Densification behavior of ZrB_2 with Co–WC as additives

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Among ultra-high temperature ceramics (UHTCs), zirconium diboride (ZrB_2) ceramics have high electrical/thermal conductivity, excellent corrosion resistance, and a chemically stable crystal structure. These properties make ZrB_2 suitable for extreme chemical and thermal environments, such as atmospheric re-entry and hypersonic aircrafts. ZrB_2 has low intrinsic sinterability due to its strong covalent bonds and low self-diffusion coefficients. In the ZrB_2 sintering process, decreased ZrB_2 particle size is an important factor for increasing the driving force of densification. SPEX mill, a type of high energy milling, was employed to decrease particle size. Co-bonded WC was used by jar and media in SPEX mill because Co–WC is hard enough to pulverize ZrB_2 particles. During SPEX milling, ZrB_2 powders were contaminated by Co–WC. Co–WC contaminant could be also used by sintering additives. This study investigated the effects of Co, WC, and Co–WC for the densification of ZrB_2 . The ZrB_2 composites were sintered by spark plasma sintering (SPS). Microstructures were observed using scanning electron microscopy (SEM) and phases of sintered samples were characterized by X-ray diffraction (XRD).

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1. Introduction

Ultra-high temperature ceramics (UHTCs) are major subjects of recent research and development in the field of structural materials. Among UHTCs, zirconium diboride (ZrB_2) has a high melting point (3250°C), high electrical conductivity, high thermal conductivity, and chemical stability. Because of these excellent properties, ZrB_2 is used for refractory materials, cutting tools, and armor.

In recent years, ZrB_2 has also been considered promising materials for thermal protection systems of hypersonic vehicles, re-entry of space shuttles, and rocket nozzles.^{1,2)}

ZrB_2 has low self-diffusion coefficients due to strong covalent bonding. Additionally, surface oxygen contaminant of both B_2O_3 and ZrO_2 disturb mass transport between ZrB_2 .^{3–6)} Thus, high temperature and external pressure are required for densification of ZrB_2 . Diverse processing methods have been studied in order to enhance the sinterability of ZrB_2 .

Previously on a study, researchers developed a two-step pretreatment method.⁷⁾ First, commercial ZrB_2 powder was pulverized to an average size of 0.5–0.6 μm using a SPEX mill (SPEX, Mixer/Mill 8000D, SPEX SamplePrep Corp., USA). Second, oxide impurities on the surface of ZrB_2 powder were removed with a dilute hydrofluoric solution. Through these two-step pretreatment, 99.5% relative density of pure ZrB_2 was obtained without any sintering aids.

Small particles size and low oxygen content are major effects on the enhanced sinterability of ZrB_2 . But, contamination with Co–WC was also considered as a sintering additive. A Co-bonded WC (Co–WC) jar and balls were used during the SPEX milling process because Co–WC is hard enough to crush ZrB_2 particles.

After the SPEX milling, X-ray fluorescence (XRF, Model XRF-1700, Shimadzu Corp., Tokyo, Japan) spectroscopy determined the presence of 6 wt.% Co–WC contaminant. In this study, Co, WC, and Co–WC are respectively investigated the effects for the ZrB_2 additives.

2. Experimental procedures

Commercially available ZrB_2 powder (99.5%, Alfa Aesar, A Johnson Matthey Co., Ward Hill, MA, USA) which had an average particle size of 2.61 μm and contained 1.23 wt.% oxide was used as a starting material. Tungsten carbide (WC, 99.5%, Alfa-Aesar, 0.8–1 μm), cobalt bonded tungsten carbide (Co–WC, 99%, Alfa-Aesar, 1 μm), and cobalt (Co, 99.8%, Alfa-Aesar, 0.8–0.6 μm) powders were mixed with ZrB_2 powder in polypropylene plastic bottles along with methanol, following the batch composition shown in Table 1.

Mixed powders were then ball milled for 48 h at 200 rpm. To obtain homogenous slurries, rotary evaporation was applied.

