TiH_2 compact (curve 1). This indicates that excess porosity forms during the heating stage. When the TiB_2 content is further increased to 10% in the powder blend (curve 3), less shrinking occurs. This indicates that there is an inverse relationship between the amount of TiB_2 used and the extent of densification. Most TiH_2 densification occurs during the dehydrogenation period. Starting when the vacuum heating process has reached approximately 300°C , the release of hydrogen atoms results in the reconstruction of the crystal lattice and significant shrinkage of each powder particle and of the entire sample due to a specific compaction mechanism that is exhibited between the particles (Ivasishin and Savvakina, 2010). Dehydrogenation is nearly complete for all samples at around $600\text{--}650^\circ\text{C}$. Phase transformations $\delta\text{-TiH}_2$ to $\beta\text{-Ti}$ and then to $\alpha\text{-Ti}$ creates a large number of crystalline defects (Ivasishin et al., 2011). This factor activates an overall diffusion that is accompanied by intensive powder sintering and $\sim 10\%$ linear reduction in total. However, as seen when comparing curve 1 with curves 2 and 3, the addition of TiB_2 particles to the titanium hydride strongly affects the shrinkage processes of the corresponding compacts, retarding densification. The presence of TiB_2 particles results in the loss of compact integrity during dehydrogenation, as well as the formation of additional gaps and voids between compacted particles at $300\text{--}650^\circ\text{C}$. When the temperature exceeds 650°C , the boride blend shrinkage intensity decreases substantially. Minor swelling even occurs when the temperature exceeds $1,000^\circ\text{C}$. These differences can be attributed to the presence of titanium diboride particles in the blend, which, unlike hydride particles, are not subject to dehydrogenation-related shrinkage. Reactions between

dehydrogenated Ti particles and TiB_2 are another reason for poor densification. Although calculations based on the densities of reacting materials indicate minor volume reductions ($\sim 1\%$) during *in-situ* formation of the TiB phase, swelling occurs because of increased porosity formation at higher boride contents. As shown in Ivasishin et al. (2019), the interfaces between TiB_2 particles and the Ti matrix are important sintering-related pore formation locations. The swelling effect observed due to this reaction strongly hinders the overall densification upon powder sintering, decreasing overall linear shrinkage from $\sim 10\%$ for TiH_2 to $\sim 4\%$ for TiH_2 admixtures that contain 5% TiB_2 and to 2% for blends that contain 10% TiB_2 .

Bulk shrinkage of TiH_2 powder particles upon hydrogen release during heating cycles creates extra interstitial spaces between the dehydrogenated titanium matrix and TiB_2 particles. These spaces further impede direct contact between the reactants, diminishing the TiB formation rate and sometimes stopping the reaction during its intermediate stages. Two more reasons for the noted excess porosity are the gap between the diffusion capabilities of titanium and boron at elevated temperatures (Baglyuk et al., 2017) and the difference between the boron diffusion velocities in TiB and TiB_2 phases. These factors can cause the formation of Kirkendall porosity during boron redistribution (Panda et al., 2003). The TiB crystals grow to form needle-like shapes via unidirectional diffusion of atomic boron. This creates a flux of vacancies in the opposite direction and forms pores, which also contribute to the swelling of the compact and the formation of residual porosity.

The presence of a particular boride cluster structure surrounded by a number of pores (Figure 2C) and the remnants of TiB_2 phase in the sintered material prove that titanium diboride is not completely reacted to single-phase titanium monoboride even after treatment at $1,250^\circ\text{C}$ for 4 h. Similar effects were observed in Ivasishin et al. (2019). Incomplete transformation of TiB_2 powder to the TiB phase can also be

induced via occasional formation of relatively coarse TiB₂ aggregates during powder blending. This also promotes the porous structure developed during heating.

