Synthesis and thermal expansion properties of ZrO₂/ZrW₂O₈ composites

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Abstract

In this work, a ceramic composite of ZW₂O₈ and ZrO₂ was synthesized, in order to investigate the possibility of compensating the positive thermal expansion of ZrO₂ with the negative thermal expansion (NTE) compound ZrW₂O₈, tailoring the thermal expansion of these composites. The NTE material was mixed with varying amounts of ZrO₂. The thermal expansion coefficients of this series of composites decrease with increasing amounts of ZW₂O₈. Nevertheless, a negative deviation from the values expected by the rule of mixtures was found to be most pronounced in the middle of the compositional region.

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1. Introduction

Most materials expand on heating and thus have a positive thermal expansion. Nevertheless, in recent years several families of materials with a negative thermal expansion (NTE) have been discovered. The ceramic material ZrW₂O₈ is one of the best known. This cubic material has an exceptionally large and isotropic negative thermal expansion over its entire stability range (−273 to 770 °C). The dimensions of this cubic material decrease linearly with temperature and at about 150 °C a phase transition from α-ZW₂O₈ to β-ZW₂O₈ can be observed.¹⁻³ A broad range of applications have been suggested for these NTE materials. One of the most obvious is the use in composites where the thermal expansion coefficient of the bulk material can be tailored to a specific value by combining a NTE material with a positive thermal expansion material. This may result in new materials with precisely matched expansion, being positive, negative or even zero, by adjusting the volume fraction of the different phases. These controlled expansion composites may be used in high precision optical mirrors, fibre optic systems, electronic devices or as a thermal package for fibre Bragg gratings. Although many applications were proposed for these new materials, the published research literature on this subject is still very limited. Only the Cu/ZrW₂O₈ composite has been more thoroughly studied.⁴⁻⁶ This combination was chosen for its possible high thermal and electrical conductivity. Preliminary studies of cement/ZrW₂O₈ composites yielding zero expansion mortars⁷ and Al/ZrW₂O₈ composites have been published.

In this work, the microstructure and thermo-mechanical properties of a two-phase ceramic composite consisting of ZW₂O₈ and ZrO₂ are studied, with special emphasis on the coefficients of thermal expansion for different compositions ranging from 0 to 100 vol.% of ZW₂O₈. Furthermore, the synthesis of the composites will be discussed, including an optimized preparation of ZW₂O₈ based on our earlier published spray drying technique.⁸

2. Experimental

2.1. Synthesis of the composites

The starting materials consisted of a commercial ZrO₂ powder (Aldrich) and ZW₂O₈ prepared using the spray drying technique. The synthesis of ZW₂O₈ involves sev-
eral successive steps as summarized in Fig. 1a. An aqueous precursor solution was prepared starting from ammonium metatungstate, (NH₄)₆H₂W₁₂O₄₀ (Aldrich), zirconium oxychloride, ZrOCl₂·nH₂O (Aldrich) and citric acid, as a complexing agent to prevent hydrolysis and precipitation of the salts. The 100 ml 0.042 M W-salt solution was slowly added to 100 ml of a solution containing 0.25 M Zr-solution and 0.25 M citric acid. NH₃ was used to raise the pH of the Zr-solution from 0.3 to 6. This transparent, colourless solution was then spray-dried using a Büchi 190 mini spray dryer with a 0.5 mm nozzle and a feeding rate of 5 ml per minute at temperatures close to 250 °C. This spray-dried powder was subsequently calcined at 700 °C for 12 h to yield an intimate mixture of ZrO₂ and WO₃. After calcination, these powders were uni-axially, cold pressed in pellets (250 mm Ø × 1 mm) at a pressure of 350 MPa. After heating in a covered Pt crucible at 1180 °C in a preheated furnace under air during 2 h, the pellets were quenched in liquid nitrogen, to prevent decomposition of the formed ZrW₂O₈ phase into ZrO₂ and WO₃.

For the preparation of the composites, the above pellets were ground in a mortar and manually mixed with different amounts of ZrO₂ (Fig. 1b). The properties of these powders are summarised in Table 1. The mixture was then uni-axial, cold pressed into bars (2 mm × 2 mm × 13 mm) at a pressure of 750 MPa. The bars were sintered at 1180 °C for 2 h under air in a covered Pt crucible, again in a preheated furnace and subsequently quenched in liquid nitrogen. A bar of pure ZrO₂ was prepared, using the same conditions.

For all prepared materials, the mass differences between the green and sintered bodies were found to fall between 1 and 2%. This indicates that, even if there is a possible contribution of the volatilization of tungsten oxide to the mass loss during the thermal treatment, the effect of it is very limited and constant.

