Metallophysics and Advanced Technologies
Металофіз. новітні технол.
Metallofiz. Noveishie Tekhnol.
2022, vol. 44, No. 2, pp. 211–222
https://doi.org/10.15407/mfint.44.02.0211
Reprints available directly from the publisher

CRYSTAL-LATTICE DEFECTS

PACS numbers: 61.43.Gt, 61.72.-y, 62.20.-x, 81.05.Mh, 81.20.Ev

Comparative Study of Microstructure and Characteristics of Ti6Al4V/TiB Composites Manufactured with Various Powder Metallurgy Approaches

Yuchao Song[*,**], Oleksandr Stasiuk[*,**,***], Dmytro Savvakin[*,**,***], Orest Ivasishin[*,**,***], and Xiaofeng Xu[*,**]

[*]*College of Materials Science and Engineering, Jilin University, CN-130012 Changchun, China*
[**]*International Center of Future Science, Jilin University, CN-130012 Changchun, China*
[***]*G. V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine, 36 Academician Vernadsky Blvd., UA-03142 Kyiv, Ukraine*

In this work, Ti6Al4V-based composites reinforced with TiB phase are comparatively synthesized by three powder metallurgy approaches: press-and-sintering of powder blends; hydrogen assisted 2-stage sintering and sintering of powders preliminary activated by milling procedure. The simplest cold compaction and vacuum sintering of TiH_2-based powder blends with Al–V master alloy (MA) and TiB_2 powder additives is used as reference approach. It results in the formation of porous Ti6Al4V matrix with inhomogeneous distribution of partially reacted boride phases. Such microstructure is not appropriate to ensure sufficient mechanical characteristics of produced composites. To achieve desirable highly dense composite microstructures with evenly distributed needle-shape TiB reinforcements, two other manufacturing approaches are comparatively tested. Hydrogen assisted 2 stage sintering is based on hydrogenation of not uniform porous composite product obtained after first press-and-sintering cycle, its milling to produce hydrogenated composite powders which are subjected to second compaction and sintering cycle. The alternative approach includes activation milling of HDH-Ti pow-

Corresponding author: Dmytro Savvakin
E-mail: savva@imp.kiev.ua

Citation: Yuchao Song, Oleksandr Stasiuk, Dmytro Savvakin, Orest Ivasishin, and Xiaofeng Xu, Comparative Study of Microstructure and Characteristics of Ti6Al4V/ TiB Composites Manufactured with Various Powder Metallurgy Approaches, *Metallofiz. Noveishie Tekhnol.*, **44**, No. 2: 211–222 (2022).
DOI: 10.15407/mfint.44.02.0211

der with TiB_2 additives, following blending with TiH_2 and MA powders, compaction and sintering operations. Both methods ensure activated sintering of powders, improves density, microstructure uniformity and mechanical characteristics of produced composites compared to reference manufacturing approach. Among all studied manufacturing approaches, Ti6Al4V/TiB composite produced with activating milling of powders exhibits the best mechanical performances owing to combination of reduced porosity, microstructure uniformity and acceptable impurity content.

Key words: titanium matrix composites, powder metallurgy, press-and-sinter, titanium boride, hydrogenation, microstructure, porosity.

В даній роботі композити на основі стопу Ti6Al4V, зміцненого фазою TiB, для порівняння синтезовано трьома порошковими технологіями: пресуванням та спіканням порошкових сумішей, двостадійним спіканням із застосуванням водневого впливу на матеріал та спіканням із попередньою активацією порошків розмелюванням. Найпростіший метод холодного пресування та спікання сумішей на основі TiH_2 із ліґатурою Al–V та порошком TiB_2 використано як стандартний для порівняння. Даний метод формує пористу матрицю Ti6Al4V з нерівномірним розподілом боридних фаз, що частково прореагували, така мікроструктура не забезпечує достатні механічні характеристики композиту. Для досягнення бажаної малопористої та однорідної мікроструктури композиту з дрібними частинками фази TiB, у порівнянні досліджено ще два підходи. Двостадійне спікання з використанням водневого впливу полягає у наводненні неоднорідної пористої композитної структури після першого спікання, та розмелювання для отримання композитного порошку, який пресували та спікали повторно. Альтернативним підходом є активація розмелюванням порошків титану та TiB_2 з наступним змішуванням з порошками TiH_2 та ліґатурою, компактуванням і спіканням. Обидва методи забезпечують активоване спікання порошків з підвищенням густини композиту, однорідною мікроструктурою та покращеними механічними характеристиками порівняно із стандартним методом виробництва композиту. З усіх вивчених методів отримання композит Ti6Al4V/TiB, одержаний з активаційним розмелюванням порошків, демонструє кращі механічні характеристики завдяки комбінації низької залишкової пористості, однорідності мікроструктури та прийнятного вмісту домішок.

