ZrO$_2$-ZrW$_2$O$_8$ COMPOSITES
WITH TAILOR-MADE THERMAL EXPANSION

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Most of the materials expand upon heating. There are a few families of materials which exhibit negative thermal expansion (NTE). ZrW$_2$O$_8$ is an example which gained a lot of interest in international literature recently. This cubic material has an exceptionally large and isotropic negative thermal expansion over its entire stability range (0.5 to 1050 K). At 430 K a phase transition occurs from α-ZrW$_2$O$_8$ (α = -9.1 × 10^{-6} K^{-1}) to ß-ZrW$_2$O$_8$ (β = -5.4 × 10^{-6} K^{-1}). At high pressures an orthorhombic phase is formed, γ-ZrW$_2$O$_8$, which possesses a small negative expansion coefficient. A broad range of applications have been suggested for these NTE materials. In composites, their thermal expansion coefficient can be tailor-made by combining a NTE material with a positive expansion material. Adjusting the volume fraction of the different phases results in a positive, negative or even zero thermal expansion. The ZrW$_2$O$_8$ - ZrO$_2$ - composites studied in this paper were prepared in two ways. The first synthesis method applied, started from off-stoichiometry mixtures of the pure oxide powders of ZrO$_2$ and WO$_3$. This novel in situ process included a heating step up to 1450 K which combines the formation and sintering of ZrW$_2$O$_8$. In the conventional synthesis the starting materials were ZrO$_2$ and ZrW$_2$O$_8$. ZrW$_2$O$_8$ was first obtained using an optimised spray drying technique. Obviously, our "in situ" method does not require such an additional step. The crystal structure, morphology, thermal expansion behaviour and mechanical properties of these composites were tested and compared.

INTRODUCTION

The thermal expansion of a material in general is due to the specific temperature dependence of the geometrical parameters under specified conditions. Although this leads to a positive thermal expansion resulting from an increase in the population of higher energy vibration levels, in some cases negative thermal expansion is also possible. In the last decennium, several families of materials which exhibit negative thermal expansion, arising from a geometrical effect in so-called framework structures, have also been discovered. Usually, this negative thermal expansion is small, anisotropic and appears in a very small temperature interval. ZrW$_2$O$_8$ is an exception because of its large and isotropic negative thermal expansion (NTE) in a temperature range from 0.5 K to 1050 K. A cubic symmetry is found over the entire stability range with a phase transition from -ZrW$_2$O$_8$ to -ZrW$_2$O$_8$ near 430 K [1-3]. This phase transition has an influence on the thermal expansion which changes from -8.7 × 10^{-6} K^{-1} for the alpha phase to - 4.9 × 10^{-6} K^{-1} for the beta phase (figure 1). The negative thermal expansion behaviour of ZrW$_2$O$_8$ is caused by the presence of Rigid Unit Modes. ZrW$_2$O$_8$ consists of a network of corner-shared polyhedra with twofold coordinated oxygen atoms. These stiff polyhedra have strong M-O bonds and short O-O distances. When coupled rotations occur of these polyhedra while the intra-polyhedra bond distances and the intra-polyhedra angles remain relatively constant, the material exhibits a decrease in volume. Broad range of applications have been suggested for these NTE materials. Their use in composites together with the possibility to tailor the thermal expansion to a specific value by the combination of a NTE material with positive expansion materials is most promising. It may result in a whole range of new materials with a thermal expansion going on from negative over zero to positive values by adjusting the volume fraction of the components. Such a new material with controlled thermal expansion could be used in electronic devices, optical mirrors, fibre optic systems or in thermal package for fibre Bragg gratings. A Cu/ZrW$_2$O$_8$ composite has been studied more thoroughly recently with the same ambitions [4-6]. Preliminary studies of ZrW$_2$O$_8$ composites with cement [7] and Al [8] have also been published.

In this work ZrO$_2$ - ZrW$_2$O$_8$ composites are studied. ZrO$_2$ was chosen because of its earlier applications in optical, electrical and energy devices and because of the absence of an intermediate phase between ZrO$_2$ and ZrW$_2$O$_8$ [9]. The composites were prepared in two ways.

