Low temperature densification of ZrB₂ by the mechanical pre-treatment of particles

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The effects of the pre-treatment of commercially available powder by high energy ball milling on the densification of highly refractory ZrB₂ were investigated. The pristine powder could be crushed into 10 nm in size by high energy ball milling. The resultant powder was densified, using spark plasma sintering apparatus under 120 MPa pressure. Dense ZrB₂ with fine microstructure was obtained after sintering at 1425°C for 1 h. The ultra-fine particle size of crushed ZrB₂, and the deformation of the powders and grains by dislocation played important roles in the low temperature densification of the pre-treated ZrB₂ powder. WC, which was incorporated during the milling process from WC–Co balls, formed a solid solution with ZrB₂, and promoted grain growth at and above 1450°C. In contrast, Co was mostly segregated at the grain boundary. The 4-point bending microstructure was obtained after sintering at 1425°C for 1 h. The ultra-fine particle size of the raw powder, and the resultant specimens had good mechanical properties.

Key-words: ZrB₂, High energy ball milling, Sintering, Nano

1. Introduction

During the last decade, intensive researches have been performed into ultra-high temperature ceramics, such as ZrB₂, due to the combination of excellent properties, such as mechanical properties and chemical/thermal stability. However, densification of ZrB₂ is difficult, because of its high melting temperature and strong covalent bonding. Without sintering additive, densification of ZrB₂ typically requires pressure-assisted sintering at 2100–2300°C. Consequently various types of sintering additives have been used during the last decades. In the late 1990’s and early 2000’s, nitride ceramics, such as Si₃N₄, HfN and AlN, were used as sintering additives of ZrB₂. More recently, additives such as boron, B₄C, carbon, MoSi₂, polycarbosilane, rare-earth oxides and ZrSi₂ have been tested. In many cases, the sintering additives promoted densification, by forming secondary phases with low melting temperature. However, the secondary phases often cause the deterioration of high temperature properties of ZrB₂. For example, ZrB₂ could be densified by pressureless sintering at 1650°C when adding 40 wt% of ZrSi₂, which has a low melting temperature (1620°C). However, the specimens lost strength at 1400°C, thus were not appropriate for application at high temperature.

In order to prevent the use of sintering additives, reactive sintering and reactive melt infiltration using Zr, Si, B, B₄C and C have been investigated. In the process, the densification of ZrB₂ was promoted by the heat that was produced during exothermic reduction reactions. Densification of ZrB₂–SiC–ZrC composite was accomplished without using sintering additives at 1700°C, by reactive hot pressing. However, industrial application of the reactive densification method has been scarcely reported, because the prices of Zr and B powders are fairly high. Also, careful handling of the process in an inert atmosphere is required, due to the high reactivity of Zr powder with humidity.

The pulverization of ZrB₂ powder into nanometer scale has been recently reported, using the high energy ball milling (HEBM) method. The primary particle size of crushed ZrB₂ was 9 nm. The effects of high energy milling on the densification of ZrB₂ have recently been reported, but at the temperature range of 1800–1900°C, or together with SiC, which may cause the formation of borosilicate glass. Also, the former reports did not consider the effects of defects and contaminants within grains, which were formed by high energy milling.

The present investigation reports the densification of mono-phase ZrB₂ without using sintering additives at 1425°C, by the pre-treatment of ZrB₂ powder using HEBM process, and subsequent densification of the powder using the spark plasma sintering (SPS) method under 120 MPa. To our knowledge, the achieved sintering temperature is more than 100°C lower than the current state of the art, which was attained using 40 wt% of low melting temperature additives (ZrSi₂). The sintering kinetics and mechanical properties of the resultant ZrB₂ were analyzed.

2. Experimental procedure

Commercially available ZrB₂ powder (ZrB₂–F, d₅₀: 2.12 μm, Japan New Metals, Co.) was used as a starting material. 5 g of the raw powder was crushed using a high energy ball mill (M-8000, Spex) equipped with WC–Co balls (diameter: 5.0 mm, 50 g) and jar for 6 h. The oxygen contents of the powders before and after the treatment were determined by a Nitrogen/Oxygen Determinator (ON900, Eltra). The phase identification and morphology of the milled powder were analyzed by X-ray diffractometry (XRD, D-Max2200, Rigaku Co.) using Cu Kα radiation (wavelength of 1.54056 Å), scanning electron microscopy (SEM, JSM-
6700F, Jeol, Japan) and transmission electron microscopy (TEM, JEM-2100F, Jeol) equipped with energy-dispersive spectroscopy (EDS, Ex-24065JGT, Jeol). A focused ion beam (FIB) equipment was used for obtaining TEM specimens, to minimize the formation of dislocation during sample preparation. Thermo-gravimetric analysis (TGA, STA 402C, Netzch) of the crushed powder was performed under flowing Ar atmosphere (20 ml/min) up to 1950°C (heating rate: 5°C/min). In order to analyze the effect of WC-Co contaminants on densification, part of the milled powder was dispersed in ethanol, and the contaminants were removed by a strong magnet. The contents of W and Co before and after the magnetic separation were measured using the inductively coupled plasma method (ICP, ICAP 6000, Thermoscientific).

