Synthesis of 30 vol% TiB₂ Containing Fe–5Ti Matrix Composites with High Thermal Conductivity and Hardness

Yujiao Ke¹, Kazuhiro Matsugi^{1,*}, Zhefeng Xu^{1,*}, Yu He², Yongbum Choi¹, Mingzhi Wang² and Jinku Yu²

¹Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

²State Key Laboratory of Metastable Material Science and Technology, Yanshan University, Hebei Street West 438#, Qinhuangdao, 066004, China

TiB₂ doped Fe system alloys composites as a new generation of novel materials in sustainable society show the great potential in hot work tool steels usage. Compared with SKD61, the new generation materials are focused on improving both thermal conductivity and hardness. For the suppression of TiB₂ decomposition and Fe₂B formation, monophase BCC structured Fe–5Ti alloy powders were fabricated by mechanical alloying method. The TiB₂ addition with 30 vol% was selected for the control of hardness. The compacts sintered at 1323 and 1373 K for 0.6 ks consisted of α -Fe and TiB₂ with almost 30 vol%, which meant no decomposition of TiB₂ occurred during sintering. The result agreed with the achievement of thermal stability of TiB₂ in Fe–5Ti during spark sintering synthesis. The thermal conductivity and Vickers hardness of compacts sintered at 1323 and 1373 K for 0.6 ks were 48.0 W/(m·K), 684.7 HV and 53.5 W/(m·K), 717.5 HV, respectively, which were 2.0, 1.3 and 2.2, 1.4 folds than those (24.0 W/(m·K), 516.0 HV) of SKD61. In addition, the compression strength of two compacts sintered at 1323 and 1373 K were measured to be 1698 and 2591 MPa, respectively. The compact sintered at higher temperature showed better mechanical properties and higher thermal conductivity due to the improvement of densification and interface bonding between Fe–5Ti and TiB₂ as proved by the fracture modes in compression tests and the crack propagations in hardness tests. Hence, this work provides a new method for fabricating Fe₂B free Fe–TiB₂ composites by powder metallurgy with both improvement of thermal conductivity and hardness in the usage of hot work tool steels. [doi:10.2320/matertrans.MT-M2019168]

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1. Introduction

Ceramic reinforced metal matrix composites (MMCs) have drawn great attention for decades since they incorporate the toughness of metals and the strength of ceramics. Of the various kinds of ceramic reinforced MMCs, Fe (steel) matrix composites are considered as promising materials since Fe (steel) is still the most widely used structural material and provides diverse mechanical properties when subjected to different treatments. In addition, Fe (steel) matrix composites can be processed like steels. Alloying elements additions,^{1–3)} thermal processing or thermo/mechanical processing,^{4–7)} which are highly sophisticated and well established in steels design to alter the constitution and mechanical properties, can be also applied to processing Fe (steel) matrix composites. As for the reinforcing particulates, TiB₂ is one of the high-profile members, due to its excellent hardness, strength, thermal/electrical conductivity and oxidation resistance, which are superior to that of TiC. Moreover, TiB₂ is relatively stable in liquid Fe^{8–10)} and the solubility of Fe in TiB₂ is lower than 4%.¹¹⁾ In addition, liquid Fe can wet TiB₂.^{12,13)} More importantly, Fe–TiB₂ composites fabricated by powder metallurgy (PM) and casting both show good interface cohesion between the matrix and TiB₂ particles.^{5,14–17)} Fracture of TiB₂ particles are inclined to occur before particles/matrices debonding.^{5,18)} Of most reported Fe–TiB₂ composites, they are expected to apply to high modulus steels^{1–3,6,7,11,16,19–23)} and wear-resistance parts,^{24–30)} on account of the improved strength, specific modulus and wear-resistance. SKD61 has been widely used as one of

hot work tool steels (HWTS). It is characterized by good abrasion resistance at both low and high temperatures, high level of toughness and ductility, outstanding high-temperature strength and resistance to thermal fatigue.^{31,32)} However, the low thermal conductivity of 24 W/(m·K) limits its further applications. As a result, Fe–TiB₂ composites also display great potential in the application of HWTS because of their possibility of high thermal conductivity.