The first synthesis is a process in which an in situ formation of ZrW_2O_8 takes place. This method is based on off-stoichiometry mixtures of the pure oxide powders of ZrO_2 and WO_3. In the second synthesis, a more conventional route based on a mixture of ZrO_2 and ZrW_2O_8 was taken. The ZrW_2O_8 necessary for this route was obtained using an optimised spray drying technique [10].
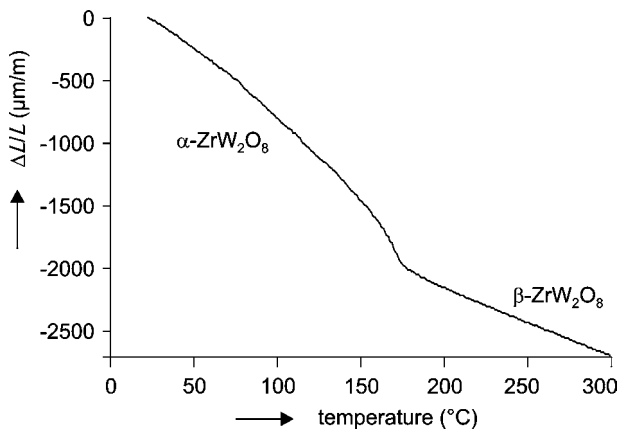

Figure 1. Thermal expansion curve of ZrW_2O_8 with phase transition from α- to β-ZrW_2O_8 at 150°C.

EXPERIMENTAL

Chemicals

ZrO_2 was purchased from Aldrich (Germany). Polyethylene glycol (MW 20000) was bought from Fluka (Germany). WO_3 was obtained from Acros Organics (Belgium).

Instrumentation

Particle size and particle size distribution of the different powders dispersed in deionised water were determined by laser diffraction (Malvern Particle Sizer Series 2600c). The microstructures of the fracture and polished surfaces were observed by optical microscopy (Leitz labolux 12 pol S) and scanning electron microscopy (FEI 200F). Identification of the different phases present in the samples was performed by X-ray diffractometer Siemens D5000. The coefficients of thermal expansion were measured with a vertical push rod thermo mechanical analyser (TA instruments 2940), using a heating rate of 2 K per minute from room temperature to 573 K under a constant force of 0.5 N. The mechanical properties of the samples were examined with a three point bending test using a Instron Series 4500 coupled with a Series IX Automated Materials Testing System with a speed of 1 mm/min.
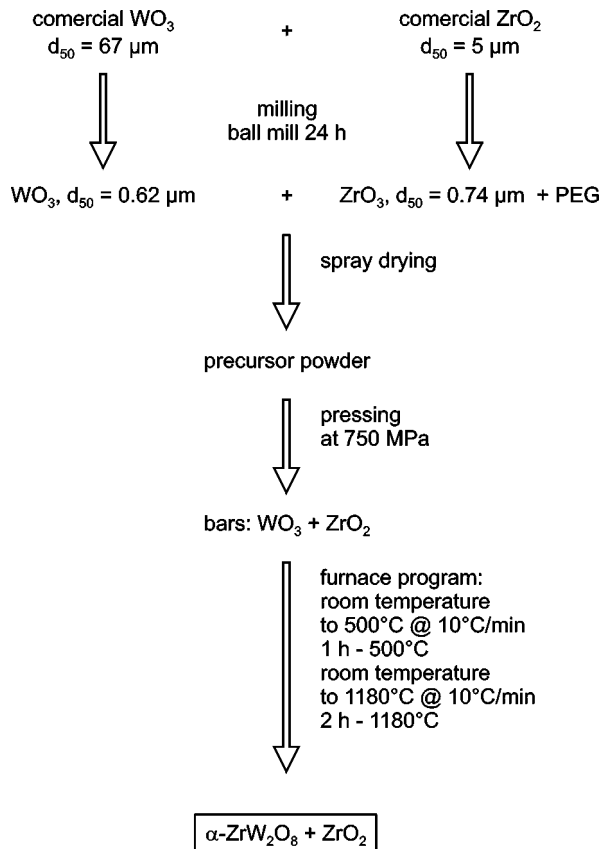
Synthesis of the composites

