Investigation of Sintering Behavior in Low-alloyed Steel Powder Containing TiB_2 Particles*¹

Nobuhiko Matsumoto^{1,*2}, Toshitake Miyake¹, Mikio Kondoh², Yusuke Oishi³ and Kazuhiro Toyama³

¹Toyota Central R&D Labs., Inc., Nagakute 480-1192, Japan.

²Former Employee of Toyota Central R&D Labs., Inc.

³Toyota Motor Corporation, Toyota 471-8572, Japan

In our previous study, TiB_2 -reinforced sintered steel with a high Young's modulus was obtained for lightweighting of automobile parts. The high Young's modulus was attributed to the combination of suitable reinforcing particles for the steel and the high relative sintered density provided by hot-working of the sintered billet.

In this study, how and why the relative sintered density is increased were investigated via single-pressing and single-sintering, by which near net shape parts were simply and easily manufactured.

In steel powder and TiB_2 powder compact, the liquid phase of the Fe-B system formed above 1448 K, enhanced the densification. For 2–15 vol% TiB_2 addition, the effect of this liquid phase on the densification was appreciable and high relative sintered densities of >98% were achieved by vacuum sintering at 1523 K. This high relative sintered density realized a high Young's modulus comparable to the calculated value for each TiB_2 contents. [doi:10.2320/matertrans.Y-M2019817]

(Received February 6, 2019; Accepted March 22, 2019; Published August 25, 2019)

Keywords: liquid phase sintering, high-density sintered steel, reinforcing particle, titanium boride, Young's modulus

1. Introduction

Weight reduction by reducing the size and thickness of structural parts used for engines and drive-train systems is highly effective for improving the fuel economy of automobiles. However, when these structural parts are subjected to high actual working stress, the increased elastic deformation accompanying the decreased size and thickness degrades automobile performance. Therefore, to reduce the size and thickness of these structural parts without degrading automobile performance, it is essential to increase their Young's moduli to exceed that of conventional steels.

Titanium boride (TiB_2) is thermally stable in steel and has a high Young's modulus of 540 GPa, approximately 2.5 times higher than that of conventional steels. With these excellent characteristics, improvement of Young's modulus of sintered steel by introducing dispersions of TiB_2 particles was investigated. A high Young's modulus far exceeding that of conventional steels was obtained using the densification method of single-pressing and single-sintering (1P1S) followed by hot-working.^{1–3)}

In the developed sintered steel, if a high relative density comparable to 100% can be obtained only by 1P1S, a reduced material production cost can be achieved by omitting the hot-working. In addition, easy manufacturing of near-net-shape parts can be achieved by 1P1S.

In this study, TiB_2 powder was mixed with a steel powder and 1P1S was applied for it. A liquid phase generated in the compact during sintering. The effect of this liquid phase on the relative density and the Young's modulus was investigated through microstructural observations.

2. Experimental

2.1 Raw material powders and compounding

Fine water-atomized steel powder ($D_{50} = 11 \mu\text{m}$, Epson Atmix Corporation) was used as a base powder pre-alloyed with 3 wt% Cr and 0.5 wt% Mo. Figure 1(a) shows the SEM (scanning electron microscopy) image of the base powder.

(a) Low-alloyed steel powder

(b) TiB_2 powder 25 μm

*¹This Paper was Originally Published in Japanese in J. Jpn. Soc. Powder Powder Metallurgy **65** (2018) 227–232.

*²Corresponding author, E-mail: e1065@mosk.tytlabs.co.jp

Fig. 1 SEM images of (a) low-alloyed steel and (b) TiB_2 powders.

Table 1 Pore-free densities of the investigated mixes for each TiB₂ content.

TiB ₂ content		Pore free density (PFD) Mg/m ³
Volume fraction vol%	Weight fraction wt%	
0	0	7.80
0.9	0.5	7.77
1.7	1.0	7.74
5.0	3.0	7.64
10.0	6.0	7.47
15.0	9.3	7.31
20.0	12.6	7.14
25.0	16.1	6.98
30.0	19.8	6.81
40.0	27.8	6.48
50.0	36.6	6.15

The base powder mainly comprised fine particles with small surface irregularities, despite water atomization.