Increased porosity, remnants of borides that are not fully transformed into TiB, and boride particle distribution irregularities in the titanium matrix harm the mechanical properties of the resulting composites. For example, Ti/8.4 vol% TiB with 7.5% porosity has a moderate Vickers hardness (260–270 HV) and moderate tensile characteristics (UTS = 770 MPa, elongation 2.4%). The Ti/16.8% TiB composite is completely brittle without the expected hardness increase due to its higher (~9%) porosity. For comparison, commercially pure titanium (CP-Ti) produced by sintering TiH₂ powder exhibits a hardness of 220 HV–230 HV, UTS of 570–600 MPa, and elongation of 16%–22% at a low (1.5%) residual porosity. Excessive porosity of Ti/TiB material is the main cause of premature fracture because pores serve as stress concentrators during tensile loading and hide the strengthening effect of boride particles during hardness testing. The strengthening potential of TiB particles cannot be used when the resulting composites exhibit excessive porosities.

EFFORTS TO REDUCE POROSITIES BY VARYING BLENDED ELEMENTAL POWDER METALLURGY PROCESSING PARAMETERS

Since high porosity of sintered Ti/TiB composite porosities, incomplete TiB₂ → TiB transformation, and non-uniform distribution of TiB crystals in the titanium matrix all contribute to property degradation, significant efforts were dedicated to improving as-sintered microstructures by varying press-and-sinter BEPM parameters. Smaller starting powders, higher temperatures, and longer sintering durations were tested. All such efforts are summarized in **Table 1**, taking Ti/8.4% TiB composite as an example. A basic set of parameters was taken, as described above.

Changing the types and sizes of starting powders did not result in a noticeable microstructural improvement. Since TiB₂ powder is responsible for compromised densification, a finer starting TiB₂ powder (<8 μm) was tested via dilatometric experiments (**Figure 4**, curve 4). Although the decreased boride powder size leads to some better shrinkage behavior at high temperatures (compare curves 3 and 4 in **Figure 4**), the final porosity is not considerably reduced (**Table 1**, #2). A minor decrease in as-sintered porosity is also observed in Stasiuk (2019)

when smaller TiH₂ powder particles are used (**Table 1**, #3). These experiments cannot reduce the average residual porosity below 5%–6%. As expected, the use of HDH titanium powder sieved to less than 100 μm (i.e., with a particle size distribution similar to that of the TiH₂ powder presented in **Figure 1**) results in even worse densification, similar to that observed in Baglyuk et al. (2017), and an increase in residual porosity to 9% for the Ti/8.4% TiB composite (**Table 1**, #6).

Increasing the temperature to 1,350°C and extending the sintering cycle duration to 8 h has a minor effect on porosity reduction (**Table 1**, #4–#5), while completion of TiB formation improves only slightly. To conclude, substantial improvement of Ti/TiB composite microstructures requires a different technique that includes more revolutionary changes to the manufacturing process.

PRODUCTION OF LOW-POROSITY COMPOSITES VIA THE BLENDED ELEMENTAL POWDER METALLURGY + PRE-ALLOYED DOUBLE HYDROGENATION/DOUBLE SINTERING METHOD

The idea for this process modification comes from the relatively good Ti/TiB composite PA powder metallurgy results in Tamirisakandala et al. (2004). It has already been mentioned that the disadvantage of the PA approach is that it requires melting for powder fabrication and further complex operations to consolidate hard, crystallized powders. In contrast, processing can be simplified significantly if the above-described BEPM solid-state sintered Ti/TiB composites are used as a specific grade of PA material for further production of PA powders and these resulting PA powders are then used in a second press-and-sinter stage.

In two-stage BEPM + PA processing, the non-uniform Ti/TiB obtained during the first sintering stage is further mixed via crushing. This promotes better boride-phase distribution uniformity in the resulting PA powder. Moreover, the absence of the TiB₂ → TiB reaction during subsequent sintering of the PA powder can improve densification as compared to the initial TiH₂ + TiB₂ powder blends. However, the problem with this processing route is the insufficient sintered Ti/TiB composite crushing ability. This hinders the production of PA powders of desirable sizes. Despite the considerable porosities of the Ti/TiB composites produced during the first sintering stage and the presence of brittle boride particles, the titanium matrix plasticity allows the material to be deformed instead of crushed. Transformation of bulk

TABLE 1 | Microstructural characteristics of Ti/8.4% TiB composites produced with various press-and-sinter BEPM parameters.

