Spark Sintering Behavior of Ubiquitously Fe-B and Fe Powders and Characterization of Their Hard Composites

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Spark sintering behaviors of 10 vol% Fe added FeB powders with 10 μm size (hereafter called FeB-10Fe) were investigated in spark sintering process for the development of alternative materials of WC-Co alloys. Spark sintering behaviors of FeB-10Fe in the temperature range of 600 to 1493 K were the same in the sintering curves although their maximum temperatures changed from 1493 to 1523 K. The densification rates, D, of FeB-10Fe and pure Fe were also obtained experimentally, and the maximum point of D was shown at the D of approximately 0.75. The plastic deformation and power law creep deformation of Fe binder phase in FeB-10Fe compacts occurred before and after reaching maximum point of D, respectively. The sinterability was improved by 10 vol% Fe addition, and apparent relative density of FeB-10Fe compacts was increased with the increment of the sintering temperature of 1493 K to 1523 K. In contrast, the mean density of FeB-10Fe compacts was decreased with the increment of sintering temperature because of the poor wettability between liquid phase (Fe and Fe2B) and FeB phase in the liquid phase state at 1505 K and 1523 K. The values of Rockwell hardness of FeB-10Fe compacts were decreased with increment of sintering temperature because of the increment of porosities in FeB-10Fe compacts. In contrast, the values of micro hardness on the interfaces between grains were increased with increment of sintering temperature, because of the promotion of atomic diffusion between particles. There were maximum values of compressive stress and strain on compacts sintered at highest temperature, also because of promotion of the sintering in the interface between grains.

Keywords: Iron borides, spark sintering behaviors, ubiquitously hard materials, compressive strength, densification mechanism

1. Introduction

Hard materials were widely used in the fields of cutting materials, wear-resistant materials, high temperature and corrosion-resistant materials. Hard materials consisted of hard phases and binder phases. The hard phases provided the properties of high strength, hardness and wear resistance, while the binder phases provided the necessary toughness for the material deformation. So far the metal-carbides, -nitrides and -borides were commonly used as hard phases. And the combinations of WC and Co were the most widely used as hard materials. However, the low reserves and refining efficiency of the W influenced the continued supply and energy conservation. Simultaneously, Co as the binder was a high-grade alloy with excellent hardness and toughness, which resulted in relatively low price compared with Co.

2. Experiment procedure

2.1 Powders

FeB (Fukuda Metal Foil and Powder Co., Ltd.) and Fe powders (DOWA IP CREATION Co., Ltd.) were used as starting materials. The mean particle size of FeB and pure Fe powders were 45 and 7.7 μm, respectively. As-received FeB powder consisted of 78.4% Fe, 19.1% B, 0.04% C, 0.48% Si, 0.02% P, 0.003% S and 1.9% Al (mass %). In order to obtain the fine powders, the as-received FeB powders were ball milled using a planetary ball mill (Fritsch Pulverisette 5) at 150 rpm for 86.4 ks. The milling was using 500 mL vial and stainless steel balls with a diameter of 10 mm. The ball to powder weight ratio was 20:1. Figure 1 showed SEM images.

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of (a) as-received-, (b) ball milled-FeB, and (c) pure Fe powders. The shape of as-received and ball milled FeB powders showed irregular. The mean particle size of ball milled FeB powder was $10 \mu m$, which was less than that of as-received FeB powder. Figure 2 shows X-ray patterns of (a) as-received- and (b) ball milled-FeB powders. The phases of both powders were FeB, Fe$_2$B, Fe and B. The predominant phase was FeB, which amounted to 65 or 77\% for as-received- or ball-milled-powders, respectively. In order to prepare the uniform distribution of Fe powders, FeB after ball milling and pure Fe powders were mechanically mixed using the ball mill for 1.8 ks at 50 rpm.

### 2.2 Spark sintering process

During the spark sintering, two graphite punches with diameter of 10 mm and height of 30 mm and a graphite die with an inner diameter of 10 mm, an outer diameter of 40 mm and height of 60 mm were used. The spark sintering process had two modes, pulse discharge sintering mode and resistance heating mode\(^{10}\). All of the powders were consolidated under a vacuum condition ($<10^{-2}$ Pa). The sintering process was shown in Fig. 3. The sintering temperature was measured using a thermocouple (R-type) inserted in the cylindrical of the die. The thermocouple tips were about 2 mm away to the compact. The voltage, current, sample temperature and compact height were monitored from a software (Naviwave System, SSAIloy Co., Ltd.) of the spark sintering.