TiB₂ powder (TiB₂-N, D₅₀ = 3 μm, Japan New Metals Co., Ltd.) was used as an additive. As shown in Fig. 1(b), fine particles of 5 μm or less are predominant, although 20–40 μm agglomerates made from fine particles were also observed.

Table 1 shows the compounding ratio by volume fraction and weight fraction of the TiB₂ powder and the pore-free density (PFD) of each mix. For the conversion of the volume and weight fractions of the TiB₂ powder and the calculation of PFD in each mix, the values of 7.80 Mg/m³ and 4.50 Mg/m³ were used as the densities of the base powder and TiB₂ powder, respectively. The compounded powder was premixed in a mortar until 1–2 mm agglomerates were broken, and then mixed by rotating for 30 minutes.

2.2 Preparation and evaluation of test pieces

Cylindrical green specimens (14 mm in diameter, 8–10 mm in height) were prepared by warm compaction at 423 K by a lithium stearate die-wall lubrication. The compacting pressure was 392–1176 MPa.

Sintering was performed for 1.8 ks in a vacuum (1–5 × 10⁻² Pa) at 1523 K using a batch-type sintering furnace (PVSG gr 20/20, Shimadzu Mectem, Inc.). After sintering, furnace cooling was performed from 1523 to 1173 K, followed by rapid cooling with 200 kPa nitrogen gas. For several TiB₂ powder mixtures, the specimens were also sintered at 1373 to 1548 K under the same cooling conditions.

The green and sintered densities and the dimensional change rate (ΔD) were calculated from the diameter, thickness, and weight of the cylindrical specimens before and after sintering. The relative green and sintered densities were respectively obtained by dividing the green and sintered densities by the PFD, which was considered the true density.

The Young's modulus was calculated using eq. (1). In eq. (1), ρ , V_l , and V_s are the sintered density, the longitudinal wave velocity, and the shear wave velocity, respectively. V_l and V_s were calculated using the thickness of the sintered specimen and the propagation times of longitudinal and shear waves, respectively, measured by the acoustic pulse method.⁴⁾

Fig. 2 Relationship between relative green density and TiB₂ content.

$$E = \rho V_s^2 (3V_l^2 - 4V_s^2) / (V_l^2 - V_s^2) \quad (1)$$

Microstructures were evaluated by SEM (SU3500, Hitachi High-Technologies GLOBAL) after polishing the cross-section of the sintered specimens and etching with nital (a mixture of 5 vol% nitric acid and ethyl alcohol). The alloying element contents of the constituent phases were analyzed in the un-etched condition after cross-sectional polishing of the sintered specimens. This elemental analysis was performed by electron probe microanalysis (EPMA, JXA-8200, JEOL Ltd.).

3. Results

3.1 Relative density of green specimens

Figure 2 shows the relationship between the relative green density and the TiB₂ content. For constant TiB₂ contents, the relative green density increased with increasing the compacting pressure. However, for constant compacting pressure, the relative green density decreased as the TiB₂ content increases. Because TiB₂ powder is harder than the base powder, the compressibility of the mix decreased with increasing TiB₂ powder in the mix.

3.2 Relative density of sintered specimens

Figure 3 shows the relationship between the relative sintered density and the TiB₂ content after sintering at 1523 K. For all nonzero TiB₂ contents and compacting pressures, the relative sintered density exceeded the relative green density. Without TiB₂, the relative sintered density increased with increasing compacting pressure; the relative sintered density of 97.7% was obtained at the compacting pressure of 1176 MPa. The relative sintered density increased with the addition of 1–2 vol% TiB₂; the increase in relative density was particularly remarkable at low compacting pressures. High relative sintered densities of ≥98% were obtained regardless of the compacting pressure for 2–15 vol% TiB₂. However, the addition of >15 vol% TiB₂ caused a decrease in the relative sintered density with increasing TiB₂ content or decreasing compacting pressure.

3.3 Dimensional change after sintering

Figure 4 shows the relationship between the dimensional change rate (ΔD) and the TiB₂ content when sintered at

Fig. 3 Relationship between relative sintered density and TiB₂ content.