#	Parameter variation	Average residual porosity, %	Effect on completion of TiB formation	Effect on TiB uniformity improvement
1	Basic set of parameters	7.5	—	—
2	Finer TiB ₂ powder (<8 μm)	5	+	-
3	Finer TiH ₂ powder (<63 μm)	6	-	+
4	Increased sintering temperature (1,350°C)	6	+	-
5	Longer sintering time (8 h)	7	+	-
6	Substitution of TiH ₂ with Ti HDH powder of the same size	9	-	-

as-sintered product into PA powders smaller than 100 μm requires long, intensive milling processes that lead to excessive contamination of the powders.

Hydrogenation of the Ti/TiB composite obtained during the first sintering stage was proposed to overcome the problems described above. This operation was intended to be the main feature of the modified process. Hydrogenation would make the Ti/TiB composite material brittle and reduce its strength, just as it affects titanium. Non-uniform, porous composite materials saturated with hydrogen would be crushed easily into composite powders of desirable sizes. Utilization of a hydrogenated, pre-alloyed powder in a second press-and-sinter stage would promote a positive influence of hydrogen on densification and hydrogen cleaning of powder once more to produce uniform, low-porosity composite structures. This approach is validated via the experimental results described below.

The Ti/TiB material hydrogenation process was thoroughly investigated and optimized based on Sieverts method, which demonstrated active hydrogen consumption above 425°C. The Ti/TiB composite obtained by sintering of the $\text{TiH}_2 + 5 \text{ wt}\% \text{ TiB}_2$ blends (1,250°C for 4 h) was saturated with hydrogen at 600°C and 0.6 MPa. Thus, the titanium matrix reverts to a $\delta\text{-TiH}_x$ lattice structure according to the X-ray data. The substantial volume change associated with this leads to stress accumulation and crack nucleation in the bulk sintered composites. As shown in **Figure 5**, wide cracks extend throughout the sintered compacts and fractures form and grow along intergranular positions.

Because of the brittle, low-strength nature of the hydride composite and ceramic reinforcement of the titanium boron compound, the sintered compacts were readily broken up and ground into powders with desirable dimensions after quick (10 s)

milling in a planetary mill. **Figure 6** shows the resulting hydrogenated pre-alloyed powders after milling. The particles of irregular morphologies are fractured during further compaction and mechanically locked to each other with the formation of dense compacts via close powder stacking. Furthermore, large TiB whiskers and incompletely reacted remnants of the initial TiB_2 powders are crushed and blended with the matrix phases, creating a prerequisite for the complete formation and homogeneous distribution of the titanium monoboride phase during the second sintering stage. The resulting PA powder was pressed into compacts at 600 MPa and sintered again using the same parameters (1,250°C for 4 h) to form the final Ti/TiB composite.

Neither TiB_2 nor other Ti-B phases were identified after the second sintering step (**Figure 3**). The intensities of the TiB peaks are enhanced after the second sintering step. This indicates that transformation to TiB is complete. Titanium hydride phases are not found in the composite after the second sintering step. This demonstrates that hydrogen has completely escaped from the base material during heating. The above X-ray findings are in accordance with our microstructure observations.