However, the challenge still remains with regard to the synthesis of Fe/TiB₂ composites, since Fe₂B, a brittle phase, will always get involved in composites as an undesired resultant which can deteriorate the toughness of composites.³³⁾ In the pursuit of obtaining Fe₂B free Fe/TiB₂ composites, according to the Fe–Ti–B ternary phase diagram,^{33,34)} over stoichiometric amount Ti (atomic ratio of Ti:B $\geq$ 0.5) is added to suppress the formation of Fe₂B. Up to date, Fe₂B free Fe/TiB₂ composites have been fabricated by different methods. Casting or eutectic solidification can not only guarantee a clean interface, but also tailor the ratio of each element. Another unparalleled advantage of casting over PM is the higher diffusion coefficient of atoms rendering a more homogeneous distribution of Ti in Fe. However, this route is still open to question due to clustering of TiB₂ particles in Fe matrix⁵⁾ and density-induced floatation of the primary TiB₂ particles,⁷⁾ contributing to inhomogeneous microstructure of composites. In addition, the large primary TiB₂ particles are more likely to fracture than the small eutectic TiB₂ particles when subjected to stress.¹⁸⁾ Therefore, more elaborate processes should be taken into consideration to overcome the aforementioned problems. Self-propagating high-temperature synthesis (SHS) or combustion synthesis is another way reported capable of producing Fe₂B free Fe/TiB₂ composites.^{24,28,29)} One of the striking merits of SHS

*Corresponding authors, E-mail: matsugi@hiroshima-u.ac.jp, xuzhefeng9972@hotmail.com

refers to the extreme high temperature caused by heat generated by an exothermic reaction, promoting the occurrence of mass transfer process. Nevertheless, high porosity and aggregation of the newly formed phases^{25–28)} are inevitably introduced in products, which is not suitable for the underlying application for structural materials where strength is valued extremely.

PM can precisely control the volume fraction and size of reinforcements in matrix though, it is still seemingly to be the least impossible method to fabricate the Fe₂B free Fe/TiB₂ composites due to the low diffusion coefficient of atoms in solid state sintering, in despite of an extra addition of Ti powder into Fe and TiB₂ powder mixtures. In contrast, mechanically alloying (MA), a non-equilibrium processing technique, has been carried out to synthesize supersaturated solid solutions, nanocrystallines, alloys, high entropy alloys (HEA),^{35,36)} etc. This offers a new possibility to fabricate a Fe–Ti alloyed powders in which Ti atoms solid solute in Fe lattice. In recent years, alloy and HEA powders synthesized by MA have been extensively used in the fabrication of alloy (HEA)/TiB₂ composites.^{37–43)} Evidently, it is also feasible to use MAed (Fe–Ti) alloy powders and TiB₂ powders to fabricate (Fe–Ti)/TiB₂ composites and further realize the synthesis of Fe₂B free Fe/TiB₂ composites. Hence, mono-phase BCC structured Fe–Ti (percentage by atom is used unless otherwise specified) alloy powders were fabricated by MA. Moreover, it is considered that Fe–5Ti is promising as the matrix in (Fe–5Ti)/TiB₂ composites. Spark sintering was chosen to sinter (Fe–5Ti)/TiB₂ composites because it has the potential to retard grain growth, suppress the thermal decomposition and purify the surface of powders through dielectric breakdown of an oxide film by proper control of process.^{44,45)} Therefore, it is a highly efficient sintering technique applying to rapidly synthesizing a wide range of materials at lower temperature.^{46–49)} It is concluded that (Fe–5Ti)–30 vol%TiB₂ composites consolidated by spark sintering are underlying materials compared with those of SKD61 mentioned above. The optimization among used powders, process parameters and system has to be carried out for achievement of fabrication of objective composites in spark sintering.^{44,45)}

In this study, the fabrication of Fe₂B free (Fe–5Ti)–30 vol%TiB₂ composites by the spark sintering with both high thermal conductivity and hardness in the application of HWTS was carried out by adjustment of both Fe–Ti alloy powders fabricated by MA and process parameters during spark sintering. The microstructures, phase composition, thermal conductivity and mechanical properties of compacts were also characterized in detail.

2. Experimental Procedure

2.1 Compositions, used materials and synthesis

As-received TiB₂ (99.9%, Pure Chemical Co., Ltd. Japan) pure Fe (99.9%, Sanwa Metal Industry Co., Ltd. Japan) and pure Ti (99.9%, Pure Chemical Co., Ltd. Japan) powders with size of 2~3, ~26 and ≤45 μm, respectively, were used as starting powder materials.