Ключові слова: титаноматричні композити, порошкова металургія, пресування та спікання порошків, борид титану, гідрування, мікроструктура, пористість.

(Received December 13, 2021)

1. INTRODUCTION

Titanium matrix composites (TMCs) doped with hard ceramic particles have been proved to be promising materials for commercial applications such as aerospace, automotive, and advanced defence areas, ow-

ing to their improved mechanical properties and excellent peculiarities at elevated temperature [1]. Compared to *ex-situ* manufacturing routes with direct addition of reinforcements into titanium-based matrix, *in-situ* formation of reinforcing phase particles is preferred in fabrication of TMCs due to clean and strong bonding interface between matrix and formed reinforcements [2]. A review of previous researches shows that TiB phase can be identified as one of the most compatible reinforcements for TMCs, exhibiting high Young modulus, brilliant thermal stability and similar thermal expansion behaviour with titanium matrix [3]. Therefore, considerable research interests have been drawn on in situ fabrication of TMCs reinforced with TiB.

Among various manufacturing methods based on casting [4] and powder metallurgy [5–11] approaches including hot isostatic pressing [5] and spark plasma sintering (SPS) [6–8] technologies, blended elemental powder metallurgy (BEPM) has received long-time attentions as a cost-effective method to fabricate TMCs with desirable microstructure and characteristics with high raw material utilization ratio. On the other hand, it has been proved that the adoption of cheap titanium hydride (TiH_2) powders instead of conventional titanium powders in simplest press-and-sinter manufacturing of Titanium-based alloys can not only further expand the cost advantages of BEPM route, but also improves the densification of powder compacts in heating cycle and reduces content of impurities in sintered alloys, thus, providing high mechanical characteristics [12–14]. In such approach, hydrogen is used as temporary alloying element which is evacuated from titanium on heating, simultaneously resulting in acceleration of diffusion, activated homogenization and densification of powder compacts. However, early trials on employment of TiH_2-based powder blends in BEPM press-and-sinter processing of titanium composites reinforced with TiB are less successful [15–17]. Porous microstructure of sintered matrix with not evenly distributed boride clusters resulted in the inferior mechanical performance of such composites.

The main objective of this work is to develop powder approaches ensuring formation of nearly dense and uniform composites on the base of Ti6Al4V alloy matrix reinforced with TiB particles without application of pressure during sintering. To activate formation of desirable composite microstructure, hydrogen assisted double compaction-double sintering and preliminary activation of powders by milling are tested in manufacturing process to compare microstructure and mechanical properties of produced composites.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

In the present research, to produce composite on the base of Ti–6Al–4V (% wt.) alloy matrix with 10% vol. TiB reinforcing phase, TiH_2

powder (3.5% wt. H, less than 88 μm), titanium HDH-Ti (44–88 μm), 60% Al–40% V master alloy (MA) (less than 88 μm) and TiB_2 (~10 μm) powders are adopted as starting materials. Figure 1 shows the actual particle distribution of corresponding raw powder particles. Three different processing routes are comparatively used for composite manufacturing to study their microstructure and characteristics.

