Z. Kristallogr. Suppl. **26** (2007) 525-530

Phase composition and thermal expansion behaviour of zirconium tungstate prepared by rapid sintering

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Keywords: zirconium tungstate, thermal expansion, phase composition, rapid sintering

Abstract. Zirconium tungstate (ZrW_2O_8) is a ceramic material with a strong negative isotropic thermal expansion in the range of -8 to -10 ppm/K. This property makes the material interesting to be used as substrate for compensation of unwanted thermal expansion of e.g. fiber bragg gratings [1]. For the preparation of this material several attempts have already been used, e.g. pressing and sintering. Unfortunately the composition is only stable within some specific temperature windows. This makes the preparation of a compact material showing this extraordinary thermal behaviour very challenging. This work summarizes the attempt to use pressure assisted rapid sintering techniques for the consolidation of this material. Thermal behaviour and phase composition of the materials are shown as well.

Introduction

Zirconium tungstate (ZrW_2O_8) shows interesting thermal expansion behaviour. When heated, the material shows an enormous shrinkage (the coefficient of thermal expansion is around -8 to -10 ppm/K). Therefore it has already been subject of many publications [2-4]. Due to a negative thermal expansion the material was already used as a filler element in metal matrix composites. Copper was added to the zirconium tungstate in order to achieve a material with high thermal conductivity combined with a reduced coefficient of thermal expansion [5-7].
Bulk materials of zirconium tungstate can be produced by reaction sintering of ZrO_2 and WO_3 [8, 9] or by compaction of ZrW_2O_8 powder [9, this work]. Unfortunately the composition is thermodynamically stable only in the temperature range from 1105°C to 1257°C. During cooling down it is metastable and it decomposes below 1050°C into the oxides. Therefore it is necessary to sinter the material either at a temperature of approx. 1125°C followed by quenching or by consolidation and sintering below the decomposition temperature of 777°C.

Experimental methods

Synthesis of the samples

Within this work we started from pure ZrW_2O_8 powder which was consolidated by two different, but similar, rapid sintering techniques: the first technique is called Spark Plasma Sintering/Field Assisted Sintering (SPS/FAST), the second is the inductively heated hot pressing method (iHP).

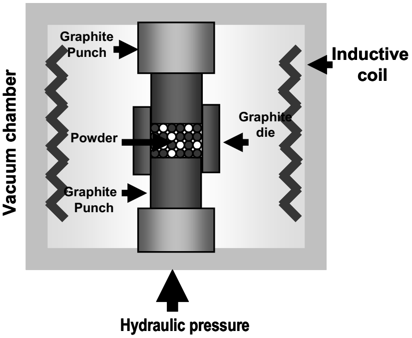


Figure 1. Schematic overview of iHP (inductive hot pressing)

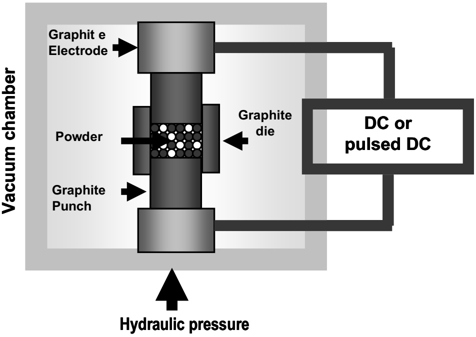


Figure 2. Schematic overview of SPS/FAST process

Both methods are quite similar and characterised by high heating/cooling rates (several 100 K/min) and short cycle times (~15-30 minutes). The characteristic difference is, that SPS/FAST uses a pulsed DC to heat the graphite die while heating is achieved for the second method by an inductive coil.

For the preparation of samples ZrW_2O_8 powder (WahChang, USA) with a particle size < 50 µm and a mean particle size in the range of 8-17 µm was filled in a graphite mould. The powder samples were pre-compacted and placed in the hot pressing/SPS device. The vacuum system was evacuated to a pressure in the order of 10^{-2} to 10^{-3} mbar. The mechanical pressure was increased to around 50 MPa and the graphite die was heated either by inductive coil or via pulsed DC. Using heating rates of around 200 – 400 K/min and a holding time of 1 minute the total cycle was finished after about 15 minutes. After the end of the process cycle the samples were removed from the graphite die. Table 1 gives an overview on the compacted samples and the corresponding hot pressing conditions.