Monophase BCC structured Fe–5Ti alloy was chosen due to the following reasons. Firstly, the solid solubility of Ti in

Fe is about 5 at% at 1373 K in equilibrium state according to Fe–Ti binary phase diagram;⁵⁰⁾ Secondly, a quasibinary behavior exists along line TiB₂–Fe containing 2–3%Ti,³³⁾ that is to say, TiB₂ is thermally stable in Fe–(2–3%Ti). Thirdly, the Ti addition should be higher than 3% to neutralize any inadvertently present C. Pure Fe and Ti powders were mixed at an atom ratio of 19:1 and mechanical alloyed in a planetary ball-miller (QM-BP, Nanjing NanDa Instrument Plant, Nanjing, China) for 108 ks at 400 rpm in an argon atmosphere. MA was paused for 1.8 ks after each 3.6 ks of running. WC vials and balls with a diameter of 2~10 mm were utilized as the milling media with a ball-to-powder mass ratio of 20:1. Ethanol served as the process control agent to avoid cold welding as well as to prevent the alloy from oxidizing.

30 vol%TiB₂ addition was selected based on previous work for achieving the target value of hardness. Hence, 30 vol%TiB₂ and 70 vol% as-alloyed Fe–5Ti powders with a total amount of 15 g were placed in a stainless-steel jar with a volume of 250 cm³, and then 25 mL ethanol was added as a wet mixing agent. Hereafter, the jars were vacuumed for 0.3 ks. Stainless-steel balls (SUS304) with a diameter of 2~10 mm were used for blending and the ball to powder mass ratio was 10:1. Mixing process was conducted in a planetary mill (Fritsch Pulverisette, Germany) at 100 rpm for 10.8 ks. Slurry of powder mixtures was dried in a fume hood and then dry mixed for 3.6 ks afterwards.

2.2 Spark sintering

Powder mixtures were loaded in a graphite die and consolidated by spark sintering (CS12567, Japan). All spark sintering experiments were carried out at an applied pressure of 50 MPa, heating rate of 100 K/min and holding time of 0.6 ks in vacuum. Hence, (Fe–5Ti)–30 vol%TiB₂ compacts were obtained at 1323 and 1373 K for 0.6 ks. The die temperature was monitored using an infrared radiation thermometer focused into the hole of die. The temperature of compacts could be estimated approximately 40 K higher than that of die.⁴⁸⁾ Compacts with height of 10 mm and diameter of 10 mm were obtained. And then compacts were ground by SiC abrasive paper and polished by diamond paste for the succedent characterizations.

2.3 Characterizations of starting powders and sintered compacts

Morphology of powders and microstructure of sintered compacts were observed by electron probe micron analyzer (EPMA, JXA-8900, JEOL, Japan). Phase identification of sintered compacts was characterized by X-ray diffraction (XRD, D/max-2500PC, Rigaku, Japan) with Cu Kα radiation (L = 0.15406 nm, 40 kV, 100 mA). Transmission electron microscope (TEM, JEM-2010, JEOL, Japan) was performed to observe the interface between Fe–5Ti and TiB₂. Image analysis was employed to obtain the particle size distributions of starting powders and area fraction of each phase in sintered compacts.

2.4 Vickers hardness, thermal conductivity and compression tests

Vickers hardness was obtained by Vickers hardness tester

(MHT-1, Japan) at a load of 5 kg and a dwelling time of 10 s. In order to observe the crack propagations, a load of 30 kg was applied to compacts by using the same hardness tester. The thermal diffusivity (α) of the samples with dimension of $\Phi 10 \times 1$ mm was measured at room temperature by a laser flash thermal constants measuring apparatus (Thermal conductivity-9000h, Ulvac-riko, Japan). The specific heat capacity (C_p) of the samples with dimension of $\Phi 4$ mm $\times$ 0.5 mm was also measured at room temperature by differential scanning calorimeter (DSC, STA449C, Germany). Density (ρ) of sintered compacts was acquired by Archimedes' principle. Thermal conductivity (λ) of sintered compacts was calculated according to the eq. (1).

$$\lambda = \alpha \cdot C_p \cdot \rho \quad (1)$$

Compression test specimens are cylindrical with the dimension of $\Phi 4$ mm $\times$ 6 mm. Room temperature compression tests were performed on a mechanical testing machine (Autograph DCS-R-5000, Shimadzu Corporation, Japan) at an initial strain rate of $1.7 \times 10^{-3} \text{ s}^{-1}$.