Table 1. Batch composition

Sample Name	Composition			Note
	WC	Co	WC–Co	
Z0WC	0			WC only
Z5WC	5			
Z10WC	10			
Z15WC	15			
Z0Co		0		Co only
Z0.1Co		0.1		
Z0.7Co		0.7		
Z1.0Co		1.0		
Z0W-C			0	Co–WC (6 wt. % Co)
Z5W-C			5	
Z10W-C			10	
Z15W-C			15	

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Slurries were strained by a -325 mesh sieve. The slurries were dried by vacuum oven at room temperature for 24 h.

Next, spark plasma sintering (SPS; Plasma Activated Sintering, ELTEK Corp., Anyang, Korea) was employed to densificate the ZrB_2 composite under the following conditions: temperature: 1400, 1500, and 1600°C; pressure: 60 MPa; mild vacuum atmosphere; heating rate: 100°C/min; and dwelling time: 15 min.

Sintered pellets were disk type with 10-mm diameters and 2-mm thicknesses. Pellets were polished by 1- μm diamond slurry. The microstructure was observed by scanning electron microscopy (SEM, Model JSM-6700F, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM, Model JED-2300, JEOL, Tokyo, Japan). Relative density was measured by the Archimedes method. Elementary analysis was conducted by an electron probe micro analyzer (EPMA, EPMA-1600, SHIMADZU, Japan). Phase analysis of the ZrB_2 powders was carried out by X-ray diffraction (XRD, UltimaIV, Rigaku, Japan) using $\text{Cu K}\alpha$ radiation ($k = 1.54178 \text{ \AA}$). Samples were scanned over a range of $2\theta = 20\text{--}80^\circ$ with scanning rate of $3^\circ/\text{min}$. From the 2θ values, d values were calculated. The data were compared with standard values from the JCPDS diffraction files (PDF) to identify phases.

Fig. 1. Relative density of the sintered ZrB_2 -WC composite as a function of WC concentration.

Fig. 3. XRD patterns of ZrB_2 -WC composites.

Fig. 2. SEM images of ZrB_2 -WC composites.

Fig. 4. SEM-EDS mapping data of ZrB₂-10WC sintered at 1500°C.

Fig. 5. Relative density of ZrB₂-Co composite as a function of Co concentration.

3. Results & Discussion

3.1 Effects of WC

As shown in **Fig. 1**, the relative density decreased as the WC concentration increased. WC is expected to have a role as a reduction agent. To enhance the sinterability of ZrB₂, oxygen contents are removed. Therefore, WC is expected to enhance densification rate of ZrB₂. During the densification process, the following reactions are expected.

Previously on a study, ZrC solid-solution in ZrB₂ could increase solid-state diffusion rates.⁸⁾ However, XRD (**Fig. 3**) could not detect ZrC phase. Therefore, relative density data (**Fig. 1**) show that the effect of ZrC is insufficient to enhance the sinterability of ZrB₂.

The microstructure of ZrB₂-WC composites is shown in **Fig. 2**. Many pores were identified, and the sintered specimen looks similar to a green body. Corresponding with the density data, as the WC concentration increased, the microstructure of the sintered specimen doesn't have any large differences among them.

By 2θ intensity values from **Fig. 3**, ZrB₂ and tungsten boride (WB) were detected. Corresponding with EDS mapping data (**Fig. 4**), WB was segregated among ZrB₂. This secondary phase (WB) could disturb mass transport between ZrB₂. Additionally, the amount of WC increased, the intensity of WB increased. Therefore, it was difficult to identify the effects of WC as a sintering additive for ZrB₂.

3.2 Effects of Co

As seen in **Fig. 5**, as sintering temperature and Co concentration increased, relative density increased. This was expected in the case of only Co, which has a role as a liquid phase sintering source due to its melting point of 1495°C.