Table 1: Hot Pressing and SPS/FAST conditions

Sample #	Consolidation	Sintering Temperature	Heating Rate	Dwell Time
#26	SPS/FAST	800 °C	400 K/min	1 min
#32	SPS/FAST	900 °C	400 K/min	1 min
#157	iHP	750 °C	400 K/min	1 min
#158	iHP	800 °C	400 K/min	1 min
#159	iHP	900 °C	400 K/min	1 min
#170	iHP	700 °C	400 K/min	1 min
#171	iHP	750 °C	400 K/min	30 min
#172	iHP	800 °C	400 K/min	30 min
#176	iHP	850 °C	400 K/min	1 min

Characterization

For the characterisation of the thermal performance of the compacted materials a dilatometer was used in order to identify the thermal expansion behaviour as a function of temperature. Therefore samples with a length of approx. 12 mm were used. The phase determination of the samples by means of X-ray powder diffraction methods were performed using an Philips X´Pert Powder diffractometer (θ – 2 θ, Bragg-Brentano geometry) using copper $K\alpha_{1,2}$ radiation at 40 kV and 40 mA. The measurements were performed in step-scan mode over the range 5 - 85° 2θ with a step size of 0.02° and a counting time of 3 s/step.

Results

Phase analyses (XRD)

The compacted samples were investigated with respect to the composition. XRD was used to identify the zirconium tungstate phase as well as the decomposition products such as ZrO_2 and WO_3. Comparing the XRD patterns of the SPS/FAST sintered samples with the pattern obtained from the starting powder no differences in the phase composition were found. This means, that due to the fastness of the process, no decomposition during heating at 800 °C for 1 minute. Increasing the temperature to 900°C leads to a decomposition into its oxides.

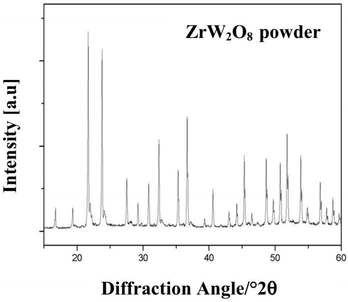


Figure 3. XRD patterns of ZrW_2O_8 powder

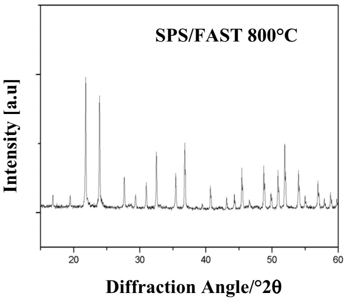


Figure 4. XRD patterns of SPS/FAST compacted samples at 800°C

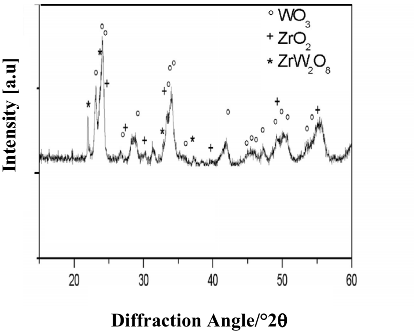
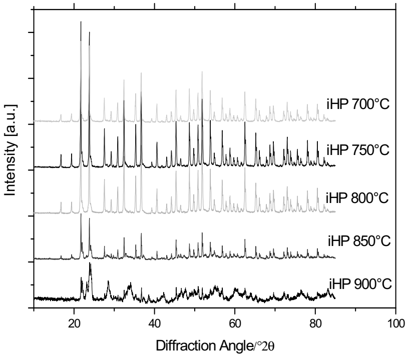


Figure 5. XRD patterns of sample prepared at 900°C using SPS/FAST process.

The inductively heated hot press was used to compact samples at different temperature and for two holding times (1 minute and 30 minutes). Using a heating rate of 400 K/min (identical to SPS/FAST) no significant differences in the composition could be seen, e.g. if the samples compacted at 800°C were compared. For both methods the main detected phase was the ZrW_2O_8 phase. Of course for hot pressing temperatures below 800°C the same phase was observed. If the consolidation temperature was increased to 850°C a first significant change in the composition is observed. A comparable phase composition in the material could be also obtained if the hot pressing process took place at lower temperature (800°C) but for a much longer hot pressing time (30 minutes). At a consolidation temperature of 900°C a clear indication of the presence of the decomposition products was visible (see figure 6/7).