The pristine or pre-treated ZrB2 powders were densified using spark plasma sintering apparatus (SPS, Dr-Sinter 4000, SPS Syntax) at 1400–1950°C for 3–120 min under 120 MPa pressure in vacuum (heating rate: 50°C/min). 1g of powders were sintered into 10 × 2.5 mm pellets at 1475–1950°C, in order to analyze the densification behavior during heating. Small samples were used, due to the limitation of the SPS apparatus for heating large samples at high temperature. Based on the data, bars having 2 × 10 × 25 mm in size were sintered at 1400–1650°C using 5 g of powder. The bars were machined to 1.5 × 2×25 mm in size, and one side of the bend bars was polished up to 1 μm finish. The 4-point bending strength was measured using 5 specimens per condition (upper and lower span length: 10 and 20 mm, respectively; crosshead speed: 0.3 mm/min). The phase identification, microstructure and chemical composition of the sintered specimens were analyzed by XRD, SEM, TEM and EDS.

3. Results and discussion
3.1 Properties of pre-treated ZrB2 powder

Figure 1 shows the morphology of the powder after HEBM treatment. The crushed ZrB2 was composed of fine particles of about 10 nm in size [Fig. 1(a)]. Dislocation was not observed within fine particles of 10–20 nm in size. Dislocation was reported to become unstable when the particle size decreases below a certain value. For example, the maximum dependency of dislocation density as a function of the energy of shocks was reported to be 35 nm in the case of Cu. However, rather large particles (50–100 nm) were also observed after HEBM [Fig. 1(b)]. The ultra-fine particles formed an agglomeration, because of the cold-welding during HEBM. The size of the agglomerates ranged between 50–500 nm [Fig. 1(c)].

The particle size calculated from the Scherrer equation using the XRD data shown in Figure 2 was 10.04 nm, which matched well with TEM data [Fig. 1(a)]. The results were in accordance with those reported by Galán et al., where the crystallite size decreased to 9 nm after HEBM treatment of ZrB2 for 3 h.

WC peaks were also identified in the XRD data of crushed ZrB2, which was caused by contamination from the milling media. The weight loss of the ball and jar, which indicated the contaminant content in the pre-treated ZrB2, increased almost linearly with time. The contaminant content was 4.5 wt% after milling for 6 h.

Figure 3 shows the TGA data of the ZrB2 powder before and after the HEBM treatment. The difference of mass loss below 1050°C was most probably caused by the different amount of humidity that was adsorbed on the surface of the powders. The mass loss of the milled powder became more distinct than that
of the pristine one above 1050°C, due to the vaporization of B₂O₃, which was formed on the particle surface. The oxygen content of ZrB₂ powder increased from 1.05 to 3.3 wt% after HEBM treatment. Because ZrO₂ was formed simultaneously with B₂O₃ during milling, the increase of B₂O₃ content after the pre-treatment was estimated to be 1.9 wt%, based on the oxygen content. The value was similar to the difference of mass loss between the pristine and milled ZrB₂ powders at 1050–1950°C (2.0 wt%, Fig. 3).

3.2 Densification of pre-treated ZrB₂ powder

Figure 4(a) shows the effect of HEBM treatment of the raw powder on the sintering shrinkage of small pellets (φ10 mm) during heating up to 1950°C using SPS. In the case of the pristine powder, the onset temperature of shrinkage was 1770°C as shown in the enlarged figure, and the shrinkage became rapid above 1870°C. In contrast, the densification of the milled powder started at 1420°C, and the shrinkage rate became slow above 1610°C, before the onset of the second shrinkage at 1690°C. Shrinkage occurred during the sintering of both the pristine and milled powders at 1950°C for 3 min, but the density of the sintered specimens (4.7 and 5.0 g/cm³, respectively) was much lower than the theoretical value of ZrB₂ (6.1 g/cm³). The relative densities of the sintered specimens were about 80% in both cases, when considering the increase of the theoretical density of the milled powder caused by the contaminants (density of WC and Co: 15.6 and 8.9 g/cm³, respectively). The strong shrinkage of milled powder at 1950°C was partly caused by the
extrusion of powder through the hole on the surface of the mold, which was made in order to measure the temperature of the specimen during sintering (Figure 5).