Fig. 4 Relationship between dimensional change (ΔD) and TiB₂ content.

1523 K. The negative value of ΔD corresponds to the shrinkage. For all nonzero TiB₂ contents the samples shrunk, as the compacting pressure was decreased. With increasing TiB₂ contents, a local maximum shrinkage was found at ~ 10 – 25 vol% TiB₂. Above the TiB₂ contents at which the local maximum shrinkage was shown, shrinkage was decreased for further TiB₂ addition. This change behavior in ΔD supported high relative sintered densities of $\geq 98\%$ for 2–15 vol% TiB₂ regardless of the compacting pressure as shown in Fig. 2 and Fig. 3.

3.4 Young's modulus

Figure 5 shows the relationship between the Young's modulus and TiB₂ content of the specimen sintered at 1523 K. This figure also shows Young's modulus of the pore-free composite material (E_c) calculated by eq. (2). In eq. (2), E_m and E_p are the Young's moduli of the Fe–Cr based matrix (207 GPa) and of the TiB₂ particle (540 GPa) respectively; V_p is the volume ratio of the added TiB₂ powder. Equation (2) is derived from the model based on a unit cell consisting of the regions in which uniform strain is imparted and in which uniform stress is imparted to Fe–Cr based matrix and TiB₂ particle.⁵⁾

$$E_c = \{(cE_p E_m + E_m^2)(1 + c)^2 - E_m^2 + E_p E_m\} / \{(cE_p + E_m)(1 + c)^2\}$$

with $c = (1/V_p)^{1/3} - 1$ (2)

Fig. 5 Relationship between Young's modulus and TiB₂ content. (Calculated Young's modulus is based on the equation derived through a unit-cell representation of the microstructure.⁶⁾)

With no added TiB₂, the Young's modulus increased with increasing compacting pressure. The Young's modulus increased for 1–2 vol% TiB₂; this tendency became more prominent with decreasing compacting pressure. For 2–15 vol% TiB₂, the Young's moduli were nearly equal each other regardless of the compacting pressure, showing a linearly increasing tendency with increasing TiB₂ content.

For >15 vol% TiB₂, the Young's moduli increased with increasing compacting pressure. The Young's moduli at each compacting pressure were locally maximized at ~ 15 – 25 vol% TiB₂, and the TiB₂ content at which the Young's modulus locally maximized increased with increasing compacting pressure.

The experimental Young's moduli for 2–15 vol% TiB₂ were almost equivalent to those calculated by eq. (2). For TiB₂ contents of <2 vol% or >15 vol%, the experimental Young's moduli were lower than those calculated by eq. (2); the difference between the experimental and calculated Young's moduli increased with decreasing compacting pressure.

4. Discussions

4.1 Mechanism of relative density improvement accompanying sintering

To clarify the mechanism of improving the relative density via sintering, the sintering process of developed sintered steel was investigated for two TiB₂ contents. They were 5 and 30 vol% and the relative sintered densities after 1523 K sintering were 99.3 and 93.6%, respectively.

4.1.1 Change behavior of relative density in sintering process

Figure 6 shows the relationship between the relative sintered density for steels with 5 and 30 vol% TiB₂ and sintering temperature.

For 5 vol% TiB₂, the relative sintered densities were nearly equal to the relative green density at sintering temperatures of ≤ 1423 K. For sintering temperatures of >1423 K, the increase in the relative sintered density became noticeable, and high relative sintered densities of $\geq 99\%$ were obtained for sintering temperatures of >1443 K.

Fig. 6 Effect of the sintering temperature on the relative sintered density.

For 30 vol% TiB_2 , the increase in the relative sintered density became noticeable at sintering temperatures of >1423 K. However, the increasing tendency of the relative sintered density in this temperature range was less prominent than that for 5 vol% TiB_2 , and the relative sintered density increased to 93.6% even at the high sintering temperature of 1523 K.