Composite produced by simplest press-and-sinter BEPM approach (Fig. 2, *a*, indicated by dashed frame) is used as reference material. In this approach, TiH_2, MA and TiB_2 powders are blended in corresponding ratios in a V-type mixer at 90 rpm for 6 hours; powder blends are die pressed under 600 MPa. The obtained compacts are subjected to standard vacuum sintering procedure (1250°C, 4 h) at 10°C/min heating rate and furnace cooling to produce dehydrogenated composite material. As revealed by Fig. 2, *a*, such press-and-sintering process can be regarded as pre-sintering stage in hydrogen assisted 2 stage (double compaction–double sintering) route. Following this flow chart, the

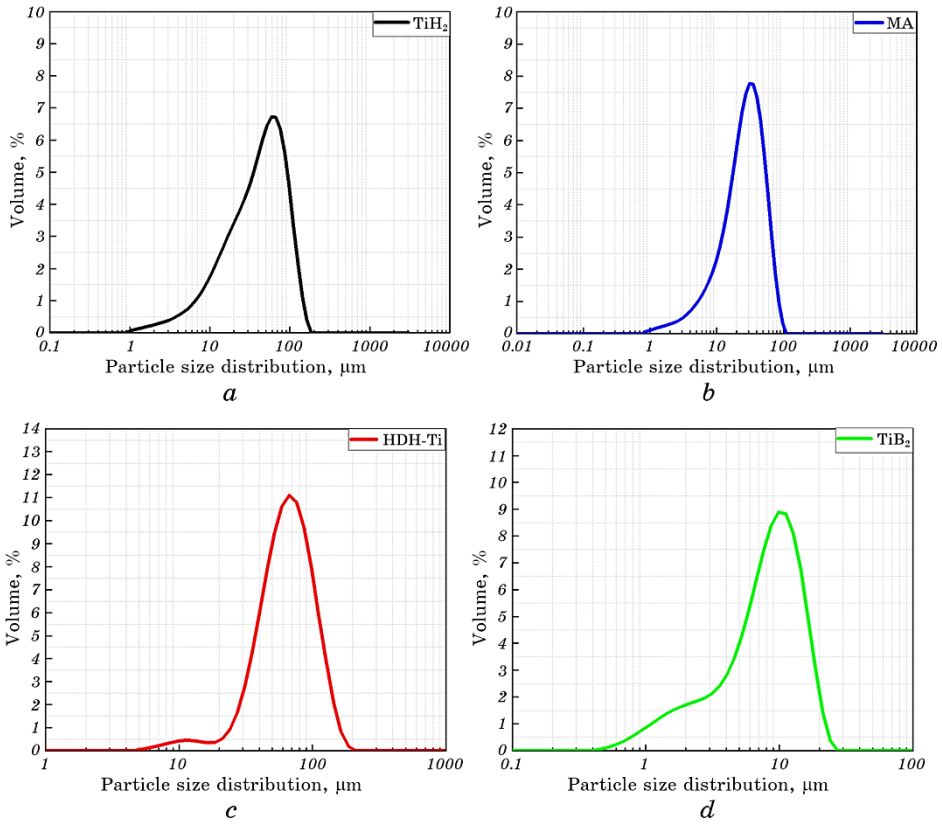


Fig. 1. Particle size distribution of the starting powders: TiH_2 (*a*), MA (*b*), HDH-Ti (*c*), TiB_2 (*d*).

sintered (reference) materials are then hydrogenated again in temperature range of 400–600°C and ball milled under argon atmosphere to obtain hydrogenated pre-alloyed composite (PA) particles less than 88 μm in size, which are used in second press-and-sintering stage (Fig. 2, *a*). For such two stage hydrogen assisted process, milling of hydrogenated pre-sintered composites ensures better uniform redistribution of fine boride particles in powder ensemble, while at second sintering stage hydrogen contributes again to activate densification and promotes formation of low porous composites.

To achieve better densification of composite, alternative approach (Fig. 2, *b*, hereinafter noted as milling-blending approach) includes initial low energy milling of HDH-Ti and TiB_2 powders at 200 rpm for 4 hours under argon atmosphere protection. Such additional processing step should result in embedding of hard TiB_2 particles into soft and ductile titanium particles, resulting in close interfaces and good bonding of their surfaces. Thus, contact of TiB_2 particles with titanium should be better than with hard and brittle TiH_2 particles, ensuring better diffusion and activated reaction at interfaces with lower porosity formation. The milled titanium and diboride powders are then blended for 6 h with TiH_2 and MA powders in required ratios. Finally, blend is compacted and sintered to produce composite structure (Fig. 2, *b*).