As shown in **Figure 7**, after hydrogenation of pre-sintered material and the second press-and-sinter operation, porosity is reduced from over 7.5% to nearly 2.2%, which is acceptable. The density improvement from 4.16 to 4.41 g/cm^3 corroborates this observation. The average pore size also decreases. This promising result is in line with dilatometric studies where hydrogenated, pre-alloyed powder compacts (**Figure 4**, curve 5) exhibit shrinkage trends similar to those for pure TiH_2 (curve 1). Hydrogen desorption from hydrogenated, pre-alloyed Ti/TiB compacts is observed at the same temperature range as for

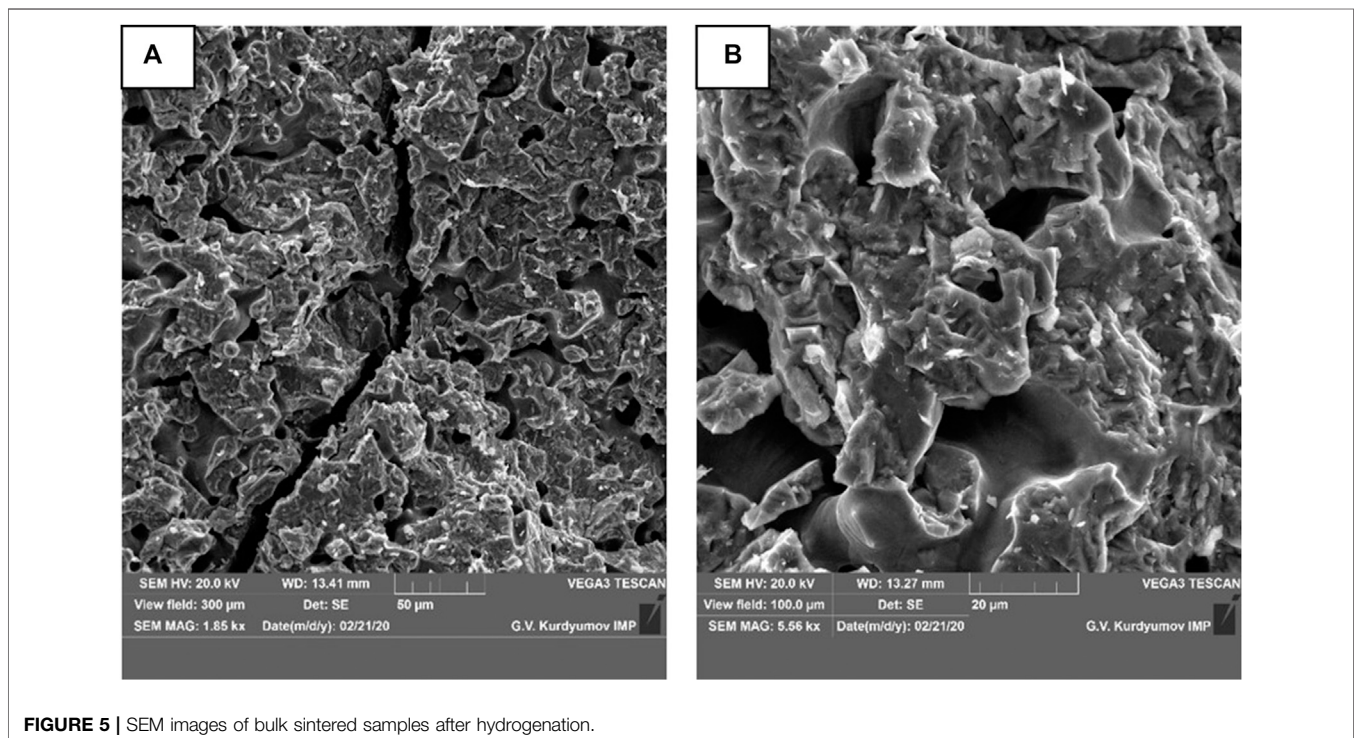


FIGURE 5 | SEM images of bulk sintered samples after hydrogenation.