### 2.3 Characterization

Densities of the compacts were measured by Archimedes’ method. Apparent relative density of compacts was calculated on the basis of the displacement of between electrodes, by the height of the compacts dividing the ideally height of 10 mm. Morphology of the powder was measured by scanning electron microscope (SEM, TOPCON SM-520; Japan). Microstructure of the sintered samples was observed by the optical microscope (Metal Microscope OPTIPHOT-2, Nikon Corporation, Japan). Average grain size, average pore size and porosity of compacts were measured by image analysis methods on the optical microscope images\(^{20}\). Phases in the compacts were characterized by X-ray powder diffraction method (XRD, MAC-M03-XHF22; Japan) using Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA. The macro hardness of the compacts were measured by Rockwell hardness testers (A scale) and micro hardness of the compacts were measured by Vickers hardness tester (MHT-1, Japan). Vickers hardness test of compacts used the load of 2.45 N and the holding time of 15 s. Compressive strength of the compacts were measured at room temperature by using a mechanical testing machine (Autograph DCS-R-5000, Shimadzu Corporation, Japan) with a constant crosshead speed of 0.5 mm/min.
3. Results and discussion

3.1 Spark sintering behaviors

The relations between electric discharged time and compact-temperature or apparent relative density by displacement between electrodes were shown in Figs. 4 and 5. There were two heating conditions in constant current values of 3.8 A/mm² and constant heating rate of 50 K/min, in these figures. Both processes of unsteady and steady at temperature were contained in sintering. The temperatures of compacts were dependent on their thermal and electrical conductivity, which resulted in the higher and lower values in temperatures for pure Fe and FeB compacts. In contrast, apparent relative densities were also increased corresponding to the behavior in temperature-change. The values of relative densities to the sintering time of 1 ks, were decided depending on the shapes of powders and pressure values (15 or 50 MPa). Figure 6 showed the relation between the sintering temperature and apparent relative density, in which were already shown in Figs. 4 and 5. There were good and poor sinterability on pure Fe and FeB powders, respectively, and FeB-10Fe showed the sintering behavior between both powders. The slope of sintering curves below about 1260 K for FeB-10Fe compacts was higher than that of FeB compacts using the 45 μm size powders during spark sintering. It was mainly because of the effect of the addition of Fe binder phase. In addition, the slope of the sintering curve of FeB powders with 10 μm size was higher than that of FeB powders with 45 μm size because of higher sinterability for the fines size of FeB powders. In other words, the high slope in the sintering curve meant high densification rate in the temperature range showing the solid state sintering.

The sintering behaviors of FeB-10Fe powders in the temperature range showing the solid state sintering.

![Fig. 4](Relation between sintering time and sintering temperature of FeB-10Fe sintered at 1493 K, 1505 K and 1523 K, FeB sintered at 1523 K and pure Fe sintered at 1330 K. 15 → 50 MPa*: applied pressure in pulse discharge to resistance heating were changed 15 to 50 MPa, respectively. 50 → 50 MPa*: applied pressure in pulse discharge to resistance heating were keep constant.)

![Fig. 5](Relation between sintering time and apparent relative density of FeB-10Fe sintered at 1493 K, 1505 K and 1523 K, FeB sintered at 1523 K and pure Fe sintered at 1330 K. 15 → 50 MPa*: applied pressure in pulse discharge to resistance heating were changed 15 to 50 MPa, respectively. 50 → 50 MPa*: applied pressure in pulse discharge to resistance heating were keep constant. Insert (b) was the enlargement of the square area of (a).)

![Fig. 6](Relation between sintering temperature and apparent relative density of FeB-10Fe sintered at 1493 K, 1505 K and 1523 K, FeB sintered at 1523 K and pure Fe sintered at 1330 K. 15 → 50 MPa*: applied pressure in pulse discharge to resistance heating were changed 15 to 50 MPa, respectively. 50 → 50 MPa*: applied pressure in pulse discharge to resistance heating were keep constant.)
temperature range below 1493 K showed good reproducibility, although their maximum temperatures changed from 1493 to 1523 K. The apparent relative density of FeB-10Fe compacts was increased monotonously in the temperature range below this temperature. And then the apparent relative density became almost constant above about 1260 K. Moreover, during holding time at the maximum temperature, the final apparent relative density of FeB-10Fe compacts sintered at 1505 and 1523 K were increased significantly, compared with FeB-10Fe compact sintered at 1493 K. It meant that the sintering at 1505 and 1523 K proceeded at partially liquid state sintering, although the sintering at 1493 K was solid state one.

