Preparation of Dense $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ Cosintered Ceramics with Controlled Thermal Expansion Coefficients

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熱膨張挙動を制御した高密度 $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ 共焼結材料の合成

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Various kinds of $\text{ZrO}_2\text{--ZrW}_2\text{O}_8$ composite ceramics were successfully prepared by cosintering of ZrO_2 and ZrW_2O_8 mixture with various ratios at 1200°C . The thermal expansion coefficient of the composite could be controlled from $-9.6 \times 10^{-6} \text{ K}^{-1}$ – $8.2 \times 10^{-6} \text{ K}^{-1}$ by varying $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ ratios and zero thermal expansion was observed in the specimen with a $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ weight ratio of 2/1. A small amount of Al_2O_3 addition less than 0.25 mass% was effective in increasing the density of the composite. It was suggested that the generation of a liquid phase of $\text{Al}_2(\text{WO}_4)_3$ improved the sintering property of the $\text{ZrO}_2\text{--ZrW}_2\text{O}_8$ mixture.

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1. Introduction

Recently, many kinds of highly functional devices including the integration of several highly functional materials are proposed and applied to fields such as optics, energy transformation and electronics. For the permeation of highly functional devices, mechanical reliability and stability under operating conditions for long periods are required. One of the causes of the destruction and/or deterioration of the properties of such devices is the generation of stress due to the thermal expansion mismatch of component materials.¹⁾ The preparation of materials with the controlled thermal expansion would increase the mechanical reliability and long-term duration. In particular, a material with zero thermal expansion is highly desired for optical devices such as the ferrules of optical fibers and Bragg gratings to be free from deviations of position and wavelength, respectively. The hybridization of materials with a positive thermal expansion and negative one is one of the promising candidates as a method of controlling the thermal expansion coefficient of components.

It has been reported that materials such as cordierite ($\text{Mg}_2\text{Al}_2\text{Si}_5\text{O}_{18}$ family), β -eucryptite (LiAlSiO_4) family, $\text{NaZr}_2(\text{PO}_4)_3$, $\text{ZrV}_{1-x}\text{P}_x\text{O}_7$ and ZrW_2O_8 show negative thermal expansion.^{2)–7)} Among them, we regard ZrW_2O_8 as the most promising material for application to optical devices because it shows isotropic contraction by temperature due to its cubic crystal structure in the wide temperature range of 0.9–1050 K⁷⁾ and a large amount of ZrW_2O_8 ceramics can be easily prepared using a simple, low-cost solid-state reaction technique.⁸⁾

At present, reports on the hybridization of ZrW_2O_8 and ceramics with positive thermal expansion are few. Nishiyama and coworkers reported the thermal expansion behavior of

$\text{SnO}_2\text{--ZrW}_2\text{O}_8$ cosintered ceramics.⁹⁾ They reported that thermal expansion could be controlled by $\text{SnO}_2/\text{ZrW}_2\text{O}_8$ ratio and specimens with a $\text{SnO}_2/\text{ZrW}_2\text{O}_8$ molar ratio of 0.87/0.13 showed zero thermal expansion. However, their observed thermal expansion behavior included large hysteresis, which might be a problem for practical application. We have succeeded in the preparation of $\text{ZrW}_2\text{O}_8/\text{ZrO}_2/\text{WO}_3$ hybrid material by rapid quenching of ZrW_2O_8 melt and observed a lower contraction by temperature in the specimen than that in pure ZrW_2O_8 .¹⁰⁾ However, the composition and thermal expansion of thus-prepared $\text{ZrW}_2\text{O}_8/\text{ZrO}_2/\text{WO}_3$ hybrid material could not be controlled intentionally.

In this study, the preparation of a hybrid material with controlled thermal expansion by cosintering of ZrO_2 and ZrW_2O_8 was examined. ZrO_2 was selected as the counterpart of ZrW_2O_8 for the following reasons.

(1) Since no intermediate phase existed between ZrO_2 and ZrW_2O_8 according to the phase diagram of the $\text{ZrO}_2\text{--WO}_3$ system,¹¹⁾ it was expected that ZrO_2 and ZrW_2O_8 composite could be prepared by heating the mixture without chemical reaction.

(2) ZrO_2 is widely applied in optical, electrical or energy devices such as the ferrules of optical fibers and the electrolytes of solid oxide fuel cells.