3. Results and Discussion

3.1 Powders characterizations

The microstructural characterizations of the starting powders are shown in Fig. 1(a)–(c), and the insets positioned in the upper-left corner of each image correspond to the areas marked by white dashed boxes. As-received Fe powders appeared to be relatively uniform particle size of about 26 μm ; but it was different for as-received Ti exhibiting an inhomogeneous size distribution with size distribution from several to several tens micrometer; The particle size also scattered in as-received TiB_2 , in addition to that, the cleavage surfaces of TiB_2 could be observed clearly, which might be due to the mechanical crush process.

The XRD patterns of as-alloyed Fe–5Ti powders milled for different times (0, 36, 72, 108 ks, respectively) are shown in Fig. 2. The pattern of Fe–5Ti powder mixture MAed for 0 ks explicitly revealed two phases of α -Fe and hexagonal Ti. As the milling time increased to 36 ks and longer, the phase constitution evolved into mainly α -Fe or body centered cubic (BCC) phase, and no peaks of hexagonal Ti was found as seen in Fig. 2(a)–(c). The disappearance of Ti peaks might be duo to, on the one hand, Ti atoms solid solute into Fe lattice by mechanical force provided by MA, on the other hand, Ti particles were amorphized during MA attributing to the degradation or even vanishing of diffraction peak of Ti.

Fig. 2 XRD patterns of as-alloyed Fe–5Ti powders milled for (a) 108 ks, (b) 72 ks, (c) 36 ks and (d) 0 ks; the inset positioned in the upper right corner is the magnified image corresponding to the area marked by dotted rectangle.

Moreover, with prolong the milling time to 72 ks, left-shift of (110) plane of Fe was observed as highlighted in the upper-right inset corresponding to the area marked by dotted rectangle. This indicated that solid solution degree of Ti into Fe was enhancing with prolonging the milling time. Left-shift of peaks ascribed to the increase of interplanar spacing according to Bragg equation. This was quite reasonable since smaller Fe atoms (0.172 nm) were substituted by larger Ti atoms (0.2 nm). However, no obvious peaks shift but much broadening peaks were observed at 108 ks milling compared with that of 72 ks milling, which meant a simple solid solution of monophase structured BCC phase was formed at 108 ks milling. Peaks broadening might be ascribed to amorphization, reduction of grain size, lattice distortion brought about by MA.^{35,36} As a result, alloyed powders milled at 108 ks were selected as the matrix in this study.

Morphologies of as-alloyed Fe–5Ti powders milled for different times are shown in Fig. 3. The powder particles appeared to be granular when milled for 36 ks demonstrated in Fig. 3(a), while most of particles evolved into severely deformed and flattened morphologies as the milling time extended to 72 ks as evidenced in Fig. 3(b). Whereafter larger particles gradually broke into finer ones after 108 ks milling as shown in Fig. 3(c). In addition, the particle size

Fig. 1 Low and high magnification of SEM images of the starting powders: (a) as-received Fe powders, (b) as-received Ti powders and (c) as-received TiB_2 powders; the insets positioned in the upper-left corner are the high magnification images corresponding to the areas marked in white boxes in (a), (b) and (c), respectively.

Fig. 3 SEM images of as-alloyed Fe–5Ti powders milled for different times: (a) 36 ks, (b) 72 ks and (c) 108 ks; (d), (e) and (f) are particle size distributions corresponding to (a), (b) and (c), respectively.

distributions are illustrated in Fig. 3(d)–(f) and the mean particle size reduced from 7.74 μm to 1.07 μm with the increase of milling time, as compared with the as-received Fe and Ti powders seen in Fig. 1(a), (b). The evolution process of particles morphology coincided well with the fundamental process in MA, in which repeated welding and fracturing of powder mixtures in a highly energetic ball charge were involved.³⁵ Consequently, controlled microstructure and size of monophase BCC structured Fe–5Ti alloy powders could be obtained by MA.