In order to investigate the mechanism of densification in spark sintering process, the densification rate of FeB-10Fe, FeB and pure Fe powders were obtained experimentally as shown in Figs. 7 and 8. The densification rate was obtained by dividing the apparent relative density, \( D \), increment by time increment, \( dt \).

\[
\dot{D} = \frac{dD}{dt} \tag{1}
\]

where \( D \) and \( t \) were currently apparent relative density and time, respectively. Three peaks of \( \dot{D} \) showed at \( D \) of 0.49, 0.52 and 0.76 for pure Fe compacts as shown in Fig. 7. The highest densification rate was found in the curve for pure Fe compacts which was applied to 50 MPa after 15 MPa application in pulse discharge. In contrast, in the \( D \) curves of pure Fe which was initially 50 MPa applied, no peaks appeared in the initial stage in below 0.5 \( D \). It was considered that the rearrangement of the particles by increment of the pressure resulted in the firstly high densification rate in \( D \) of approximately 0.5 showing the start of resistance heating. The secondary peak of \( \dot{D} \) at the 0.52 was caused by the particle-rearrangement due to the plastic deformation in local heat generated areas between particles at a little higher temperature.

There also were three peaks of \( \dot{D} \) at 0.5, 0.52 and 0.75 for FeB-10Fe in Fig. 8. The values in \( \dot{D} \) peaks and the final \( D \) of FeB were lower than those of FeB-10Fe powders. The deformation of FeB phase could not be expected in this temperature range below 1260 K, as shown in Fig. 6. Therefore, the plastic deformation of Fe binder phase caused by Joule’s heat generation between particles played a dominant role in increasing the apparent relative density for FeB-10Fe compacts, which meant the increase of relative density from about 0.7 for FeB to 0.8 for FeB-10Fe by the 10 vol\% Fe addition.

Generally, the densification process could be divided into three stages. The first stage was performed in the pulse sintering process. The second and third stages were plastic deformation and creep deformation stages\(^{21}\). In order to further investigate the sintering mechanism after rearrangement of the particles, the follow eq. (2) as plastic deformation (2nd stage) and the eq. (3) as power law creep deformation (3rd stage) were used for theoretical analysis\(^{22}\).

\[
\dot{D} = AV_\text{ex}^m \Delta \sigma \kappa(D)^{n-1} \left(\frac{\sigma}{\sigma_{\text{yield}}}\right)^{m-n} e^{-\frac{Q}{RT}} \tag{2}
\]

\[
\dot{D} = AV_\text{ex}^m \Delta \sigma \kappa(D)^{n-1} \left(\frac{\sigma}{\sigma_{\text{yield}}}\right)^{m-n} \tag{3}
\]

where \( T, \dot{T}, P, \sigma_{\text{yield}}, A, Q, m, n \) and \( R \) were temperature, heating rate of compact, applied pressure, yield stress of powder material, creep constant, activation energy of power lay creep, stress exponent, coefficient representing the contribution of macroscopic stress and gas constant respectively. And \( \kappa(D) \) was the function of apparent relative density and \( V_\text{ex} \) was an extended volume fraction for densification\(^{23}\). In this study, the values of \( k, m, n \) and \( Q \) were used to be 3.5\(^{21}\), 0.3\(^{21}\), 4.8\(^{21}\) and 326 kJ \( \cdot \) mol\(^{-1}\)\(^{24}\), respectively. Assuming \( V_{eq} \) was equal
The relationship between 0.2% proof stress and temperature of pure Fe was obtained by high temperature tensile tests. In our laboratory, the densification processes of Cu and mixture powder of Cu and Al₂O₃ were investigated by experiments and theoretical calculation of the $\dot{\varepsilon}$ using the eqs. (2) and (3) mentioned above. The experimental results were consistent with the estimated results calculated by eqs. (2) and (3) for Cu, Cu+Al₂O₃. It was considered that plastic deformation of the Cu powders occurred before reaching maximum point of the $\dot{\varepsilon}$ at the $\dot{D}$ of approximately 0.7~0.75. The power law creep deformation of Cu powders occurred after that.

In this study, the experimental results of $\dot{\varepsilon}$ both of pure Fe and FeB-10Fe compacts were consistent with the estimated results using eqs. (2) and (3), as shown in Figs. 7 and 8. Therefore, it was considered that the increment of the densification rate of FeB-10Fe compacts was caused by the plastic deformation of Fe binder phase before reaching maximum point of the $\dot{\varepsilon}$ at the $\dot{D}$ of 0.75. After that power law creep deformation of Fe binder phase occurred above $\dot{D}$ of 0.75.