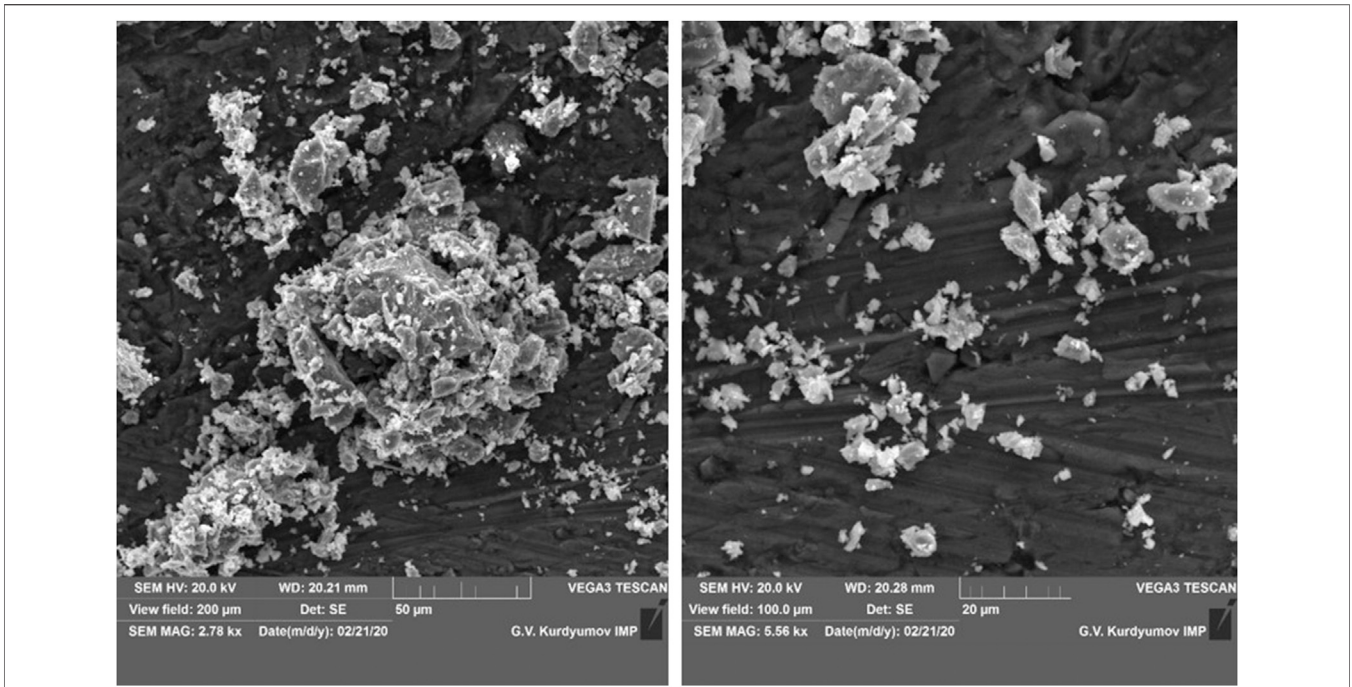


FIGURE 6 | SEM images of hydrogenated pre-alloyed powders.