Liquid phase sintering process is widely used for densification of ceramics. Because, low sintering temperatures, homogenization and high relative density are easily obtained. Also, resulting microstructures often provide mechanical or physical material properties superior to solid-state sintered materials.⁹⁾

As shown in **Fig. 6**, Co formed a dense sintered body without any secondary phases (also see **Fig. 7**). Because the operating temperature was higher than the Co melting point, Co could have a role as the liquid phase sintering source.

To clarify the existence of Co, TEM was employed. Co was identified at the triple points. Also, Co has a good wettability (contact angle $\leq 90^\circ$) with ZrB₂, as shown in **Fig. 8** (corresponding with **Table 2**). Therefore, Co has a great effect on densification of ZrB₂ caused liquid phase sintering process accelerating mass transfer through liquid phase of Co.

3.3 Effects of Co–WC

Previous researches on sintering additives for ZrB₂ have only studied WC and Co. As mentioned earlier, we expected that Co–WC composite contamination generated by SPEX mill process could enhance the sinterability of ZrB₂. Therefore, to clarify the influence of Co–WC compound as an additive, additional experiments were conducted.

From **Fig. 9**, relative density increased as the amount of Co–WC increased. For Co–WC compound, carbothermal reduction of WC and liquid phase sintering of Co were expected simultaneously.

As shown in **Fig. 10**, with increasing amounts of Co–WC, the microstructure of sintered specimens became denser. Specifically,

Fig. 6. SEM images of ZrB_2 -Co composites.

Fig. 7. XRD data of ZrB_2 -Co composites.

Fig. 8. TEM image of Z0.7Co sintered at 1600°C showing Co located at the triple junction.

Table 2. TEM-EDS analysis data at the triple junction

Element	Mass (%)	Atom (%)
Co	15.44	22.04
Zr	84.56	77.96

Fig. 9. Relative density of ZrB_2 -WC-Co composite as a function of WC-Co concentration.

Fig. 10. SEM images of ZrB_2 –WC–Co composites.

Fig. 10(c) shows the most common resultant system of liquid phase sintering, which consists of spheroidal grains that substantially increase in size during the process.^{10)–13)}

Microstructure of the Z15W–C specimen could easily divide into three areas: black, white, and grey. Corresponding with Figs. 11 and 12, the black area consists of Co, B, and C. The white area consists of tungsten composites, both WB and WO_3 . The grey area consists of ZrB_2 respectively.

This ternary system (black area) is likely generated by re-precipitation and dissolution during liquid phase sintering. And both WB and WO_3 , these secondary phases were generated by exceeding the solubility limit of WC concentration for ZrB_2 .^{14),15)} Furthermore, these secondary phase (black, white areas) could interrupt mass transport between ZrB_2 . Thus, the Co–WC sintered specimen could not obtain full density.

Overall, Co–WC contamination by SPEX mill has a positive effect on densification of ZrB_2 . However, among the contamination contents, Co is a major reason for full density through the liquid phase sintering process.

4. Conclusion

In this study, WC, Co, and Co–WC were investigated as additives for ZrB_2 densification. WC was expected to have a role as a carbothermal reduction agent, but its influence was inadequate. Also, WC generates secondary phase (WB) which disturbs mass transfer between ZrB_2 . Therefore, WC does not have any effects on densification of ZrB_2 . Co–WC compounds were considered for both carbothermal reduction and liquid phase sintering. However, due to residual WO_3 , WB which disturbs mass transfer between ZrB_2 , Co–WC compound additive could not obtain full density of ZrB_2 .

As mentioned earlier, we expected that Co–WC contamination generated by SPEX mill process could enhance the sinterability of ZrB_2 . But, the enhanced sinterability was due to contamination of Co, which gives rise to a liquid phase sintering process. Thus, the case with only Co as a sintering additive had the highest relative density value.

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Fig. 11. XRD data of ZrB_2 –WC–Co composites.

Fig. 12. EPMA mapping data of Z15W-C sintered at 1600°C.

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