

The Study on Thermal Expansion of Ceramic Composites with Addition of ZrW_2O_8

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Abstract. The studies on structure, phase composition and thermal properties of ($\text{Al}_2\text{O}_3 - 20$ wt% ZrO_2) – ZrW_2O_8 ceramic composites obtained using nanosized, initial powders were conducted. Homogeneously distributed white particles on the polished surface of composites were observed. Phase composition of the composites was represented with corundum, monoclinic ZrO_2 and two modifications of ZrW_2O_8 (tetragonal and cubic). Linear thermal expansion coefficient values of the composites were determined. The difference in experimental and calculated coefficient of thermal expansion values for composites obtained may be attributed to phase transformations, features of the structure, internal stresses due to thermal expansion mismatch, which contribute significantly to thermal expansion of the ceramic composites.

1. Introduction

Development of new composites with specific thermal properties, for example low thermal expansion, for today is a significant and perspective research task. Recently one can observe a growing number of studies on the creation of ceramic composites with controlled coefficient of linear thermal expansion to provide dimensional stability of the object during the operation from very low to high temperatures. The solution of the problem lies in a combination of materials with positive and negative coefficients of thermal expansion (CTE). Zirconium tungstate is considered as most effective material for such application due to its isotropic negative thermal expansion coefficient ($\alpha = -9 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$) in a wide temperature range from -273 to $770 \text{ }^\circ\text{C}$ [1]. Ceramic materials with unique mechanical, thermal properties, with a near zero CTE can be applied in various fields such as rocket engineering, high-precision optics, electronics, oil and gas industry and others. However, the interaction between zirconium tungstate and ceramics during thermal treatment is not fully investigated. Phase transitions or formation of internal stresses can lead to a change of physical and mechanical properties of the material. A detailed study on these processes is required in order to obtain material that retains mechanical properties on sufficient level and the required value of the coefficient of thermal expansion.

The main aim of the work is to study the structure and thermal properties of the ($\text{Al}_2\text{O}_3 - 20$ wt.% ZrO_2) ceramic composite with addition of zirconium tungstate ZrW_2O_8 .



2. Materials and Experimental Procedure

The powder mixtures of Al_2O_3 – 20 wt.% ZrO_2 and ZrW_2O_8 were used as initial components. Zirconium tungstate was obtained using hydrothermal method based on low-temperature decomposition of the precursor $\text{ZrW}_2\text{O}_7(\text{OH}_{1.5}\text{Cl}_{0.5})2\text{H}_2\text{O}$ [2]. The mixing of Al_2O_3 and ZrO_2 powders was carried out in a ball mill for 25 hours. The volume fraction of zirconium tungstate powder in the powder mixture was 10 wt. %. Samples were prepared by uniaxially cold pressing the mixtures in a cylindrical shaped steel press mold with diameter 7 mm under 10 MPa. (Al_2O_3 - 20 wt.% ZrO_2) – ZrW_2O_8 ceramic composites were obtained by free sintering the green compacts in air at 1550 °C. Structure and phase composition were studied using XRD analysis on “DRON” diffractometer with $\text{CuK}\alpha$ radiation. Particle shapes and sizes were characterized using optical and scanning electron microscopy (SEM). Thermal expansion was investigated using quartz mechanical dilatometer in temperature range 100 - 600 °C.

3. Results and Discussion

3.1. ZrW_2O_8 powder

According to SEM analysis the ZrW_2O_8 powder synthesized was represented with elongated particles with block structure, Figure 1. The mean size of individual elongated particles in the transverse direction was 200 nm, the block size –50 nm [3].

Thermal behavior of zirconium tungstate was described in detail in [4]. ZrW_2O_8 has cubic crystal structure in temperature range from 25 to 540 °C. The further increase of temperature causes rearrangement of atoms in crystal structure of ZrW_2O_8 intended to form sublattices of zirconium and tungsten oxides. The rearrangement is a predecessor of the decomposition process of zirconium tungstate. The decomposition process of zirconium tungstate into constituent oxides ends at 850 °C.

The lattice parameter (a) of cubic ZrW_2O_8 decreased with increase of temperature from 25 to 1000 °C indicating the negative thermal expansion of the material. The linear thermal expansion coefficient of ZrW_2O_8 in temperature range from 20 to 200 °C was equal to $\alpha = -9.4 \cdot 10^{-6} \text{ C}^{-1}$ and $\alpha = -3.8 \cdot 10^{-6} \text{ C}^{-1}$ in temperature range from 200 to 1000 °C, Figure 2. Increase of the CTE value at $200 \pm 25 \text{ }^\circ\text{C}$ corresponds to a phase transition from a low temperature (α -) to high-temperature (β -) modification of zirconium tungstate.