The morphology of the FeB-10Fe compact sintered at the solid state was shown in Fig. 9. The Fe phase with steep shaped grain boundary was observed in FeB-10Fe compacts which corresponded to the morphologies of pure Fe and FeB particles showed in Fig. 1. As shown in Fig. 9 (b), it was considered that the plastic deformation of Fe phase and movement of the FeB hard particles toward the Fe phase were performed together in the plastic deformation as the 2nd stage. This phenomenon was illustrated as shown in Figs. 10. The plastic deformation of the Fe phase surrounded by the FeB hard phase was largely caused to the higher temperature of 1100 K showing the $\dot{D}$ of 0.75, seen in Figs. 6 and 8, because of just 10 vol% Fe amount in the uniaxial die press at the lateral pressure condition. However, it was interesting that exchanging value of the $\dot{D}$ from plastic deformation to powder law creep deformation was shown to be approximately 0.76, even for the different powders and various binder contents.

### 3.2 Microstructures

Figure 9 showed the microstructure of FeB-10Fe compacts sintered at (a) 1493 K, (c) 1505 K and (d) 1523 K, FeB compacts using (e) 10 $\mu$m size powders and (f) 45 $\mu$m size powders sintered at 1523 K. (b) was the enlargement of the square area of (a).
size powders sintered at 1523 K. In addition, (b) was the enlarged image of the square area of (a). The average sizes of pores in FeB-10Fe compacts sintered at 1493, 1505 and 1523 K were 9.7, 13.6 and 15.7 μm, respectively. Moreover, the shape of pores in FeB-10Fe compacts gradually changed from the irregular shape to round shape with the increment of sintering temperature. It was mainly because the liquid phase consisting of Fe and Fe2B in FeB-10Fe compacts sintered above 1505 K was appeared during the holding time according to the sintering curves of Fig. 6. As reference, the average size of pores of FeB compacts using 10 and 45 μm size powders were 15.9 and 19.1 μm. As shown in Table 1, the porosities of FeB-10Fe compacts were increased with the increment of sintering temperature. This attributed to the liquid phase in FeB-10Fe compacts squeezed out from die during holding time at 1505 K and 1523 K because of the poor wettability between liquid phase and FeB28).

The densities of FeB-10Fe compacts measured by Archimedes’ method were shown in Table 1. The increment of the porosity with the sintering temperature resulted in the decrease of the densities of FeB-10Fe. As reference, the porosities and densities of FeB compacts using 10 and 45 μm size powders were also shown in Table 1. It was found that manufacturing of compacts using fine particle size of FeB contributed to decrease the porosity compared that of FeB compacts using large particle size powders. The average grain sizes of FeB-10Fe compacts were slightly increased as the sintering temperatures were increased, compared with average particle sizes of starting powder, as shown in Table 1. High sintering temperature promoted the atomic diffusion between particles, and the liquid phase resulted in the further grain growth of FeB-10Fe compacts.

Figure 11 showed the XRD patterns of FeB-10Fe compacts sintered at 1493 K, 1505 K and 1523 K and FeB compacts using 10 and 45 μm size powders sintered at 1523 K.

![Fig. 10 Deformation process of Fe binder around FeB powders at lateral pressure condition as seen in Fig. 9 (b).](image)

![Fig. 11 XRD patterns of FeB-10Fe compacts sintered at 1493 K, 1505 K and 1523 K and FeB compacts using 10 and 45 μm size powders sintered at 1523 K.](image)

<table>
<thead>
<tr>
<th>Powders</th>
<th>Sintering temperature/K</th>
<th>Average grain size/μm</th>
<th>Porosity(%)</th>
<th>Density×10⁻³ kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeB-10Fe with 10 μm</td>
<td>1493</td>
<td>9.7</td>
<td>19</td>
<td>6.18</td>
</tr>
<tr>
<td></td>
<td>1505</td>
<td>13.8</td>
<td>25</td>
<td>6.16</td>
</tr>
<tr>
<td></td>
<td>1523</td>
<td>18.1</td>
<td>29</td>
<td>6.07</td>
</tr>
<tr>
<td>FeB with 10 μm</td>
<td>1523</td>
<td>11.3</td>
<td>28</td>
<td>6.01</td>
</tr>
<tr>
<td>FeB with 45 μm</td>
<td>1523</td>
<td>50.1</td>
<td>31</td>
<td>5.88</td>
</tr>
</tbody>
</table>
atomic diffusion, which resulted in the increment of FeB amount as equilibrium phase in mean composition of Fe-19%B received powders.