The spray drying technique was used in the preparation of pure ZrW_2O_8 [10]. For the preparation of the composites, two different methods were used as can be seen in figure 2a and b. In the in situ method (figure 2a), the commercially obtained oxide powders are first milled in an agate ball mill during 24 h to reduce the particle size and thus improve the homogeneity of the mixture and the sintering ability. Hereby an average particle size of 0.62 μm for WO_3 and 1.12 μm for ZrO_2 was obtained. The particle size and particle size distribution of these powders are given in table 1. For further manipulation of the mixed powders, they have to be pressed into bars but the bars were of poor quality. Therefore, aqueous slurry was prepared containing polyethylene glycol as dispergens. This additive possesses the additional benefit of reducing the friction during pressing of the bars. Using a polymer means that this organic material most be removed before sintering. An additional heating stage of 60 min at 773 K ensures that all organic material will be expelled. During this evaporation, pores are formed in the composites as can be seen in figure 3. This will have its effect on the mechanical properties of the composites. The amounts of oxides used in the preparation of the different composites are mentioned in table 2. Therefore the desired mixture of ball-milled oxides was suspended in 250 ml
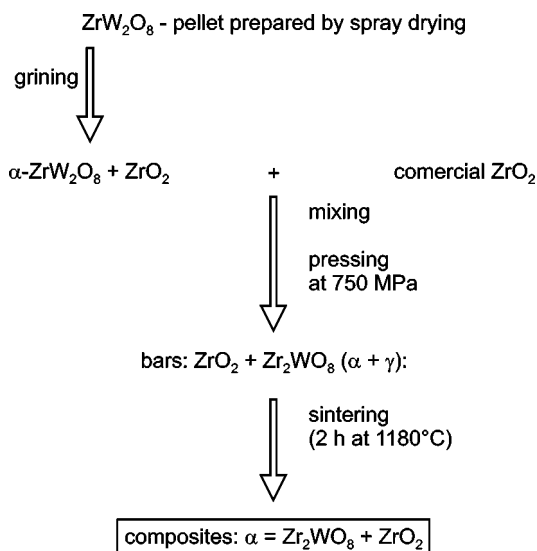
Table 1. Powder particle size.

Material	Particle size d_{50} (μm)	Particle size d_{90} (μm)
ZrW_2O_8 (Spray dried)	12.77	32.46
ZrO_2 (Aldrich)	5.27	8.72
ZrO_2 (milled 24h)	0.74	0.94
WO_3 (Aldrich)	66.56	130.39
WO_3 (milled 24h)	0.62	0.94

Table 2. Composition of the in- situ composites before heat treatment.

Desired ZrW_2O_8 in the composites (wt.%)	Mass WO_3 (g)	Mass ZrO_2 (g)	Mass PEG (g)
100	6.32	1.68	0.24
99	4.69	1.31	0.18
80	6.32	3.68	0.30
33	5.27	4.73	0.30

comercial WO₃
d₅₀ = 67 µm

+

comercial ZrO₂
d₅₀ = 5 µm

milling
ball mill 24 h

WO₃, d₅₀ = 0.62 µm   +   ZrO₃, d₅₀ = 0.74 µm + PEG

spray drying

precursor powder

pressing
at 750 MPa

bars: WO₃ + ZrO₂

furnace program:
room temperature
to 500°C @ 10°C/min
1 h - 500°C
room temperature
to 1180°C @ 10°C/min
2 h - 1180°C

α-ZrW₂O₈ + ZrO₂

a)

ZrW₂O₈ - pellet prepared by spray drying

grining

α-ZrW₂O₈ + ZrO₂   +   comercial ZrO₂

mixing

pressing
at 750 MPa

bars: ZrO₂ + Zr₂WO₈ (α + γ):

sintering
(2 h at 1180°C)

composites: α = Zr₂WO₈ + ZrO₂

b)