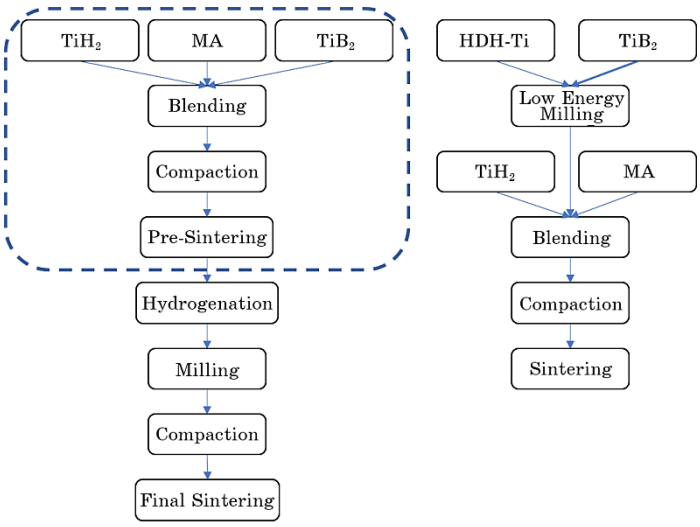


Fig. 2. Processing flow charts for Ti6Al4V/TiB composites: hydrogen assisted 2 stage press-and-sintering process, where composite produced after first stage (within dashed frame) is used as reference material (*a*), milling–blending approach which includes preliminary activation of powders by milling (*b*).

Microstructure evolution and phase composition during processing steps are investigated by light microscopy (LM, LEICA DMI8A), scanning electron microscopy under both BSE and SE modes (SEM, JSM-IT500A) and X-ray diffraction (XRD, Rigaku, Japan). The distilled water immersion method is used to evaluate the bulk density of sintered composites. Porosity status is based on the ratio of theoretical density value and actual density results. Hardness values are measured by a hardness tester (HV 1000-IS). An automatic universal testing machine is adopted to room temperature compressive test on cylindrical samples (6 mm in diameter and 9 mm in height) at a constant crosshead speed of 60 μm/min following the ASTM standards. Impurity contents in sintered samples are determined by LECO ONH 836 tester. At least three measurements are taken for each of abovementioned tests to ensure the accuracy of results.

3. RESULTS AND DISCUSSION

X-ray diffraction patterns of Ti–6Al–4V/10% vol. TiB composites fabricated with used powder technologies are shown in Fig. 3. The presence of α- and β-titanium, and TiB diffraction peaks without traces of TiH_2 for all sintered materials indicates that dehydrogenation of

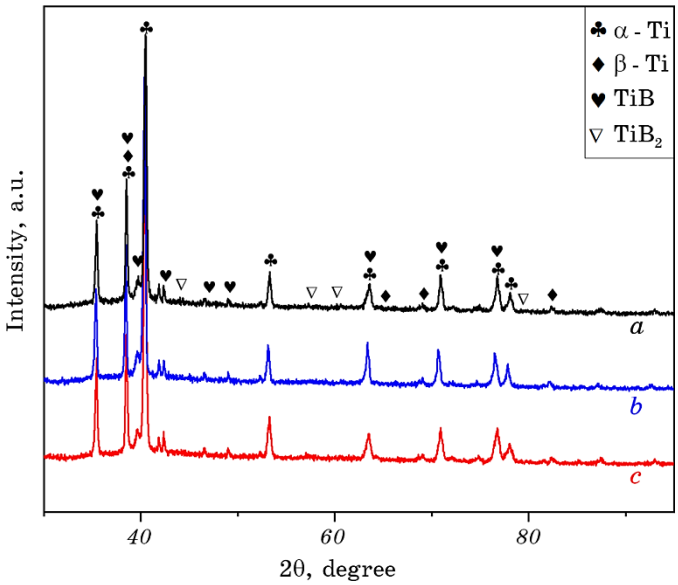
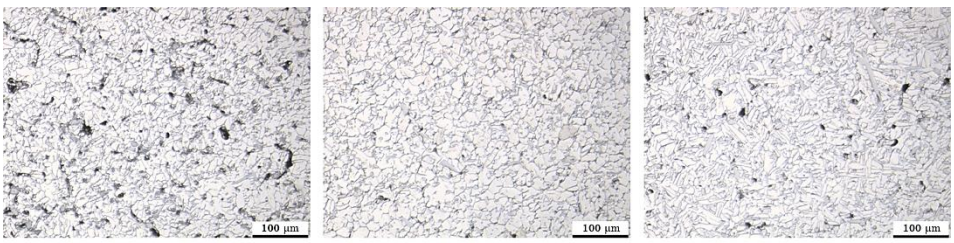