When sintering 1 g of milled powder for 1 h at 1475–1500°C, which is the first shrinkage region, the shrinkage started at 1430°C, and the behavior continued for 5–15 min during holding at the target temperature [Fig. 4(b)]. The density of the specimens was 6.2 and 6.25 g/cm³ after sintering at 1475 and 1500°C, respectively. The results clearly show that fairly dense specimens (relative density: 96–97%) could be obtained at 1475–1500°C without using sintering additives, by the pre-treatment of ZrB₂ powder using HEBM, and subsequent SPS under high pressure (120 MPa).

The onset temperature of shrinkage of the bar type specimens (1290–1340°C) was lower than that of the 10 mm pellets [1430°C, Fig. 4(c)]. In addition, sintering shrinkage occurred during holding at and above 1400°C. The vertical lines of the shrinkage curve at the sintering temperature in Figs. 4(b) and 4(c) shows the occurrence of sintering shrinkage during holding at the target temperature. The results indicated that the densification temperature of large bar-type specimens was lower than that of small pellets.

There have been several reports showing the beneficial effects of current on the initial stage of sintering. A higher current was required to sinter large specimens than small ones at the same temperature in the present experiment (980 vs. 1150A at 1400°C). Consequently the large current is believed to promote the sintering of bar type specimens.

The actual temperature of a specimen during SPS may be different from the measured value using a pyrometer. Matsugi et al. compared the temperature of electrically insulating Al₂O₃ and conductive Ti samples in graphite molds, and reported that Ti was 10°C hotter than the mold, while the temperature of Al₂O₃ was 30°C lower than the surrounding graphite. Electrical current through conductive Ti powder induced Joule heat of the sample, thus caused heat flux from the sample to the mold. In contrast, the insulating sample was heated by conduction from the surrounding mold, because electrical current cannot pass through Al₂O₃. Likewise, the actual temperature of the specimens shown in Fig. 4 might be slightly higher than the measured values, due to the low electrical resistivity of ZrB₂ (9.2 μΩ cm).

Table 1 summarizes the relative density of bar type specimens sintered under different conditions. The relative density was 93.6% after sintering at 1400°C for 2 h. The value increased to 96.4% after sintering at 1425°C for 1 h, indicating that the minimum temperature for the densification of pre-treated ZrB₂ powder was 1425°C. The required sintering time to obtain dense specimens decreased at a higher sintering temperature.

Walker et al. investigated the sintering behavior of milled ZrB₂–SiC powder mixture and reported that the relative density was 96% after sintering at 1900°C. They reported that B₂O₃, which was on the surface of ZrB₂, melted and segregated at the triple point during heating. The melt evaporated, and caused the formation of large pores in the sintered ZrB₂. The relative density was reported to be increased by the removal of B₂O₃ through the heat treatment of the milled powder at 1150°C for 8 h. Likewise, 2 wt% of B₂O₃ was formed during HEBM in the present investigation, which is believed to suppress the complete densification of ZrB₂.

### Table 1. Relative density (R. D.) of bar type specimens after sintering at 1400–1600°C under 120 MPa pressure

| Sintering condition | R. D. | Sintering condition | R. D. |
|--------------------|------|--------------------|------|
| 1400°C, 2 h        | 93.4 | 1450°C, 15 min     | 96.1 |
| 1425°C, 1 h        | 96.4 | 1550°C, 10 min     | 96.9 |
| 1450°C, 5 min      | 93.3 | 1600°C, 10 min     | 97.1 |

### 3.3 Densification mechanisms

The decrease of particle size, the deformation of the powder by dislocation, and contamination during the milling process are considered to be the possible reasons to explain the low temperature sintering of ZrB₂ after HEBM treatment.

Particle size has an important effect on the solid state sintering in terms of temperature and time reduction. The sintering temperature was reported to decreases with particle size, according to the following formula:

\[ T_2 = \frac{T_1}{\alpha m \cdot \ln \frac{D_2}{D_1}} \]  

\(T_1\): required sintering temperature when particle size is \(D_1\)  
\(T_2\): required sintering temperature when particle size is \(D_2\)  
\(m\): exponent value

The sintering of tungsten, which is also a refractory material, was reported to start at 825°C for 31 nm particles, while the temperature decreased to 625°C when using 9 nm powder. Consequently, the formation of ultra-fine particles (d<sub>50</sub> 10 nm) is one of the major reasons for the low temperature sintering of HEBM-treated ZrB₂ powder.

Figure 6 is a TEM image of a ZrB₂ grain sintered at 1450°C using HEBM-treated powder, showing the formation of imperfections within the grains. The presence of dislocation within ZrB₂ grains has been reported, in spite of the high covalent bonding strength between Zr and B. The multiplication and movement of dislocation within ceramic grains occur at rather high temperature. For example, the dislocation within Al₂O₃ grain moves actively at 700–1200°C. The imperfections that remained within relatively large ZrB₂ particles after HEBM treatment, as shown in Fig. 1(b), were believed to have multiplied, and promoted the deformation of ZrB₂ particles under high pressure of 120 MPa above 1290°C.