Figure 2. Synthesis scheme for (a) composites according to the in situ method and (b) preparation of the composites using a conventional method.

deionised water together with 3 wt.% polyethylene glycol, calculated on the mass of the oxides. The mixture was stirred for 2 h followed by an ultrasonic treatment of 1 h to break the agglomerates down. The resulting slurry was spray dried using a Büchi mini spray dryer with a 0.5 mm nozzle and a feeding rate of 5 ml per minute (Inlet temperature: 430 K; Outlet temperature: 370 K; gas flow: 800 Nl/h). Afterwards, the powder was uni-axially, cold pressed to bars (dimensions: $2 \times 2 \times 13$ mm) at a pressure of 750 MPa. The bars were thermally treated under air in a covered Pt crucible in a high temperature furnace following the temperature program described in figure 2a. After heat treatment, the bars were quenched in liquid nitrogen to avoid decomposition of ZrW_2O_8.

In the conventional method, the ZrW_2O_8 pellets synthesized using the spray drying process, are ground in an agate mortar and are manually mixed with different amounts of ZrO_2. Again, bars were pressed and thermally treated under air in a covered Pt crucible in a preheated furnace at 1450 K for 2 h followed by quenching in liquid nitrogen. Using this conventional route, a single composite with 80 wt.% ZrW_2O_8 was made by manually mixing with 20 wt.% ZrO_2 and pressing these powders into bars, followed by a thermal treatment of 2 hours at 1450 K.
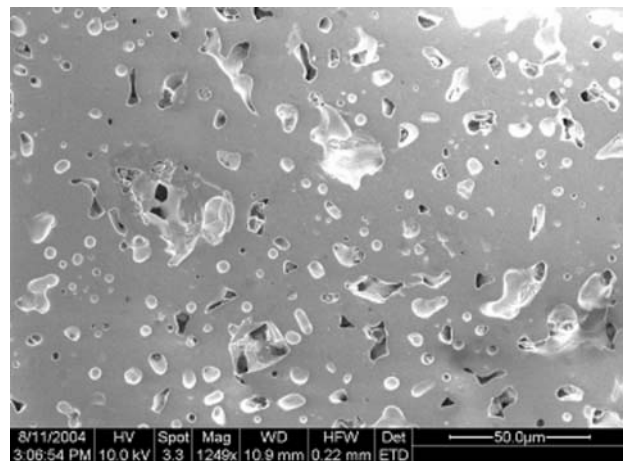

Figure 3. SEM micrograph of a surface of a 100 vol% ZrW_2O_8 bar.

RESULTS AND DISCUSSION

Analysis of the ZrO_2 - ZrW_2O_8 composite

Most of the bars prepared by the in situ method remained stable and showed no cracks after thermal treatment. Nevertheless the bars containing less than 40 wt.% ZrW_2O_8 showed some cracks after quenching, due to the high sintering temperature of ZrO_2 (more than

1700 K) in comparison to the synthesis temperature of 1450 K [11]. Examination of the mechanical properties of these samples was therefore not possible. X-ray diffraction shows that only 2 phases are found in the composite which can be identified as α-ZrW_2O_8 and monoclinic ZrO_2 as illustrated in figure 4 for a in situ - 40 wt.% ZrW_2O_8 sample.

The microstructure of the fracture surfaces of composites with identical composition is strongly dependent on the synthetic route chosen. Figure 5a shows a SEM view obtained from a 80 wt.% composite prepared by the conventional method, where as figure 5b reflects the same wt.% composite but as the result of an in situ process. The difference is clear. In the conventional obtained composite, ZrO_2 remains as loose powder between the larger ZrW_2O_8 grains, which is caused by the high sinter temperature of ZrO_2, which lies above the melting temperature of ZrW_2O_8. The reason why the micro-structure of the in-situ composite is different can be explained by the small dimensions of the starting powder which results in a much more homogeneous mixture. Furthermore, because ZrW_2O_8 is formed in situ, the ZrO_2 grains are more dispersed in the composite instead of the large agglomerates encountered in the conventional method.