3.2 Microstructure of sintered compacts

The XRD patterns of (Fe–5Ti)–30 vol%TiB₂ compacts sintered at 1323 and 1373 K for 0.6 ks are shown in Fig. 4. The main phase constitutions of both compacts were α -Fe and TiB₂ phases. The peaks shift of Fe of sintered compacts was also observed due to some Ti solubility in Fe when compared with reference cards. The peaks of α -Fe in sintered compacts were shifted toward to low angle compared with that of pure Fe and located between peaks of pure Fe (PDF#89-7194) and that of Fe–3.6Ti alloy (PDF#65-7743). In contrast, the peaks of TiB₂ were not shifted regardless of sintering temperature. This result was consistent with the aforementioned introduction that 2–3 at%Ti solubility in Fe is essential for the thermal stability of TiB₂ in Fe at high temperature.³³

Noticeably, No peaks of TiC and Fe₂B was observed in the XRD patterns. These two phases were the most reported intermetallic in literatures^{11,16,24,28,29} while not desirable in Fe–TiB₂ system, as they will deteriorate the mechanically properties of composites, especially the existence of the brittle Fe₂B phase as mentioned in introduction. Besides, no

Fig. 4 XRD patterns of (Fe–5Ti)–30 vol%TiB₂ compacts sintered at (a) 1373 and (b) 1323 K for 0.6 ks.

peaks of Fe₂B also proved that the decomposition of TiB₂ was suppressed, and thus, the thermal stability of TiB₂ in the Fe–5Ti alloy was achieved successfully. It might be possibly interpreted that the introduction of Ti into Fe balanced the chemical potential of Ti atom in both sides of TiB₂ and Fe–5Ti alloy. The crystallization of Fe–5Ti also occurred during sintering process as the diffraction peaks became narrower and sharper, compared the XRD pattern in Fig. 4 with that in Fig. 2. However, TiO₂ with minor amount was observed as well in XRD pattern in both compacts as indicated in Fig. 4. This might derive from oxide layers on as-received Ti particles or oxidation of titanium during MA process. Further measures should be taken to prevent the titanium from being oxidized in the future study.

The microstructural characterizations of (Fe–5Ti)–30 vol%TiB₂ compacts are shown in Fig. 5. TiB₂ (black areas) and Fe–5Ti alloy (gray areas) were indicated in Fig. 5(a), (b). TiB₂ particles were homogeneously distributed in matrix in both compacts due to well-designed mixing process introduced in section 2.1. The sintering pores were indicated in the upper-left insets corresponding to the areas marked by white boxes and more sintering pores were observed in Fig. 5(a) than that in Fig. 5(b). The defects which were described in later text corresponded to the sintering pores. TiO₂ was not indicated in SEM images, because the size of TiO₂ was of several hundred nanometer, which was difficult to be observed in the SEM images. Thereafter, the area fractions of TiB₂ in both compacts were predicted to be 29.3% for 1323 K and 31.4% for 1373 K by image analysis, almost the same amount with initial TiB₂ addition. This result indicated that TiB₂ was barely decomposed after sintering. And thus, Fe–5Ti alloyed powders are an effective matrix for the purpose of preventing the TiB₂ from decomposing and the fabrication of Fe₂B free Fe/TiB₂ composites by PM is feasible.

Elemental mapping analysis of Fe, Ti and B elements in (Fe–5Ti)–30 vol%TiB₂ sintered compacts are displayed in Figs. 6 and 7. The Ti and B distributed in highly overlapping regions which were right corresponding to the TiB₂ areas as illustrated in Fig. 6 and the same situation was observed in Fig. 7, suggesting that TiB₂ particles were barely decom-

Fig. 5 SEM images of (Fe-5Ti)-30 vol%TiB₂ compacts sintered at (a) 1323 and (b) 1373 K for 0.6 ks; pores are indicated in the upper-left insets corresponding to the marked areas by white boxes in (a), (b).

Fig. 6 Mapping analysis of Fe, Ti and B elements in (Fe-5Ti)-30 vol%TiB₂ compacts sintered at 1323 K for 0.6 ks: (a) a BSE image of the compact, (b), (c) and (d) are the element distribution of Ti, Fe, and B, respectively.