4.1.2 Change behavior of microstructure in sintering process

Figure 7 shows the microstructures of steels with 5 and 30 vol% TiB_2 at sintering temperatures of 1423, 1448, and 1523 K. In these micrographs, the black areas are pores. Based on the element analysis shown in Table 2, the matrix didn't contain boron, the dark gray particles are Ti-based borides, and light-gray particles and the areas are (Fe,Cr)-based borides.

At 5 vol% TiB_2 , 10–40 μm agglomerates of fine Ti-based borides of 3–5 μm and granular (Fe,Cr)-based borides ($\sim 5 \mu\text{m}$) were dispersed in the matrix, and the pores were

Table 2 EPMA analyses of sintered compacts containing 30 vol% TiB_2 : (a) dark-gray particles, (b) light-gray particles and areas, (c) matrix.

(a) Dark-gray particles

Temperature (K)	Compositions (wt%)				
	B	Ti	Cr	Fe	Mo
1423	31.0	67.8	0.1	1.1	0.0
1448	30.8	67.8	0.1	1.3	0.0
1523	30.7	67.8	0.1	1.4	0.0

(b) Light-gray particles and areas

Temperature (K)	Compositions (wt%)				
	B	Ti	Cr	Fe	Mo
1423	6.7	1.8	9.8	80.8	0.9
1448	8.0	2.1	9.5	79.8	0.6
1523	7.9	1.1	9.7	80.6	0.7

(c) Matrix

Temperature (K)	Compositions (wt%)				
	B	Ti	Cr	Fe	Mo
1423	0.0	0.4	2.7	96.5	0.4
1448	0.0	0.5	2.8	96.4	0.3
1523	0.0	0.6	2.9	96.2	0.3

mainly distributed around and inside the agglomerates of Ti-based borides at the sintering temperature of 1423 K. At sintering temperature of ≥ 1448 K, the distribution of the Ti-based borides was similar to that at 1423 K. However, the distribution of (Fe,Cr)-based borides was greatly different from that at 1423 K; (Fe,Cr)-based borides were distributed around and inside the agglomerates of Ti-based borides almost without pores.

Fig. 7 Microstructures of the sintered compacts containing 5 and 30 vol% TiB_2 . (a) 1423 K, (b) 1448 K, (c) 1523 K.

Fig. 8 Calculated Fe-rich corner of Fe-B phase diagram.

At 30 vol% TiB₂, the microstructure was similar to that at 5 vol% TiB₂ for the sintering temperature of 1423 K, although more agglomerates of Ti-based borides could be seen. At the sintering temperature of ≥ 1448 K, the distribution of (Fe,Cr)-based borides differed from that at 1423 K; (Fe,Cr)-based borides were distributed around and within agglomerates of Ti-based borides. Although the porosity decreased with increasing sintering temperature, pores remained mainly within agglomerates of Ti-based borides at the high sintering temperature of 1523 K.

From Fig. 6 and 7, the change in the distribution of (Fe,Cr)-based borides seemed to decrease in pores, consequently. The relative sintered density increased with increasing sintering temperature. For 30 vol% TiB₂, high sintered densities like 5 vol% TiB₂ were not obtained at the high sintering temperature of 1523 K because the pores remained in the high-frequency agglomerates of Ti-based borides.

The form of the (Fe,Cr)-based boride changed from 1423 to 1448 K and it can be explained as followings. According to the calculated phase diagram of the Fe-B binary system shown in Fig. 8 (used software: Thermo-Calc software; database: TCFE 6), for coexisting Fe₂B and γ -Fe phases, an Fe-B based liquid phase forms at ≥ 1449 K. For 30 vol% TiB₂, the amount of B in the (Fe,Cr)-based boride was 6.7 wt% at the sintering temperature of 1423 K, according to Table 2(b). This amount of B in the (Fe,Cr)-based boride was similar to that in the Fe₂B phase (8.8 wt%) shown in the calculated phase diagram in Fig. 8. At the sintering temperature of ≥ 1448 K, the Fe-B based liquid phase therefore formed by the reaction between the (Fe,Cr)-based boride and the γ -Fe matrix phase; this Fe-B based liquid phase penetrated the pores around and inside the agglomerates of Ti-based borides. As the Fe-B based liquid phase was transformed into (Fe,Cr)-based boride during furnace cooling to 1173 K after sintering, the distribution form of (Fe,Cr)-based boride at the sintering temperature of ≥ 1448 K differed from that at 1423 K.