Mechanical analysis of the in-situ composites

For composite materials, the thermal expansion can be theoretically predicted at a certain temperature by using the rule of mixtures ($\alpha_c = \Sigma\alpha_i V_i$). α_i is the thermal expansion of the individual component at that temperature and V_i is the volume fraction present of that component. For a series of in-situ composites the experimental results obtained at 500 K are compared with those calculated by the rule of mixtures (figure 6).
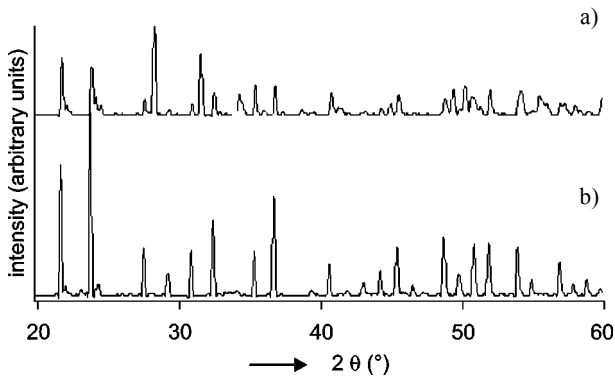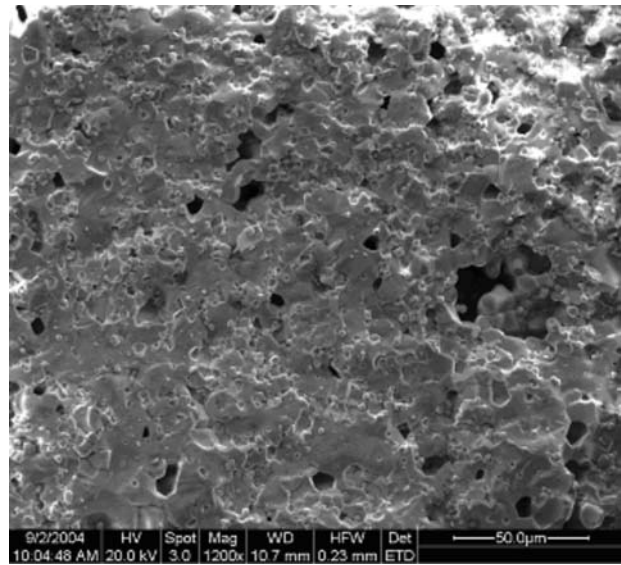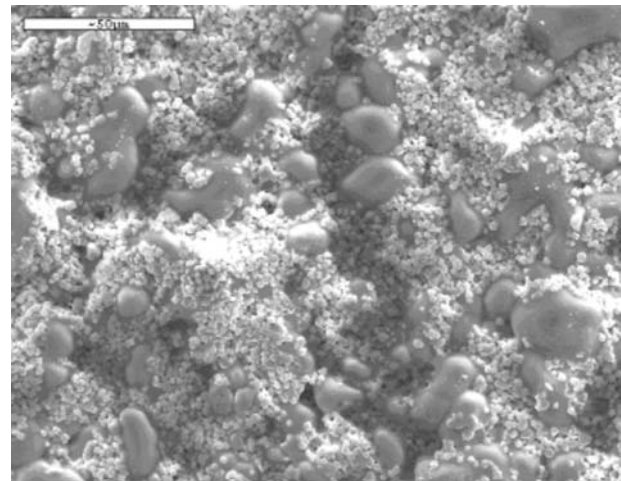

a)

b)

Figure 5. SEM micrograph of a) 80 wt.% ZrW_2O_8 bar prepared by conventional method and b) 80 wt.% ZrW_2O_8 bar by in situ.