Fig. 7 Mapping analysis of Fe, Ti and B elements in (Fe-5Ti)-30 vol%TiB₂ compacts sintered at 1373 K for 0.6 ks: (a) a BSE image of the compact, (b), (c) and (d) are the element distribution of Ti, Fe, and B, respectively.

posed and well preserved after sintering at 1323 and 1373 K for 0.6 ks, which was consistent with the results from XRD patterns. The color change from the center to edge via TiB₂ phase might be caused by the insufficient spatial resolution of WDS, although the phase had homogeneous concentration of Ti and B. Inhomogeneity of the Fe and Ti distribution in Fe-5Ti matrix in Figs. 6 and 7 was caused by MA process. Because one of the noticeable features of MA process is that as-alloyed powders are macroscopically uniform but microscopically uneven.

TEM observations of Fe/TiB₂ interface cohesion of compacts sintered at 1323 and 1373 K for 0.6 ks are demonstrated in Fig. 8. The compact sintered at 1373 K for 0.6 ks showed better interface cohesion as marked by dashed white arrows in Fig. 8(b), in contrast, the compact sintered at 1323 K for 0.6 ks showed the insufficient interface cohesion as indicated by solid white arrow in Fig. 8(a) accompanying a few defects. This might be ascribed to that higher temperature can enhance the interface bonding of (Fe-5Ti)/TiB₂. There was no reaction layers between the interface of Fe-5Ti and TiB₂, which was in line with the result that TiB₂ was barely decomposed as seen in Figs. 6 and 7. Apparently, these TEM images are not sufficient enough to interpret the interface bonding condition between TiB₂ and Fe-5Ti. However, it is believed that the interface between TiB₂ and Fe-5Ti will enhance with the increase of sintering temperature. Therefore, for a better and further understanding of the interface bonding conditions at different sintering temperatures, fracture modes in compression tests and crack propagations in hardness tests from the macroscopic perspective were discussed in the following text.

3.3 Thermal conductivity and mechanical properties

As shown in Fig. 9, the thermal conductivity and Vickers hardness of compacts sintered at 1323 and 1373 K for 0.6 ks were 48.0 W/(m·K), 684.7 HV and 53.5 W/(m·K), 716.2 HV, respectively. With the increase of sintering temperature, both thermal conductivity and Vickers hardness were improved owing to the lower porosity as shown in Fig. 9 and enhanced interface bonding between Fe-5Ti/TiB₂ and less sintering pores in the compact sintered at 1373 K as shown in Fig. 5(b). Defects⁵¹⁾ and interface thermal resistance⁵²⁾ are two predominant factors which influence thermal conductivity of composites, as they can scatter electron or phonon during heat transfer and then decrease the mean free length of

Fig. 8 TEM images of (Fe–5Ti)–30 vol%TiB₂ compacts sintered at (a) 1323 and (b) 1373 K for 0.6 ks.

Fig. 9 Vickers hardness, thermal conductivity and relative density of (Fe–5Ti)–30 vol%TiB₂ compacts sintered at 1323 and 1373 K for 0.6 ks.

Fig. 10 Compressive stress–strain curves of (Fe–5Ti)–30 vol%TiB₂ compacts sintered at 1323 and 1373 K for 0.6 ks.

the path of electron or phonon, leading to the decrease of thermal conductivity. In this case, in addition to lattice distortion and interface thermal resistance, TiO₂, confirmed by XRD in Fig. 4, was another unfavorable factor decreasing the thermal conductivity, on account of the low thermal conductivity of TiO₂ itself and the increase of heterophase interface. The thermal conductivity of Fe and Ti were measured to be 80.0 and 24.5 and that of TiB₂ was reported to be about 100.0 W/(m·K).⁵³⁾ Therefore, the theoretical thermal conductivity of fully-dense (Fe–5Ti)–30 vol%TiB₂ was estimated to be 84.0 W/(m·K), based on the rule of mixtures. Apparently, the thermal conductivity of both sintered compacts was lower than the theoretical value. This could be attributed to the defects such as pores and lattice distortion in the sintered compacts and the formation of TiO₂ with low thermal conductivity as explained above. In addition to that, interface thermal resistance was not taken into consideration in the calculation of the theoretical value. As consequence, the experimental values of both sintered compacts were inferior to the theoretical value. Nevertheless, a higher thermal conductivity of (Fe–5Ti)–30 vol%TiB₂ composite can be expected if the TiO₂ is further suppressed in sintered compacts.