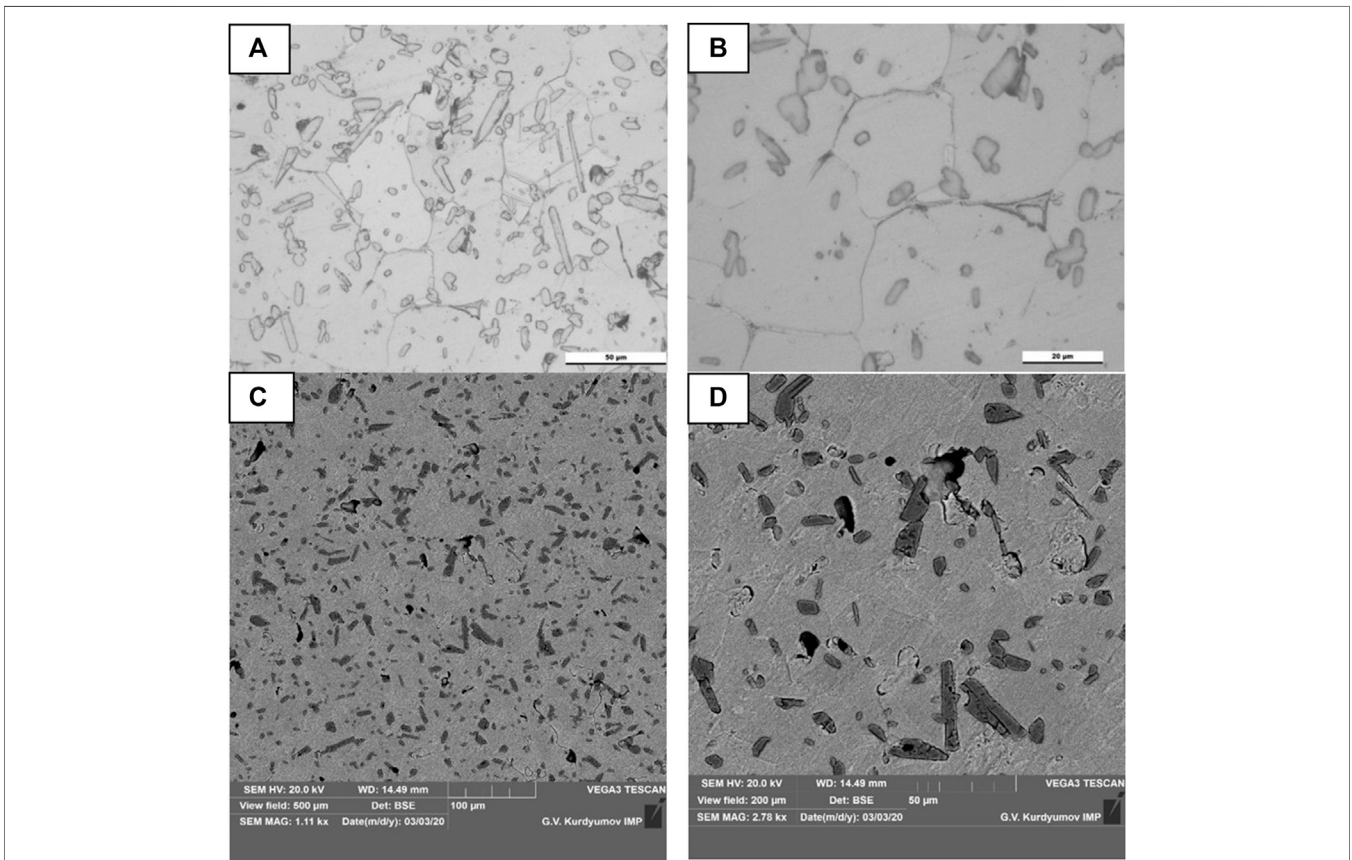
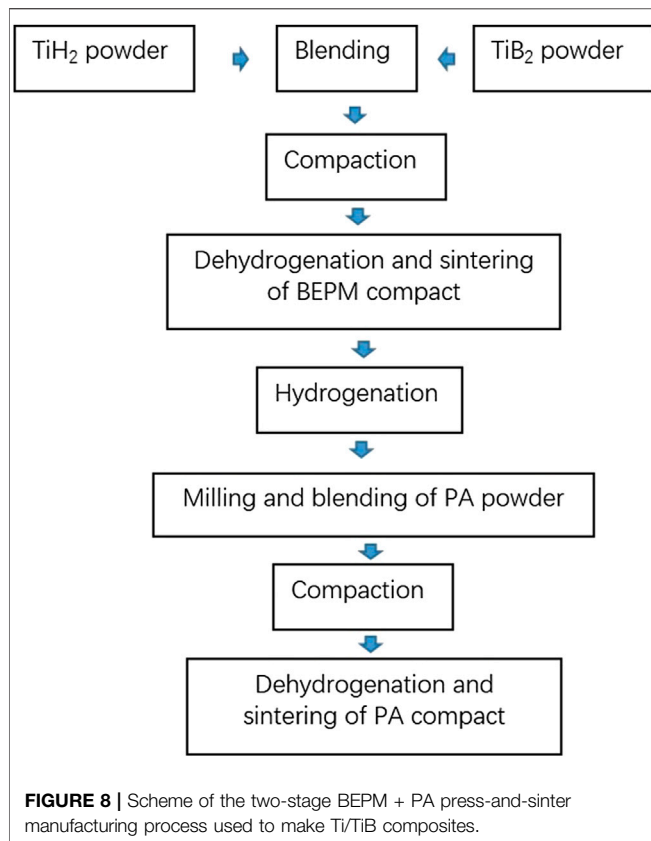