2. Experimental

2.1 Sample preparation and characterization

A ZrW_2O_8 ceramic specimen was prepared by the solid-state reaction method.⁸⁾ Powdery ZrO_2 (99.9%; Furuuchi Chemical Corp.) and WO_3 (99.9%; Furuuchi Chemical Corp.) were mixed in the correct stoichiometric proportion in ethanol. The mixture was poured into a Pt crucible, covered with a Pt cap

to prevent vaporization of WO_3 during the heat treatment, followed by heat treatment at 1200°C for 48 h in open air. The heated specimen was quenched to room temperature and pulverized using an automatic Al_2O_3 mortar. The obtained powder was confirmed to be single-phase cubic ZrW_2O_8 with a lattice constant of 0.9155 nm using powder X-ray diffraction (Rigaku Co., Ltd.: RINT-2500), which agreed well with the previously reported values.^{4),5)}

Obtained ZrW_2O_8 powder was mixed with ZrO_2 (99.9%; Furuuchi Chemical Corp.) powder at various $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ ratios using an automatic Al_2O_3 mortar for more than 24 h. In some samples, a small amount of Al_2O_3 was added as a sintering aid. The obtained powder mixture was pressed into a cylindrical pellet of 5 mm diameter and 12–15 mm height. The pellets were set on the Pt crucible covered with a Pt plate to avoid vaporization of WO_3 and heated in air for more than 48 h. Although the sintering temperature of ZrO_2 is more than 1400°C ,¹²⁾ the temperature employed for the cosintering of ZrO_2 and ZrW_2O_8 was 1200°C since the melting point of ZrW_2O_8 was reported to be $1220\text{--}1250^\circ\text{C}$.¹⁰⁾ The heated pellets were subjected to quenching to room temperature in order to prevent ZrW_2O_8 from decomposing into ZrO_2 and WO_3 at $600\text{--}1000^\circ\text{C}$.¹³⁾

The composition of the specimens was analyzed by X-ray diffraction using Rigaku RINT-2500 ($\text{Cu K}\alpha$; 50 kV, 250 mA). The thermal expansion behavior of the specimens was measured by dilatometry using Rigaku TMA8310. The cylindrical specimen of approximately 4.5 mm diameter and 10–13 mm height was employed for the measurement. The SiO_2 was employed as a material for reference and as a push rod. The measurement was carried out in the temperature range from $-100\text{--}300^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$ in static air. The morphology of the obtained specimens was measured by secondary electron microscope (SEM) using JSM-5200, JEOL Co., Ltd.

2.2 Evaluation of cosintering behavior of ZrO_2 and ZrW_2O_8

In order to evaluate the cosintering behavior of the powdery mixture composed of ZrO_2 and ZrW_2O_8 , dilatometry was used on the as-pressed pellet composed of ZrO_2 and ZrW_2O_8 . The powdery mixture was uniaxially pressed into a cylindrical pellet of 5 mm diameter and 18 mm height. The variation of length of the as-pressed pellet on temperature was measured using Rigaku TMA8310. The range of measurement temperature and heating rate was room temperature $\sim 1200^\circ\text{C}$ and $10^\circ\text{C}/\text{min}$. A Pt thin plate was inserted between the as-pressed specimen and the Al_2O_3 push rod to prevent a chemical reaction between Al_2O_3 and W.¹⁴⁾ A Pt plate was also placed between the as-pressed specimen and the dilatometer stage made of Al_2O_3 .

3. Results and discussion

3.1 Cosintering of ZrO_2 and ZrW_2O_8

Figure 1 shows the thermal expansion behavior of the cosintered specimen prepared from the mixture with a 2/1 weight ratio of $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$. Al_2O_3 was not added in the preparation procedure. Thermal expansions of sintered ZrO_2 and ZrW_2O_8 are also shown in Fig. 1 for comparison. The cosintered specimen showed almost zero thermal expansion, i. e., $0.3 \times 10^{-6} \text{ K}^{-1}$ in the range of $30\text{--}100^\circ\text{C}$, which was almost medium expansion behavior between that of ZrO_2 , i. e., $8.2 \times 10^{-6} \text{ K}^{-1}$, and ZrW_2O_8 , i. e., $-9.6 \times 10^{-6} \text{ K}^{-1}$.

X-ray diffraction patterns of the cosintered specimen, ZrO_2 and ZrW_2O_8 are depicted in Fig. 2. All the diffraction peaks of the cosintered specimen could be indexed as either

monoclinic ZrO_2 or ZrW_2O_8 , indicating that no chemical reaction occurred between ZrO_2 and ZrW_2O_8 during heat treatment as predicted in the phase diagram of ZrO_2 and WO_3 .¹¹⁾

Figures 1 and 2 apparently indicate that materials whose thermal expansion is controlled can be prepared with the cosintering of ZrO_2 and ZrW_2O_8 . However, the cosintered specimen shown in Fig. 1 was fragile probably due to insufficient sintering. Figure 3 shows an SEM image of the cosintered specimen. The specimen consists of small particles less than $\sim 10 \mu\text{m}$ diameter and a number of pores, which are in agreement with the fragility of the specimen. For the preparation of dense and tough ZrO_2 ceramics, heat-treatment at higher than 1400°C has been generally required.¹²⁾ However, the cosintering cannot be carried out at such a high temperature because ZrW_2O_8 melts at approximately 1230°C .^{10),11)}