Fig. 3. X-ray diffraction pattern of sintered composites with varied powder technologies: press-and-sintering (reference approach) (*a*), hydrogen assisted 2 stage sintering (*b*), milling–blending approach (*c*).

TiH_2 has been completed with formation of $\alpha + \beta$ phase composition of the titanium matrix and the reaction $TiB_2 + Ti \rightarrow TiB$ between TiB_2 additives and matrix has occurred. However, traces of TiB_2 peaks found in X-ray diffraction patterns for reference press-and-sintered samples (Fig. 3, *a*) declare the presence of partially reacted boride inclusions. In contrast, peaks of the TiB phase became more intense with absence of TiB_2 in Fig. 3, *b*, *c*, revealing that the TiB_2 additives transformed entirely into the TiB phase following noted reaction under 2 stages sintering or with applying activated milling of HDH-Ti and TiB_2 powders. LM and SEM microstructure observations (Figs. 4, 5) are entirely consistent with the above X-ray diffraction analysis.

As shown in Fig. 4, *a* and Fig. 5, *a*, *d*, coarse pores and boride clusters are observed in lamellar ($\alpha + \beta$) matrix for composite manufactured following reference approach. Large TiB needles precipitated and growed into matrix grains, while equiaxed boride particles which can be remnants of raw TiB_2 powder are observed along grain boundaries and accompanied with residual voids. Fig. 5, *d* illustrates the 'sea-urchin' like morphology of partially reacted boride particles surrounded by residual voids. Observed variations in boride morphology are due to the reactions between varied sizes of TiB_2 particles and titanium and one-way boron diffusion into titanium matrix. Contrary, composite produced following 2 stage hydrogen assisted sintering (Fig. 5, *b*, *e*) demonstrates finer short bar or needle-like TiB particles evenly distributed in the low porous matrix. So, it is confirmed, ball milling procedure after first sintering promotes the breaking of large boride particles and their clusters with redistribution of borides over the powder system and, hence, in matrix after second sintering. Temporary saturation of titanium alloy matrix with hydrogen induced $\alpha + + \beta \rightarrow TiH_2 \rightarrow \alpha + \beta$ phase transformations, inspiring high density of crystal lattice defects, which accelerates diffusion and activates the overall densification process during 2nd sintering stage. Homogeneously distributed fine precipitations of TiB phase act as inhibitors for excessive β grain



a *b* *c*

Fig. 4. Microstructures of composites produced with different approaches: press-and-sintering (reference) (*a*), hydrogen assisted 2 stage sintering (*b*), milling–blending approach (*c*).

growth on sintering, while subsequent slow furnace cooling results in the formation of thick (nearly equiaxed) α crystals inside the refined β grains. In comparison, samples sintered using milling-blending procedure (Fig. 2, *b*) exhibit typical (α + β) lamellar microstructure of alloy matrix with few pores detected (Fig. 5, *c*, *f*). It should be mentioned that TiB needles with varied thickness and length evenly distributed in the matrix with seldom agglomerations (Fig. 5, *c*) are observed with this manufacturing approach.