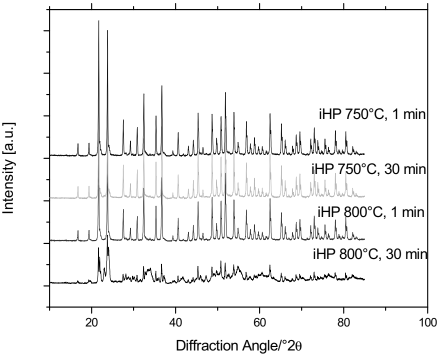


Figure 6. XRD patterns of iHP compacted samples (different temperatures between 700°C and 900°C, holding time: 1 min)

Figure 7. XRD patterns of iHP compacted samples (different temperature: 750°C and 800°C; holding time: 1 and 30 min)

Thermal expansion measurements (CTE)

As mentioned in the introduction, the ZrW_2O_8 phase is a material with a strong negative Coefficient of Thermal Expansion (CTE). In figures 8 and 9 the results of the CTE measurements are shown for the SPS/FAST compacted samples. The CTE measurements have been done using a dilatometer.

The sample compacted at 800°C contains mainly the ZrW_2O_8 phase and therefore a strong negative CTE over a broad temperature range. To study the CTE in different temperature ranges for possible applications, three different runs have been performed. The first cycle was done in the temperature region -50°C to 125°C, the second cycle was from 50°C to 250°C and the third CTE cycle from -50°C to 450°C.

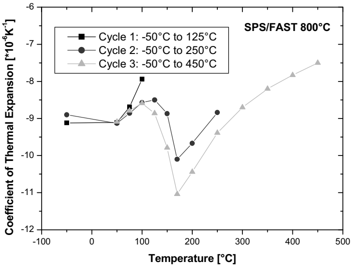


Figure 8. Coefficient of thermal expansion of SPS/FAST sample compacted at 800°C.

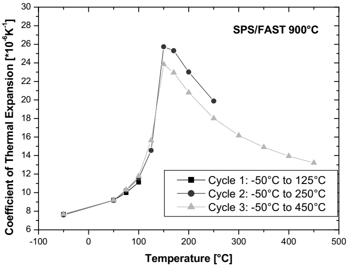


Figure 9. Coefficient of thermal expansion of SPS/FAST sample compacted at 900°C.

Figure 8 shows the CTE values of the sample compacted at 800°C. Here over the whole temperature range a strong negative CTE is observed. The CTE in the range of -50°C to around 100°C is in the about -9 to -8 ppm/K. Since ZrW_2O_8 has a reversible phase change at 150°C this is related to significant changes in the CTE. Nevertheless in the temperature range -50°C to 100°C the CTE of the material is almost constant.

For the material compacted at 900°C the influence of a phase change on the CTE is much more pronounced. Here the CTE varies in the temperature range -50°C to 100°C between +8 to 10 ppm/K. Of course this is directly related to the reduced amount of ZrW_2O_8 in the material. Here the main contributions to a positive CTE (approx. 6 to 10 ppm/K) are coming from the two phases ZrO_2 and WO_3.

Concluding remarks

Rapid sintering techniques are a promising method for the consolidation of ZrW_2O_8 powders to obtain a bulk material with a strong negative CTE. Both investigated consolidation techniques displayed a similar decomposition behaviour with increasing sintering temperature. Samples consolidated at 800°C show ZrW_2O_8 as a major phase resulting in a material with a strong negative CTE of -8 to -9 ppm/K in the temperature range of -50°C to 100°C. Using temperatures far above the decomposition temperature, a positive CTE is measured mainly coming from contributions of the oxide phases (approx. 10 ppm/K from ZrO_2 and approx. 16 ppm/K from WO_3). This of course means, that by an appropriate choice of the sintering temperature and time a specified partial decomposition of ZrW_2O_8 into its oxides can be obtained. This can surely be used to tailor the amount of negative and positive CTE phases to obtain a material with zero expansion, at least in a temperature range of -50°C to 100°C.

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