3.2 Effect of Al_2O_3 additive on cosintering of ZrO_2 and ZrW_2O_8

In order to prepare a dense and tough $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ composite, a sintering method at temperatures as low as 1200°C should be developed. One of the possible methods involves the addition of a sintering aid. Al_2O_3 is regarded as a promising sintering-aid material since Mori and coworkers reported an improvement in the bending strength of a ZrO_2 sintered specimen by the addition of Al_2O_3 .¹⁵⁾

Table 1 lists the weight of ZrO_2 , ZrW_2O_8 and Al_2O_3 , which

Fig. 1. Thermal expansion behavior of $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ cosintered specimen. The weight ratio of $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ is 2/1. Thermal expansions of ZrO_2 and ZrW_2O_8 are shown together for comparison.

Fig. 2. X-ray diffraction patterns of the specimens depicted in Fig. 1.

Fig. 3. SEM image of the $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ cosintered specimen shown in Fig. 1.

Table 1. Weights of ZrO_2 , ZrW_2O_8 and Al_2O_3 Employed as Raw Materials of the Composites

No.	ZrO_2 / g	ZrW_2O_8 / g	$\text{ZrO}_2/\text{ZrW}_2\text{O}_8$	Al_2O_3 / mg
1	4.0	2.0	2/ 1	0
2	4.0	2.0	2/ 1	50
3	4.0	2.0	2/ 1	100
4	4.0	2.0	2/ 1	15
5	3.0	3.0	1/ 1	15
6	4.5	1.5	3/ 1	15
7	4.8	1.2	4/ 1	15
8	5.0	1.0	5/ 1	15

Fig. 4. Apparent density of specimens #1–#4 in Table 1 as a function of additional Al_2O_3 weight.

are the raw materials of the composites. The total amount of ZrO_2 and ZrW_2O_8 was 6 g. Additions of Al_2O_3 were 15, 50 and 100 mg. **Figure 4** shows the apparent density of specimens #1–#4 calculated from weight and volume. Relative density also presented in Fig. 4 was calculated by dividing the apparent density by the ideal density of the cosintered specimen, which was estimated using the ideal densities of ZrW_2O_8 ($5.09 \text{ g}\cdot\text{cm}^{-3}$) and ZrO_2 ($5.817 \text{ g}\cdot\text{cm}^{-3}$) measured by X-ray diffraction.

Fig. 5. Thermal expansion behavior of composites #1–#4 in Table 1.

Fig. 6. X-ray diffraction patterns of specimens #1–#4 in Table 1. ZrW_2O_8 phase disappeared and $\text{Al}_2(\text{WO}_4)_3$ was generated in specimens #2 and #3.

tion. Even 15 mg Al_2O_3 addition was effective in increasing the density of the composite, resulting in the preparation of a specimen with $\sim 93\%$ density. **Figure 5** shows the thermal expansion behavior of specimens #1–#4 in Table 1. Specimens of #1 and #4 showed almost zero thermal expansion, whereas those prepared with 50 mg (#2) and 100 mg (#3) Al_2O_3 addition showed positive thermal expansion. The variation of thermal expansion coefficient due to the second-order phase transition^{5),16),17)} was observed at $\sim 160^\circ\text{C}$ in thermal expansion of specimens #1 and #4, however, that was not in the specimens #2 and #3. This indicates the decomposition of the ZrW_2O_8 phase by Al_2O_3 addition in specimens #2 and #3, which was also confirmed by X-ray diffraction patterns of the specimens depicted in **Fig. 6**. **Figure 7** shows an SEM image of specimen #4. The composite consists of larger grains and fewer pores than those of the composite prepared from the Al_2O_3 -free mixture (#1), depicted in Fig. 3, corresponding to an increase in the toughness of the specimen by Al_2O_3 addition.

Thus, the amount of Al_2O_3 addition was optimized to be 15 mg. **Figure 8** shows X-ray diffraction patterns of specimens #4–#8. Even though a small amount of $\text{Al}_2(\text{WO}_4)_3$ was observed in specimen #8, whole peaks could be indexed as ZrO_2 or ZrW_2O_8 in every X-ray diffraction pattern. Since the intensity of the diffraction peaks of ZrO_2 increased with increasing $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ ratio, it was concluded that $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$

Fig. 7. SEM image of specimen #4. Larger grains and fewer pores than those of specimen #1 were observed.