In order to clearly understand the effects of the contaminants on the densification of pre-treated ZrB₂ powder, magnetic separation of the contaminants was performed. The W and Co contents within the crushed powder decreased from 3.62 and 0.39 wt% to 2.28 and 0.25 wt%, respectively, by magnetic separation.
ever, the reduction of contaminants did not change the relative density after sintering.

Figure 7 is a TEM image and EDS mapping of a specimen sintered at 1450°C, showing that W was homogeneously distributed within ZrB₂ grains, due to the formation of a solid solution with ZrB₂ [Figs. 7(a) and 7(b)]. Zhang et al. also reported the formation of solid solution between ZrB₂ and WC by XRD analysis. The solubility limit was reported to be 8 wt%.

The sintering behavior of a material is affected by the formation of solid solution due to the change of diffusion coefficient for matter transport within grains, and at the grain boundary. Consequently, WC has been used as a sintering additive of ZrB₂. However, dense ZrB₂ was obtained by hot pressing at 1800°C, when using 1–5 wt% of WC as a sintering additive.

Co was preferentially segregated at the grain boundary [Fig. 7(c)]. Co has also been used as a sintering additive of ZrB₂, but pressure-assisted sintering at 1800°C was required for densification.

The results of magnetic separation, together with the high sintering temperature of ZrB₂ when using WC or Co sintering additive, showed that neither contaminant had a strong effect on the densification of HEBM treated ZrB₂ powder at 1400–1600°C.

The above discussion indicates that the first shrinkage of the HEBM treated powder shown in Fig. 4(a) at 1420–1610°C was mainly caused by the ultra-fine particles and the deformation of particles by imperfections under high temperature and pressure. The shrinkage rate decreased above 1650°C due to the rapid grain growth, which will be discussed in detail in the following paragraphs, and the decrease of the number of imperfections by annihilation. Because both the sintering mechanisms became inefficient above 1700°C, the relative density of the milled powder was only 80% after heating at 1950°C for 3 min, when the first shrinkage region was rapidly passed through during heating [Fig. 4(a)].

Figure 8(a) shows the morphology of the fractured surface of a specimen sintered at 1450°C for 5 min, with the average grain...
size of about 200 nm. The fine microstructure was attributed to the ultra-fine raw powder (~10 nm), low sintering temperature, and short holding time. Grain growth occurred rather rapidly above 1450°C. The grain size became 1 micrometer after sintering at 1500°C for 5 min [Fig. 8(b)].

Different from the rapid grain growth during sintering under pressure above 1450°C, the growth of ZrB2 within a pile of powder did not intensively occur. TEM analysis showed that the average particle size of ZrB2 was 25 nm after heating a pile of ZrB2 powder at 1550°C for 15 min [Fig. 8(c)], which increased to 50 nm at 1750°C [Fig. 8(d)]. The results indicated that the rapid grain growth of ZrB2 during densification above 1450°C was most probably caused by the formation of solid solution with WC, and/or by the Co-based grain boundary phase, because the growth of ZrB2 particles did not strongly occur at this condition.

The growth of ceramic grains has been expressed by the following formula:32)

\[ G^m = G_0^m + Kt \]  

where, \( G \): grain size,  
\( G_0 \): initial grain size,  
\( K \): temperature dependent growth factor,  
\( t \): time,  
\( m \): exponent.

The exponent value \( m \) is decided by the growth mechanism. The \( m \) value of lattice diffusion and diffusion through the continuous second phase is 3, while that of the solution of second phase is 1. Accordingly, the growth rate strongly depends on temperature during the formation of solid solution. On the other hand, solute drag phenomenon suppresses the grain growth when a secondary phase such as Co is segregated at the grain boundary.32) The results indicated that the rapid grain growth of ZrB2 at 1450-1500°C was caused by the formation of solid solution with WC.

Table 2 summarizes the 4-point bending strength of the specimens sintered under different conditions.

| Sintering condition | Strength (MPa) | Sintering condition | Strength (MPa) |
|---------------------|----------------|---------------------|----------------|
| 1425°C, 30 min      | 437 ± 7        | 1500°C, 15 min      | 461 ± 35       |
| 1450°C, 15 min      | 481 ± 27       | 1650°C, 5 min       | 461 ± 20       |

4. Conclusions

Densification of ZrB2 was attained at 1425°C without using sintering additives, by the application of high energy ball milling and spark plasma sintering under high pressure. The average grain size of sintered specimens was 200 nm after densification at 1450°C. Densification was promoted by ultra-fine powders of 10 nm in size. The deformation of grains caused by the imperfections within ZrB2 grains was another reason for low temperature sintering. WC contaminants induced grain growth above 1450°C. In spite of the low sintering temperature, the specimen had fairly high strength, of up to 481 MPa.

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