It can be easily deducted that preliminary milling of HDH-Ti and TiB_2 powders enables deformation of large Ti particles with covering of their surface with relatively fine TiB_2 additives, which means increased contacting areas between matrix and TiB_2 with sufficiently increased Ti sources for TiB formation during further sintering. Because of brittle and low-strength TiH_2 powder is crushed for fine fragments on compaction, blending of TiH_2 powder with milled (HDH-Ti + TiB_2) particles promotes better filling of the voids between large HDH-Ti particles during compaction, and, hence, achievement of higher density of compacts. Also, addition of titanium hydride purifies the overall powder compact with atomic hydrogen evolved during dehydrogenation process and creates condition for diffusion activation between dehydrogenated titanium and MA particles. In this way, formation of porosity due to reaction of TiB_2 with matrix and Kirkendall's porosity

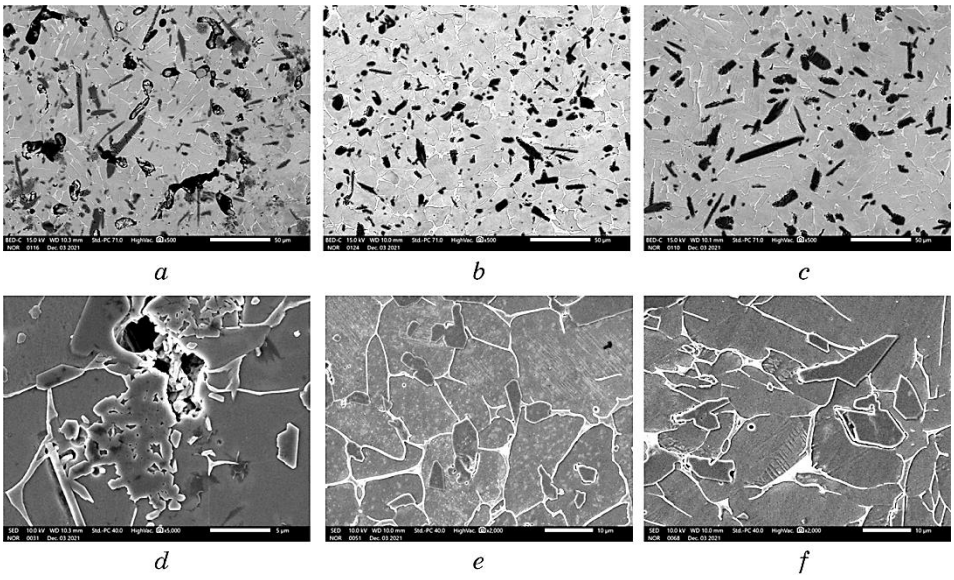


Fig. 5. Microstructures (SEM) of sintered composites produced with different approaches: press-and-sintering (reference) (*a*, *d*), hydrogen assisted 2 stage sintering (*b*, *e*), milling–blending approach (*c*, *f*).

due to mutual diffusion between titanium and MA particles is effectively inhibited.

Figure 6 shows the hardness and porosity variations for composites manufactured with different processing routes. Excessive porosity (~7%) and not uniformly distributed boride phases of various size are the main reasons for the poor hardness (~260 *HV*) for press-and-sintered reference composite. Reduced compressive strength of such composite is accompanied with relatively high compressive strain (Fig. 7). At the same time, the lowest impurity content observed for reference material (Table 1) among all studied composites promotes highest compressive strain characteristic (Fig. 7). It is apparent that application of both 2 stage sintering and milling–blending–sintering approaches are effective in pore healing and hardness improving. The absence of large pores and boride agglomerations after second sintering stage plays distinctive role in enhancing the hardness results. However, the impurity contents listed in Table 1 and compressive properties shown in Fig. 7 reveals the abnormal impurity pick-up (oxygen contents nearly doubles from 0.32% wt. to 0.67% wt., while nitrogen content is increased to more than 0.2%) which can be another reason for hardness and compressive strength improvement but loss in compressive strain for samples after 2nd sintering. Hence, the extended processing route for hydrogen assisted 2 stage sintering (including additional hydrogenation, milling, compaction and sintering operations) enables more risks for material contamination with atmospheric impurities. It is apparent that the expected hydrogen cleaning effect during hydrogenation and dehydrogenation processes in 2nd sintering cycles is