Fig. 8. X-ray diffraction patterns of composites #4–#8. Peaks represented by $\circ$, $\square$ and $\times$ originate from ZrW_2O_8 , ZrO_2 and $\text{Al}_2(\text{WO}_4)_3$, respectively.

composite ceramics with high toughness could be prepared through the process employed in this study. **Figure 9** shows the thermal expansion behavior of specimens #4–#7. The thermal expansion coefficient estimated from Fig. 9 is shown in **Fig. 10** as a function of $\text{ZrO}_2/(\text{ZrO}_2 + \text{ZrW}_2\text{O}_8)$ weight ratio. Thermal expansion increased monotonically with $\text{ZrO}_2/(\text{ZrO}_2 + \text{ZrW}_2\text{O}_8)$ ratio and specimen #4 showed a nearly zero thermal expansion coefficient.

3.3 Cosintering mechanism of ZrO_2 and ZrW_2O_8 ; the effect of Al_2O_3 addition

It was revealed that the addition of a small amount of Al_2O_3 was effective in improving the density of the $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ composite. In order to clarify the mechanism of cosintering, the sintering process of the $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ mixture was analyzed by dilatometry. **Figure 11** shows the variation in length of the as-pressed pellet composed of ZrO_2 and ZrW_2O_8 mixture with temperature. The ratio of $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ was 2/1. Dashed and solid curves represent the results for the Al_2O_3 -free sample and one containing 0.25 mass% Al_2O_3 , respectively. Both samples show the onset of shrinkage owing to sintering at 950°C . Larger shrinkage was observed in the specimen containing Al_2O_3 than the Al_2O_3 -free specimen, which showed consistency with the result of the density of the specimens

Fig. 9. Thermal expansion behavior of specimens #4–#7. The expansion behavior of ZrW_2O_8 ceramics is shown for comparison.

Fig. 10. Thermal expansion coefficients of composites #4–#8 and ZrW_2O_8 as a function of $\text{ZrO}_2/(\text{ZrO}_2 + \text{ZrW}_2\text{O}_8)$ weight ratio.

depicted in Fig. 4. Besides 950°C , an anomaly was observed at 1190°C in the Al_2O_3 -containing specimen, which could be attributed to further shrinkage.

Although the cause of the improvement of sintering properties by Al_2O_3 addition in the temperature range of 950°C – 1190°C has not been clarified, the origin of the anomaly at 1190°C in the Al_2O_3 -containing specimen shown in Fig. 11, which contributes to the improvement of sintering properties, could be speculated as follows. Since the $\text{Al}_2(\text{WO}_4)_3$ phase was observed in the specimens prepared from the mixture containing more than 50 mg Al_2O_3 , the behavior of $\text{Al}_2(\text{WO}_4)_3$ at high temperatures was investigated to clarify the origin of the improvement of sintering properties with the addition of Al_2O_3 . $\text{Al}_2(\text{WO}_4)_3$ powder was prepared by solid-state reaction of the mixture of Al_2O_3 and WO_3 . The mixture was heated at 1000°C for 17 h in air and quenched to room temperature. The obtained sample was confirmed to be a single-phase of $\text{Al}_2(\text{WO}_4)_3$ by X-ray diffraction measurement. **Figure 12** shows a TG-DTA curve of $\text{Al}_2(\text{WO}_4)_3$. The endothermic peak and anomaly of weight variation, which indicate the melting point of $\text{Al}_2(\text{WO}_4)_3$, were observed at $\sim 1190^\circ\text{C}$. Since the temperature coincided with that at which large shrinkage was observed in the Al_2O_3 -containing specimen, it was speculated that the liquid-phase sintering by melting of $\text{Al}_2(\text{WO}_4)_3$ occurred in the Al_2O_3 -containing specimen, resulting in the

Fig. 11. Variation in length of the as-pressed specimen composed of $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ mixture with a 2/1 weight ratio with temperature. Dashed and solid curves represent results for the Al_2O_3 -free sample and the sample containing 0.25 mass% Al_2O_3 , respectively.

Fig. 12. TG-DTA curve of $\text{Al}_2(\text{WO}_4)_3$.

improvement in the sintering density of the $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ composite.

4. Conclusions

Cosintered ceramics composed of ZrO_2 and ZrW_2O_8 were successfully prepared. The thermal expansion of the composite could be varied from $-9.6 \times 10^{-6} \text{ K}^{-1}$ to $8.2 \times 10^{-6} \text{ K}^{-1}$ by changing $\text{ZrO}_2/\text{ZrW}_2\text{O}_8$ ratio. A specimen composed of

ZrO_2 and ZrW_2O_8 with a weight ratio of 2/1 showed nearly zero thermal expansion. A small amount of Al_2O_3 addition, less than 0.25 mass% was effective in increasing the density of the composite. It was suggested that liquid-phase sintering by melting of $\text{Al}_2(\text{WO}_4)_3$ occurred in the specimen containing Al_2O_3 .

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