Figure 10 shows the typical compressive stress–strain curves at room temperature for the sintered (Fe–5Ti)–30 vol%TiB₂ compacts sintered at 1323 and 1373 K for 0.6 ks. The compression strength of the compact sintered at 1373 K was higher than that of the compact sintered at

1323 K, which were 1698 and 2591 MPa, respectively. This was due to the better interface bonding and higher densification at 1373 K as shown in Figs. 8 and 9. Both compacts were fractured before remarkably plastic deformation. The same fracture mode was also reported in Fe–15Cr–8Al–20Mn/30 vol%TiB₂ composites sintered at 1373 K for 0.6 ks.³⁸⁾ The fracture modes of two sintered compacts were different, which resulted in the difference of compression strength. As shown in Fig. 11(a), (b), the fracture modes were a mixture of TiB₂ cleavage marked by solid arrows and interface debonding indicated by dashed arrows for both compacts. Whereas, the difference lied in the interface debonding dominated the fracture behavior in Fig. 11(a), on the contrary, TiB₂ cleavage governed the fracture behavior in Fig. 11(b). Under the external stress, fracture of TiB₂ particles are prone to occur before particles/matrices debonding due to the good interface cohesion between Fe/TiB₂ interface.^{5,18)} Hence, it could be interpreted that dominance of interface debonding occurrence in the compact sintered at lower temperature was attributed to the insufficient interface bonding. It is reported the existence of TiO₂ can improve the mechanical properties of composites.^{54,55)} It applies to this study as well. The TiO₂, mainly derived from MA process, partially accounted for the improvement of hardness and compression strength of composites as TiO₂

Fig. 11 Fracture surface images of (Fe-5Ti)-30 vol%TiB₂ compacts: (a) 1323 K, (b) 1373 K for 0.6 ks; and dashed and solid white arrows refer to interface debonding and TiB₂ cleavage, respectively.

Fig. 12 Crack propagation images of (Fe-5Ti)-30 vol%TiB₂ compacts sintered at: (a) 1323 K, (b) 1373 K for 0.6 ks; and interface debonding in (a) and TiB₂ breakage in (b) are marked by white arrows.

played as a strengthening hard phase. The hardness values were 3400 HV⁵³⁾ and 150 HV in TiB₂ and Fe-5Ti phases, respectively. In contrast, the Vickers hardness of TiO₂ is reported to be 480 HV.⁵⁶⁾ Therefore, TiO₂ also affected the mechanical properties. Despite of the positive effect of the TiO₂ on the mechanical properties of composites, it is still an undesirable phase, because added Ti is consumed by the formation of TiO₂ and it is low in thermal conductivity. According to the Ref. 57), the strengthening mechanism can mainly be ascribed to the following aspects. Firstly, the load transfer from the soft and compliant matrix to the stiff ceramics under an applied external load, contributes to the strengthening of the base material. Secondly, the particles can play a fundamental role in grain size refinement in metal matrices of composites since they could serve as pinning points, impeding grain growth. It was considered that above factors correspond to the strengthening reasons for (Fe-5Ti)-30 vol%TiB₂ composites. Besides, in the case of present work, solution strengthening or Ti atom solid solution into Fe was another reason responsible for strengthening of matrix.

There was no crack occurrence in the indented compacts when the applied load was 5 kg. And thus, a load of 30 kg was applied to sintered compacts in order to observe the crack propagations. Figure 12 shows the principal crack propagation images of compacts sintered at different temperatures. The crack mainly propagated along the interface of (Fe-5Ti)/TiB₂ as proved by the interface debonding in Fig. 12(a), but it extended primarily through the TiB₂ particles as demonstrated by TiB₂ breakage in Fig. 12(b). The result indicated the interface strength of the compact sintered at 1373 K was stronger than that of the compact

sintered at 1323 K. Coupled with the result obtained from the fracture modes, the difference in crack propagations in the HV indented compacts confirms that higher sintering temperature guarantees a better (Fe-5Ti)/TiB₂ interface bonding.