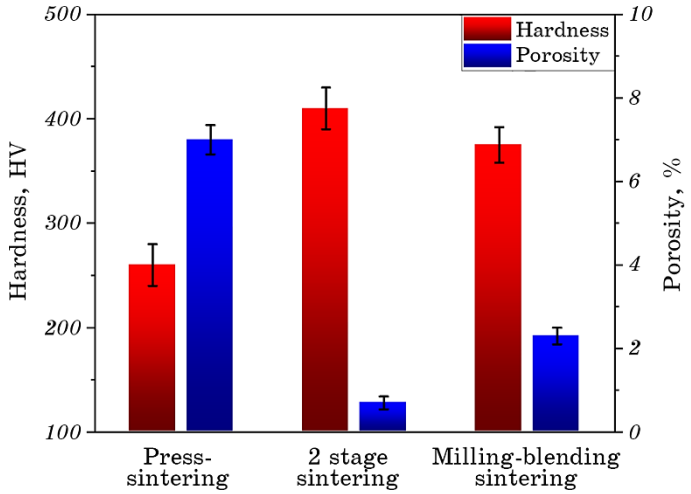


Fig. 6. Hardness and residual porosity characteristics of composites produced with used approaches.

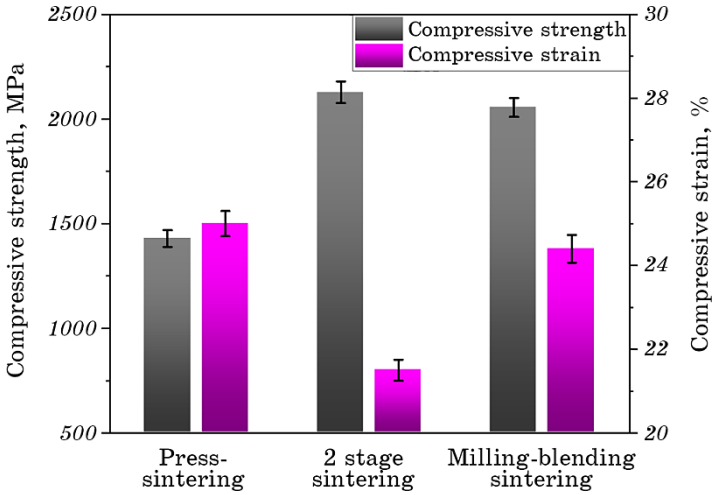


Fig. 7. Compressive characteristics of composites produced with used approaches.

overpassed by excessive environment pollutions. Although intensive impurity controlling strategy can be adopted to lower the impurity contents, thus improving mechanical properties, these extra treatments, however, will negatively impact the production efficiency with extra expenditures.

On the other hand, sintered composite produced with milling–blending approach exhibits obvious improvement in hardness and reduced porosity with slight rise in impurity contents when compared with reference composite material as revealed by Fig. 6 and Table 1. The obtained highly dense microstructure (reduced porosity of 2.3%) and evenly distributed TiB needles support the improved hardness performance (~375 *HV*). The relatively simple and short milling–blending processing route with one step sintering and hydrogen cleaning effect

TABLE 1. Impurity (O, N, H) contents of Ti6Al4V/10% TiB composites produced following used various processing.

Processing	Oxygen, % wt.	Nitrogen, % wt.	Hydrogen, % wt.
Press-and-sintering (reference)	0.32	0.022	0.0021
Hydrogen assisted 2 stage sintering	0.67	0.236	0.0017
Milling–blending + sintering approach	0.35	0.027	0.0061

on material engages acceptable impurity contents for composite produced. Distinctive increase in compressive strain (from ~21.5% to ~24.4%) as shown in Fig. 7 can be good demonstration for the obvious advantages of milling–blending approach when compared to hydrogen assisted 2 stage sintering. Since the porosity level for the two promoted processings are similar, so the slightly lower compressive strength obtained by milling-blending approach (2055 MPa) can be explained by lower content of oxygen and nitrogen impurities.