2.2. Experimental techniques

Particle size and particle size distribution of the different powders dispersed in de-ionized water were determined by laser diffraction (Malvern Particle Sizer Series 2600c). The geometrical density of the samples was measured. The microstructures of the polished cross-sections and fracture surfaces were observed by optical microscopy (Leitz labolux 12 pol S), scanning electron microscopy and EDX (Philips 501). Identification of the different phases present in the samples was performed by XRD analysis (Siemens D5000 diffractometer) using Cu Kα radiation on ground samples. The quantitative phase composition was estimated by whole pattern quantitative analysis of the X-ray diffraction patterns using the program FULLPROF.10 The coefficients of thermal expansion were measured with a vertical push rod thermomechanical analyzer (TA Instruments) 2940, using a heating rate of 2 °C per minute from room temperature to 300 °C under a constant compressive force of 0.5 N, low enough to prevent deformation of the bars.

| Table 1
<table>
<thead>
<tr>
<th>Powder specifications</th>
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<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>ZrW₂O₈</td>
</tr>
<tr>
<td>ZrO₂ (Aldrich)</td>
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</tbody>
</table>
ZrW$_2$O$_8$ were prepared by manually mixing varying amounts of synthesized ZrW$_2$O$_8$ and commercial ZrO$_2$ powders after 2 h calcinating at 1180°C. Expansion curves of cubic ZrW$_2$O$_8$ have an average particle size of 12.77 μm and a pycnometric density of 6.55 g/cm$^3$, which is sufficiently high to drive a phase transition from cubic ZrW$_2$O$_8$ ($\rho = 5.081$ g/cm$^3$) to the high pressure phase, orthorhombic γ-ZrW$_2$O$_8$ ($\rho = 5.375$ g/cm$^3$), see Fig. 3. This is reflected in the thermal expansion data of this bar, containing approximately 20 vol.% γ-ZrW$_2$O$_8$ and 80 vol.% α-ZrW$_2$O$_8$ (Fig. 4a). An expansion curve of cubic α-ZrW$_2$O$_8$ has been included for reference (Fig. 4b). Experimental thermal expansion coefficients obtained from this experiment are listed in Table 2. γ-ZrW$_2$O$_8$ is known to possess a negative coefficient of thermal expansion (−1.0 × 10$^{-6}$ °C$^{-1}$) which is almost an order of magnitude less than for α-ZrW$_2$O$_8$ (−9.07 × 10$^{-6}$ °C$^{-1}$ from 0 to 100 °C). It reverts to the cubic form by heating to 120 °C, accompanied by a volume expansion of 5 vol.% As was expected, the high pressure sample shows negative thermal expansion behaviour below 100 °C. A large volume expansion can be seen between 100 and 150 °C, due to the γ to α transition. After this transition, the thermal expansion of this bar is, unexpectedly, still positive indicating that the transition to the low pressure phase is still ongoing. The behaviour depicted in Fig. 4 suggests the existence of two different regimes of dimensional change: (1) a fraction of the γ-phase is free to undergo the γ to α transition in an unconstrained manner, which corresponds to the large step at 120 °C and (2) a second fraction may be partially encapsulated and become subjected to such mechanical stresses that a different structural behaviour ensues and this is responsible for the tailing of the curve above 120 °C. Consider the high pressure phase surrounded by a majority of shrinking cubic ZrW$_2$O$_8$ as in Fig. 5a. Heating the bar to 120 °C starts the transition of the high pressure phase to the less dense cubic low pressure phase which is associated expansion of 5 vol.%

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal expansion coefficient (× 10$^{-6}$ °C$^{-1}$)</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bar pressed at 750 MPa</td>
<td>α-ZrW$_2$O$_8$</td>
<td>−4.30</td>
</tr>
<tr>
<td>Bar pressed at 750 MPa</td>
<td>γ-ZrW$_2$O$_8$</td>
<td>23.45</td>
</tr>
<tr>
<td>α-ZrW$_2$O$_8$</td>
<td>−12.11</td>
<td>0–150</td>
</tr>
<tr>
<td>β-ZrW$_2$O$_8$</td>
<td>−0.12</td>
<td>200–300</td>
</tr>
</tbody>
</table>
with a large volume expansion while the surrounding cubic fraction is contracting. This gives rise to very large thermal stresses, high enough to prevent the complete transition of the orthorhombic high pressure to the cubic low pressure phase. One could say, the thermal stresses cause a shift of the \( \gamma \) to \( \alpha \) transition to higher temperatures as presented in the phase diagram proposed in Fig. 5b. Upon cooling, the normal thermal expansion coefficients were again measured, proving the reversibility of the phenomenon. Finally, it is important to note that the \( \gamma \)-phase does not occur in the composites because it is completely transformed to \( \alpha \)-phase during subsequent sintering at 1180°C.