Figure 4. X-ray diffraction pattern from the (a) pure α-ZrW_2O_8 and (b) In situ composite of 40 wt.% ZrO_2. (*) indicates the most characteristic diffraction lines for monoclinic ZrO_2.
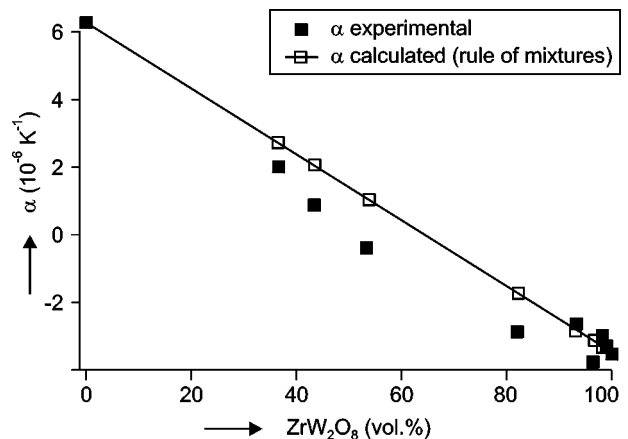

Figure 6. Thermal expansion coefficients, calculated and experimental, at 498 K.

A discrepancy is found which is most pronounced in the middle area of the graph. Such a deviation can be expected taking into account that the rule of mixtures requires a sample without voids, no thermal stress and that the combined phases should have the same elastic modulus [12-13]. Our composites do certainly not fulfil these characteristics. In the middle of the region, the differences in thermal expansion coefficient and elastic modulus are the most pronounced, resulting in the highest stress and the largest deviation of the rule of mixtures. Our results can also help us to predict the composition required to obtain the desired zero thermal expansion: 64 % ZrW_2O_8 accompanied by 36 % ZrO_2. In literature [9], a composite prepared by the conventional method and consisting of 66 wt.% ZrO_2 and 33 wt.% ZrW_2O_8 was suggested to result in zero expansion. This composition was tested for the in situ measurements. The change in linear dimensions as a function of temperature is given in figure 7. From 450 K onwards, a sleight thermal expansion is noted. This is coincident with the occurrence of the α to β transition and can be explained as follows. The -phase possesses a lower negative thermal expansion coefficient (-4.9×10^{-6} K^{-1}) than the β-phase (-8.7×10^{-6} K^{-1}) and this obviously changes the compensatory effect of the ZrO_2 which exhibits a strongly positive expansion coefficient (9.6×10^{-6} K^{-1}) which remains constant in the entire temperature region.
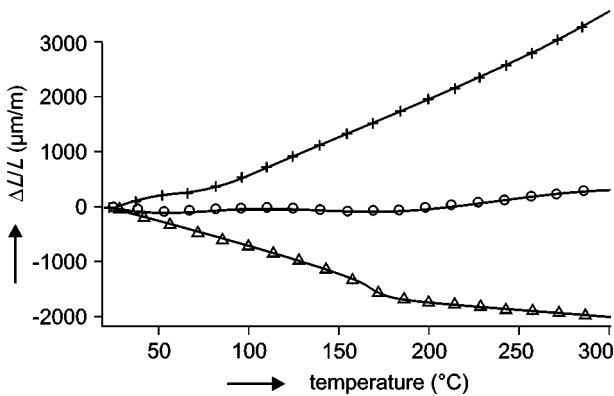

Figure 7. Thermal expansion for ZrO_2 (+), ZrW_2O_8 ($\triangle$) and 33 wt.% in situ composite($\bigcirc$).

Handling the bars is not simple because of the brittle nature of these ceramics. The mechanical properties were measured by a three points bending test [15]. In figure 8, the flexural strengths were plotted for the ZrW_2O_8 pure phase and 2 composites with the same composition (80 wt.% ZrW_2O_8) but with a different preparation.