3.4 Comparison with SKD61

For comparison, the mechanical and thermal properties of compacts sintered in this work and the alloy from other published literature⁵⁸⁾ were listed in Table 1. The Vickers hardness and thermal conductivity of SKD61 quenched and tempered were measured to be 516.0 HV and 24.0 W/(m·K) in this study, respectively. The illustration of heat treatment process of SKD61 is listed in Fig. 13. Relatively high thermal conductivity of 40CrMnMo7 alloy⁵⁸⁾ (Fe-0.37C-1.7Cr-1.4Mn-0.21Si-0.16Mo) for high-pressure die casting as one of HWTS was revealed in Table 1, but its hardness was not given. Meanwhile, the (Fe-5Ti)-30 vol%TiB₂ compacts sintered in this work exhibited either higher or comparable values in both Vickers hardness and thermal conductivity compared with other alloys. More specifically, the Vickers hardness and thermal conductivity of (Fe-5Ti)-30 vol%TiB₂ compact sintered at 1373 K for 0.6 ks were the highest among all listed items. The thermal conductivity and Vickers hardness of the two compacts sintered at 1323 and 1373 K for 0.6 ks were 2.0, 1.3 and 2.2, 1.4 folds than those of SKD61. And hence, in terms of thermal conductivity and Vickers hardness, Fe₂B free (Fe-5Ti)-30 vol%TiB₂ composites with improvement of hardness and thermal conductivity were fabricated successfully by PM. SKD61 is a martensite matrix with a proper grain size and uniform carbides

Table 1 Vickers hardness and thermal conductivity of (Fe–5Ti)–30 vol%TiB₂ compacts and other alloys measured at room temperature.

Materials	Vickers hardness (HV)	Thermal conductivity (W/(m·K))	Refs
(Fe–5Ti)/30TiB ₂ –1323K	684.7	48.0	This study
(Fe–5Ti)/30TiB ₂ –1373K	717.5	53.5	This study
SKD61	516.0	24.0	This study
40CrMnMo7	--	45.0	58)

Fig. 13 Illustration of heat treatment process of SKD61.

precipitation distribution in it.⁵⁹⁾ A series of heat treatments have to be applied in order to acquire desirable properties, such as annealing, stress relieving, preheat prior to hardening, hardening, quenching and tempering as illustrated in Fig. 13. Those complex processes are not cost effective and energy saving in the pursuit of sustainable society. In contrast, the synthesis of (Fe–5Ti)–30 vol%TiB₂ compacts with improvement of thermal conductivity and Vickers hardness can be achieved by simplex spark sintering process which leads to cost effective and relative energy saving, compared with those complex manufacturing treatments of SKD61. That is to say, (Fe–5Ti)–30 vol%TiB₂ compacts are very promising in the application of HWTS in the future.

4. Conclusion

Monophase BCC structured Fe–5Ti alloy powders had been successfully fabricated by MA and were used as the matrix for a substitution for pure Fe. Their compacts consisted of α -Fe and TiB₂ with almost 30 vol%, which meant no-decomposition of TiB₂. Their results agreed with the achievement of thermal stability of TiB₂ in Fe–5Ti during spark sintering synthesis, which might be possibly interpreted that the introduction of Ti into Fe balanced the chemical potential of Ti atom in both sides of TiB₂ and Fe–5Ti alloy. The thermal conductivity and Vickers hardness of compacts sintered at 1323 and 1373 K for 0.6 ks were 48.0 W/(m·K), 684.7 HV and 53.5 W/(m·K), 717.5 HV, respectively, which were 2.0, 1.3 and 2.2, 1.4 folds than those of SKD61. Besides, the compression strength of two compacts at 1323 and 1373 K were measured to be 1698 and 2591 MPa, respectively. The compact sintered at higher temperature showed better mechanical properties and higher thermal

conductivity due to the improvement of densification, interface bonding between (Fe–5Ti)/TiB₂ and less defects. This work provides a new method for fabricating Fe₂B free Fe–TiB₂ composites by PM with both improvement of thermal conductivity and hardness. Furthermore, simplex spark sintering process leads to low cost and relative energy saving compared with those complex manufacturing treatments of SKD61. In terms of improvement of thermal conductivity and Vickers hardness, (Fe–5Ti)–30 vol%TiB₂ compacts show great potential in the usage of HWTS.

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