FIGURE 7 | Low-porosity microstructure of the Ti/8.4 vol% TiB composite after a second sintering stage performed at 1,250°C for 4 h.



titanium hydride powder (300–700°C) and results in analogous compact shrinkage during dehydrogenation (curves 5 and 1 in **Figure 4**). The apparent shrinkage difference between curve 5 and curves 2–4 demonstrates that the considerably more intense densification of the hydrogenated pre-alloyed powder compact naturally results in low residual porosities after isothermal exposure at 1,250°C. The presence of boron mainly as a TiB phase embedded into hydrogenated titanium powder provides better densification kinetics than those observed with the TiB₂ + TiH₂ powder blend during dehydrogenation (curves 5 and 2 in **Figure 4**). The absence of a pronounced Ti + TiB₂ → 2TiB reaction above 900°C in the pre-alloyed Ti/TiB compact minimizes factors that negatively affect densification and reduce porosity.

The second sintering stage improves the TiB reinforcement distribution uniformity in the Ti matrix considerably and produces a grain size of approximately 40 μm (**Figure 7**). Finer TiB particles are attained and uniformly distributed among the α-Ti grains in equiaxial or whisker morphologies, as shown in **Figure 7**. The markedly reduced residual porosity is observed with few voids near single TiB particulates (**Figure 7D**). The two-stage hydrogen-assisted processing schematically summarized in **Figure 8** significantly contributes to the tailored microstructures and composite homogeneity.

Vickers hardness tests were carried out using a Wolpert Wilson 452 SVD hardness meter in order to provide preliminary evaluations of the mechanical properties of the Ti/8.4 vol% TiB composites fabricated using the present approach. The hardness values obtained demonstrate that the

proposed hydrogen-assisted two-stage BEPM + PA approach contributes to a nearly 50% increase in hardness (390–410 HV) relative to the traditional one-step BEPM press-and-sinter route (260–270 HV). This is a clear reflection of the finer grain size, minimized residual porosity, and better TiB redistribution uniformity in Ti/TiB composites fabricated via the hydrogen-assisted BEPM + PA technique. The Ti/TiB composite hardness values suggest the feasibility of this manufacturing approach for practical use.

CONCLUSIONS

- (1) BEPM press-and-sinter manufacturing of Ti/TiB composites using TiH₂ + TiB₂ powder blends results in highly porous structures, non-uniform distribution of borides throughout the titanium matrix, and incomplete *in-situ* transformation of TiB₂ into the TiB phase. Addition of TiB₂ particles to TiH₂ powder hinders densification kinetics because of the loss of compact integrity that results from differences in the powder constituent volume changes that occur during the hydrogen emission stage. Development of a high-temperature *in-situ* Ti + TiB₂ → TiB reaction is another reason for poor densification.
- (2) The microstructures of BEPM-produced Ti/TiB composites could not be markedly improved via optimization of press-and-sinter processing parameters, such as powder size or the sintering time-temperature regime.
- (3) A new approach was developed based on the hydrogen-assisted two-stage press-and-sinter BEPM + PA method. The microstructurally and chemically non-uniform, highly porous Ti/TiB composite received after the first sintering stage was hydrogenated again to produce PA powder. The second stage of processing focuses on sintering the hydrogenated PA powder. This finally produces a Ti/TiB composite with improved densification kinetics, as well as the desired chemistry and microstructure.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

YS and OS conceived and designed the study and experiment plan and performed the experiments. YS wrote the paper. YS and SD analyzed the experiment result. DS and OI reviewed and edited the manuscript. All authors read and approved the manuscript.

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Conflict of Interests: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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