$$\sigma = \frac{3LF}{2bh^2} \qquad (1)$$

The flexural strength σ calculated by formula 1 where L is the distance between the support points, F the load at rapture, b the cross section of the sample and h is defined as the thickness. As can be seen in figure 8, these flexural strength is similar for the pure phase and the in situ composite where as the composite prepared by the conventional method shows much lower flexural strength which was expected from the morphological analysis.
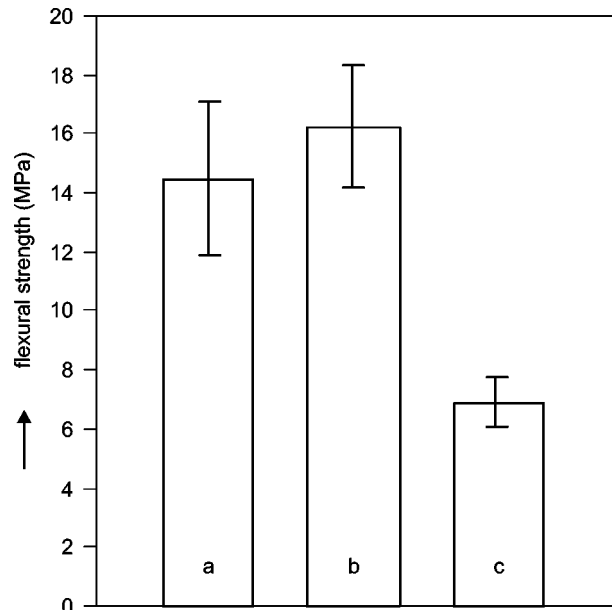

Figure 8. Flexural strength for a) pure ZrW_2O_8, b) 80 wt.% in situ and c) 80 wt.% conventional.

CONCLUSIONS

A first attempt to modify the thermal expansion of ZrW_2O_8 by the formation of composites with ZrO_2 has been demonstrated, using two preparation methods. In a conventional synthetic approach, the variation of the thermal expansion coefficient is shadowed by poor mechanical properties. However by using an in situ method, there is no loss in flexural strength. The use of polyethylene glycol as pressing aid largely improves the mechanical characteristics of the composite materials. Nevertheless, the formation of pores was observed due to the evaporation of organic material during thermal treatment. Further research will be performed to minimize the pore formation and improve the mechanical strength.

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SMĚSNÝ MATERIÁL ZrW_2O_8 - ZrO_2 S NEGATIVNÍ TEPLOTNÍ ROZTAŽNOSTÍ

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Většina materiálů se při zahřívání rozpíná. Existuje ale několik skupin materiálů s negativním teplotní roztažností (NTE). ZrW_2O_8 je příkladem, který v poslední době přitahoval velký zájem v mezinárodní literatuře. Tento kubický materiál má výjimečně velkou a izotropní negativní teplotní roztažnost v celém rozmezí své stability (0,5 až 1050 K). Při 430 K dochází k fázové transformaci α-ZrW_2O_8 (α = -9.1 × 10^{-6} K^{-1}) na β-ZrW_2O_8 (β = -5.4 × 10^{-6} K^{-1}). Při zvýšeném tlaku se tvoří ortorhombická fáze γ-ZrW_2O_8, která má malý negativní koeficient roztažnosti. Pro materiály s NTE byly navrženy pro celou řadu použití. Ve směsích může být jejich roztažnost ušita na míru kombinací s materiálem s normální teplotní roztažností. Ve vhodných objemových poměrech fází bude tepelná roztažnost záporná, nulová nebo kladná. Směsné materiály ZrW_2O_8 - ZrO_2 studované v této práci byly připraveny dvěma způsoby. První metoda začínala z nestechiometrické směsi ZrO_2 a WO_3. Tento nový "in situ" proces pokračoval zahříváním na 1450 K, kdy společně probíhá tvorba a slinování ZrW_2O_8. Při druhém, obvyklejším postupu byly výchozími látkami ZrO_2 a ZrW_2O_8. ZrW_2O_8 byl připraven technikou nástřiku a sušení (spray drying). Je zřejmé, že naše „in situ" metoda nevyžaduje tento přídavný krok. U obou směsných materiálů jsme zkoumali a srovnávali jejich krystalovou strukturu, tvar částic, tepelnou roztažnost a mechanické vlastnosti.