4. CONCLUSIONS

In this paper, the effects of various powder metallurgy processing routes on microstructure and characteristics of Ti6Al4V–10% TiB composites are investigated, and the conclusions are drawn as follows.

Press-and-sintering BEPM process results in enhanced residual porosity and not homogeneously distributed boride clusters in produced composites. These characteristics lead to poor hardness and compressive strength.

Nearly dense composite microstructure with evenly distributed finer TiB needles is produced with hydrogen assisted 2 stage sintering approach. Significant improvement in hardness and compressive strength can be attributed to low residual porosity, formation of refined microstructure and high impurity content. However, the poor compressive strain is unwanted result due to enhanced oxygen and nitrogen contents.

An alternative way to produce desirable composite microstructure is activation of *in situ* TiB phase formation with preliminary milling of powders. Combination of powder milling, blending, cold compaction and sintering operations is effective in fabrication of highly dense composites with uniform microstructure and acceptable impurity contents. Such material demonstrates promising combination of high hardness, compressive strength and ductile characteristics intending potential for practical applications.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from the International Centre of Future Science, Jilin University, China and the National Academy of Sciences of Ukraine.

REFERENCES

1. K. Morsi, *J. Mater. Sci.*, **54**: 6753 (2019).
2. K. S. Ravi Chandran, K. B. Panda, and S. S. Sahay, *JOM*, **56**: 42 (2004).

3. G. Singh and U. Ramamurty, *Prog. Mater. Sci.*, 100653 (2020).
4. R. Pederson, R. Gaddam, and M.-L. Antti, *Open Engineering*, **2** (2012).
5. Chao Cai, Shan He, Lifan Li, Qing Teng, Bo Song, Chunze Yan, Qingsong Wei, and Yusheng Shi, *Composites Part B: Engineering*, **164**: 546 (2019).
6. O. E. Falodun, B. A. Obadele, S. R. Oke, A. M. Okoro, and P. A. Olubambi, *Int. J. Adv. Manuf. Technol.*, **102**: 1689 (2019).
7. X. X. Li, C. Yang, H. Z. Lu, X. Luo, Y. Y. Li, and O. M. Ivasishin, *J. Alloys Compd.*, **787**: 112 (2019).
8. R. Chaudhari and R. Bauri, *Mater. Sci. Eng. A*, **587**: 161 (2013).
9. R. Ramaswamy, B. Selvam, P. Marimuthu, and N. Elango, *IJMPERD*, **8**: 433 (2018).
10. H. Z. Niu, H. R. Zhang, Q. Q. Sun, and D. L. Zhang, *Mater. Sci. Eng. A*, **754**: 361 (2019).
11. M. Selva Kumar, P. Chandrasekar, P. Chandramohan, and M. Mohanraj, *Mater. Characterization*, **73**: 43 (2012).
12. O. M. Ivasishin, D. G. Savvakin, D. V. Oryshych, O. O. Stasiuk, and L. Yuanyuan, *MATEC Web Conf.*, **321**: 3009 (2020).
13. D. H. Savvakin, M. M. Humenyak, M. V. Matviichuk, and O. H. Molyar, *Mater. Sci.*, **47**: 651 (2012).
14. O. M. Ivasishin, D. G. Savvakin, F. H. Froes, and K. A. Bondareva, *Powder Metall. Met. Ceram.*, **41**: 382 (2002).
15. G. A. Baglyuk, O. M. Ivasyshyn, O. O. Stasyuk, and D. G. Savvakin, *Powder Metall. Met. Ceram.*, **56**: 45 (2017).
16. S. V. Prikhodko, P. E. Markovsky, D. G. Savvakin, O. O. Stasiuk, M. N. Rad, C. Choi, and O. M. Ivasishin, *Microsc. Microanal.*, **24**: 2218 (2018).
17. P. E. Markovsky, D. G. Savvakin, O. M. Ivasishin, V. I. Bondarchuk, and S. V. Prikhodko, *J. Mater. Eng. Perform.*, **28**: 5772 (2019).