4.2 Effect of the relative sintered density and additional TiB₂ content on Young's modulus

In conventional sintered steels, the porosity greatly affects

Fig. 9 Effect of the relative sintered density on the Young's modulus of the sintered compact. (Calculated Young's modulus is based on the equation derived through a unit-cell representation of the microstructure.⁶⁾)

the Young's modulus.⁶⁻⁸⁾ As the porosity is calculated from 100 (%) – the relative sintered density (%); the influence of the relative sintered density on the Young's modulus or TiB₂ contents of 0–50 vol% was discussed.

Figure 9 shows the relationship between the relative sintered density and Young's modulus for 0–50 vol% TiB₂ with sintering at 1523 K after compaction at 392–1176 MPa. In this figure, the Young's moduli of the composite materials (E_c) calculated by eq. (2) are also plotted for the assumed relative sintered density of 100%.

The Young's modulus increased as the relative sintered density increased. For relative sintered densities of $>85\%$, the Young's modulus increased with increasing TiB₂ content. This became more prominent as the relative sintered density increased. In this study, because a relative sintered density comparable to 100% was not obtained for TiB₂ contents of >20 vol%, the Young's modulus at the relative sintered density of 100% was estimated by extrapolating the plots shown in Fig. 9 to higher relative sintered densities for TiB₂ contents of 20–40 vol%. These estimated Young's moduli were close to the values calculated by eq. (2) for the TiB₂ contents of 20, 30, and 40 vol%.

Based on the above consideration, a high Young's modulus according to the additional TiB₂ content should be obtained if a high relative sintered density comparable to 100% is achieved even for TiB₂ contents of >20 vol%. Accelerating the penetration of the liquid phase into the pores around and within agglomerates of Ti-based borides is needed for the high relative density.

5. Conclusion

In the low-alloyed sintered steel containing TiB₂ particles, the improvement of relative density and Young's modulus was investigated by the 1P1S process comprising compacting and vacuum-sintering at 1523 K. The following conclusions could be made.

- (1) High relative sintered densities of $\geq 98\%$ were obtained with 2–15 vol% TiB₂ regardless of the compacting pressure. The formation of the Fe-B-based liquid phase affected increasing the relative density.

- (2) The Young's modulus for 2–15 vol% TiB_2 increased linearly with increasing TiB_2 . These Young's moduli were almost equal to the calculated values for the varying TiB_2 contents.
- (3) For >20 vol% TiB_2 , the relative sintered density and the Young's modulus decreased with increasing TiB_2 content.
- (4) A high Young's modulus according to the TiB_2 content can be realized for >20 vol% TiB_2 if a high relative sintered density comparable to 100% is achieved by accelerating liquid-phase penetration of the pores around and inside the agglomerates of Ti-based borides.

REFERENCES

- 1) K. Tanaka, T. Oshima and T. Saito: [Tetsu-to-Hagané](#) **84** (1998) 586–591.
- 2) K. Tanaka, T. Oshima and T. Saito: [Tetsu-to-Hagané](#) **84** (1998) 747–754.
- 3) N. Matsumoto, K. Tanaka, T. Saito *et al.*: Proceedings of 2000 Powder Metallurgy World Congress, (2000) 28–31.
- 4) Japanese Industrial Standards Committee: JIS Z2280, (1993).
- 5) K.S. Ravichandran: [Acta Metall. Mater.](#) **42** (1994) 1113–1123.
- 6) N. Hirose, J. Asami, A. Fujiko and K. Oouchi: [J. Jpn. Soc. Powder Powder Metallurgy](#) **51** (2004) 515–521.
- 7) N. Hirose, J. Asami, A. Fujiko and K. Oouchi: [J. Jpn. Soc. Powder Powder Metallurgy](#) **52** (2005) 562–565.
- 8) H. Miura, A. Sakamoto and Y. Tokunaga: [J. Jpn. Soc. Powder Powder Metallurgy](#) **27** (1980) 82–87.