### 3.3. Analysis of the ZrW\(_2\)O\(_8\)/ZrO\(_2\) composites

After sintering the respective mixtures containing different molar ratios of zirconium tungstate/zirconium oxide for 2 h at 1180°C and subsequent quenching, the bars retained their original shape and did not show visible cracks. This indicates that these bars are able to withstand the thermal stresses created during heating and quenching remarkably well. These stresses originate from the large thermal volume expansion accompanying the gamma to alpha zirconium tungstate transition as shown before, in addition to the differences in thermal expansion coefficient between ZrW\(_2\)O\(_8\) (\(-9.1 \times 10^{-6}\) °C\(^{-1}\) from 0 to 100°C and \(-5.4 \times 10^{-6}\) °C\(^{-1}\) from 200 to 350°C) and ZrO\(_2\) (9.6 \(\times 10^{-6}\) °C\(^{-1}\)).

X-ray diffraction analysis confirms that only \( \alpha \)-ZrW\(_2\)O\(_8\) and monoclinic ZrO\(_2\) are present, as shown for a 50 vol.% ZrW\(_2\)O\(_8\) sample in Fig. 6. No high pressure \( \gamma \)-ZrW\(_2\)O\(_8\) was found.

The geometrical densities of the green and sintered composite bars were measured. The theoretical density for the different bars was calculated from the theoretical values for ZrW\(_2\)O\(_8\) (5.08 g/cm\(^3\)) and ZrO\(_2\) (5.83 g/cm\(^3\)) and compared to the experimental geometrical densities. The obtained results are graphically shown in Fig. 7. Each data point presents the results of one or two bars. For the composite with the highest ZrW\(_2\)O\(_8\) content, the sintering treatment results in a reduction of the porosity of the bars. For the compositions of 50%:50% ZrO\(_2\)/ZrW\(_2\)O\(_8\) and those with lower concentrations of ZrW\(_2\)O\(_8\), the sintering treatment doesn’t result in a further reduction of the porosity. The final density equals the initial green density of the composite bars. This is also reflected in their microstructures (Fig. 8). The pure ZrW\(_2\)O\(_8\) sample is micro-structurally very different from the 50 vol.% composite. As ZrO\(_2\) sinters at much higher temperatures than ZrW\(_2\)O\(_8\) (2100°C), only the latter phase is sintered during the heating step at 1180°C and the ZrO\(_2\)-phase remains as loose powder between the larger ZrW\(_2\)O\(_8\) grains. Furthermore, its presence hinders the sintering of the ZrW\(_2\)O\(_8\) phase. This assumption was confirmed by closer investigation of the microstructures presented in Fig. 8. EDX-mapping of Fig. 8d showed that the sintered, homogene areas, indicated with an asterisk (*) contain Zr and W atoms while in the area consisting of non-sintered grains, indicated with a (°), predominantly Zr atoms were found.

### 3.4. Thermal expansion of the composites

As can be expected, the thermal expansion coefficient of the composite decreases, when the zirconium tungstate to zirconium oxide ratio increases. In Fig. 9 the thermal expansion coefficients calculated from the rule of mixtures (\( \alpha_c = \Sigma \alpha_i V_i \)) are shown.
at 225 °C are compared to the experimental data. The greatest deviation is found in the middle of the compositional range, which can be explained as follows: the rule of mixtures is only valid for a sample without voids, free of thermal stresses and when the different phases have the same elastic modulus.\textsuperscript{11,12} Here, none of these conditions is fulfilled. Clearly in the middle of the compositional region, where the differences in thermal expansion coefficient and elastic modulus cause the highest stresses, the thermal expansion coefficient deviates the most from the expected coefficient. Using the rule of mixtures, the value of the thermal expansion coefficient was predicted to remain negative down to a volume ratio of 55 vol.% (at 225 °C). However, we found that volume ratios well below 55% still yielded negative expansion. This may have important technological consequences because it shows that a relatively low volume fraction of ZrW\textsubscript{2}O\textsubscript{8} is sufficient to compensate effects of thermal expansion in a powderous matrix. This negative deviation relative to the rule of mixtures was found in many other composite systems.\textsuperscript{12} This can be attributed to effects related to porosity, differences in elastic moduli and the incomplete sintering of these composites.

4. Conclusion

This study demonstrates the possibility of synthesizing ceramic composites with a tailored thermal expansion
coefficient by introducing the NTE material ZrW$_2$O$_8$. ZrO$_2$/ZrW$_2$O$_8$ composites were synthesized that are able to withstand the thermal stresses, arising during sintering and subsequent quenching. The composites’ coefficients of thermal expansion, measured between room temperature and 300 °C, decrease with increasing amounts of ZrW$_2$O$_8$. The coefficients of thermal expansion did not completely comply with the rule of mixtures since experimentally, lower volumes of ZrW$_2$O$_8$ were necessary to compensate for the positive thermal expansion of the ZrO$_2$ phase than those calculated using this rule.

Pressing the powder mixtures resulted in a partial transition of the α-ZrW$_2$O$_8$ into γ-ZrW$_2$O$_8$. This transition was still ongoing well above 120 °C, which was explained by considering the large thermal stresses originating from the α-phase encapsulating the γ-phase.

Acknowledgments

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