3.3 Mechanical properties

Figure 12 showed HRA of FeB-10Fe compacts sintered at 1493, 1505 and 1523 K and FeB compacts sintered at 1523 K. The value of HRA of FeB-10Fe compacts sintered at 1493 K was higher than that of compacts sintered above 1505 K. It was mainly because the mean densities of FeB-10Fe compacts were decreased with increment of sintering temperature. Moreover, the grain coarsening in FeB-10Fe compacts sintered above 1505 K corresponded to the decrement of the values of HRA. Moreover, the values of HRA of FeB compacts with 10 and 45 μm powders sintered at 1523 K were 82 and 78, respectively. As mentioned above, the FeB compacts using small size powder sintered at 1523 K possessed the smaller porosity and larger mean density, which resulted in the increment of values of HRA of FeB compacts. On the other hand, the value of HRA of FeB-10Fe compact sintered at 1493 K was close to that of FeB compact using 10 μm size powders sintered at 1523 K. The values of HRA of FeB compact mainly depended on the porosity. The porosity of FeB-10Fe compact sintered at 1493 K was lower than that of FeB compact using 10 μm size powders sintered at 1523 K. However, the hardness of FeB-10Fe compact sintered at 1493 K was not high, because of the addition of 10 vol% Fe binder (Hv 0.608 GPa). Therefore, the value of HRA of FeB-10Fe compact sintered at 1493 K was close to that of FeB compact (Hv 16.5 GPa) using 10 μm size powders sintered at 1523 K.

Figure 13 showed Vickers hardness of the interfaces of FeB/FeB, FeB/Fe2B and Fe2B/Fe2B in FeB-10Fe compacts. The inserted dotted lines showed the Vickers hardness of FeB and Fe2B intra-grains. Vickers hardness values of FeB and Fe2B intra-grains in FeB-10Fe compacts were 16.5 and 12.0 GPa, which were consistent with hardness values in the literature29. As shown in Fig. 13, Vickers hardness values of some interfaces in FeB-10Fe compacts sintered at 1505 and 1523 K were higher than that of compacts sintered at 1493 K. It was because the higher sintering temperature promoted the diffusion of atoms between grains, which resulted in the increment of the interfac hardness between grains. It was probable that the atomic diffusion coefficients of Fe and B atoms in the interface of FeB/FeB and Fe2B/Fe2B grains were different, which should be studied more in the future. In addition, the Vickers hardness of the interfaces of FeB/FeB and Fe2B/Fe2B in FeB-10Fe sintered at 1523 K was close to the hardness of their intra-grains. It was considered that the atomic diffusion was well completed at 1523 K.

Figure 14 showed the compressive stress-strain curves of FeB-10Fe compacts sintered at 1493 K, 1505 K and 1523 K. As shown in Fig. 14, the maximum compressive stress and strain of compacts were increased with increment of the sintering temperature. Moreover, the maximum compressive stress of FeB-10Fe compacts sintered at 1523 K with larger grain size and high porosity were larger than that of compacts sintered at 1493 K. It was considered that the high strength between grains in compacts sintered at high sintering temperature resulted in the increment of compressive stress and strain. However, Young’s modulus of FeB-10Fe compacts sintered at 1493 K, 1505 K and 1523 K were 26.8, 26.4 and 21.1 GPa, respectively.
The values of Rockwell hardness on FeB-10Fe compacts were investigated in this study.

4. Conclusions

The spark sintering behaviors and some properties of FeB-10Fe were investigated in this study.

(1) The sinterability was improved by 10 vol% Fe addition, and relative density of FeB-10Fe compacts were increased with the increment of the sintering temperature of 1493 K to 1523 K. The densification rate, $D$, of FeB-10Fe and pure Fe were also obtained experimentally, and its maximum point of $D$ was shown in the $D$ of approximately 0.75. The plastic deformation and power law creep deformation of Fe binder phase in FeB-10Fe compacts occurred before and after reaching maximum point of $D$, respectively.

(2) The values of Rockwell hardness on FeB-10Fe compacts were decreased with increment of sintering temperature because of the increment of porosities in FeB-10Fe compacts.

(3) The values of micro hardness on the interfaces between grains were increased with increment of sintering temperature, because of the promotion of atomic diffusion between particles. There were maximum value of compressive-stress and -strain on compacts sintered at highest temperature, also because of promotion of the sintering in the interfaces between grains.

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