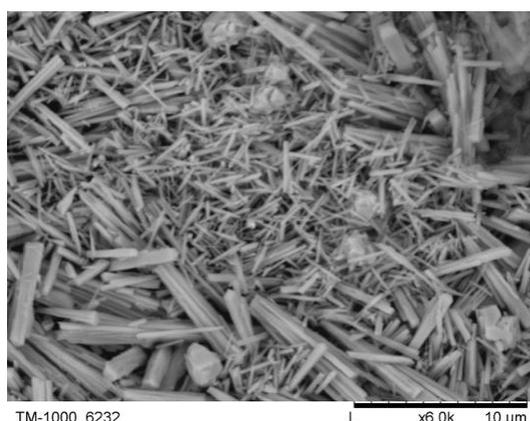


Figure 1. SEM image of ZrW_2O_8 powder.

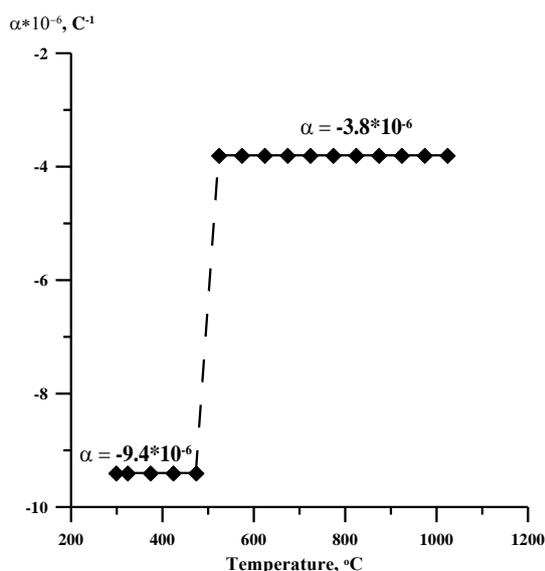


Figure 2. Lattice parameter-temperature dependence.

3.2. (Al_2O_3 - 20 wt.% ZrO_2) - ZrW_2O_8 ceramic composites

Nanosized plasmochemically synthesized alumina and zirconia powders were used to obtain the (Al_2O_3 - 20 wt.% ZrO_2) - ZrW_2O_8 ceramic composites.

The morphology of ZrO_2 powder was represented with nanocrystals, spherical particles with mean size 0.1 μm and agglomerates without regular shape with mean size 5 μm , Figure 3. The specific surface area, which is the total surface area of a material per unit of mass, was 20 m^2/g . Bulk density, which is density of a loose material, was 0.7 g/cm^3

Phase composition of the powder was represented with cubic, tetragonal and monoclinic ZrO_2 with prevalence of cubic modification (75%). The mean coherent diffracting domain (CDD) size was 20 nm for cubic ZrO_2 , 30 nm for monoclinic ZrO_2 and 15 nm for tetragonal ZrO_2 .

According to SEM analysis Al_2O_3 powder was represented with agglomerates formed by particles with irregular shapes and spherical particles with mean size of 1.3 μm , Figure 4.

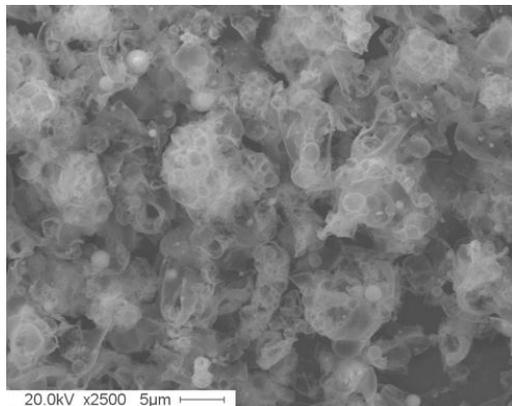


Figure 3. SEM image of ZrO_2 powder.

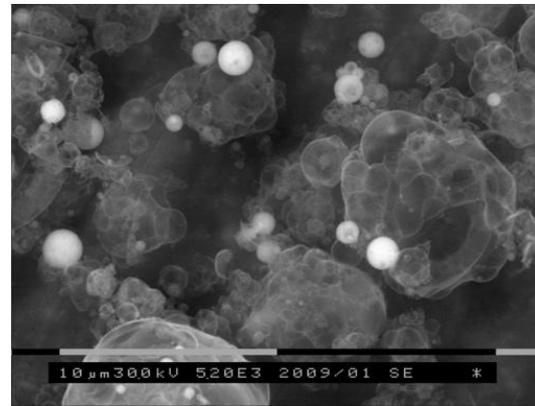


Figure 4. SEM image of Al_2O_3 powder.

According to XRD analysis in the composites obtained alumina is represented with α -modification (corundum), zirconia is represented with monoclinic modification, and two modifications of ZrW_2O_8 – cubic and tetragonal (t) were identified, Figure 5. On the X-ray diffraction pattern also appeared peaks corresponding to tetragonal ZrO_2 and WO_3 . For cubic ZrW_2O_8 $a = 9.8019 \text{ \AA}$, the lattice parameter increased by 7% compared with the literature ($a = 9.1540 \text{ \AA}$) [1]. The presence of tetragonal ZrW_2O_8 was an unexpected result. Tetragonal modification of zirconium tungstate at the moment is reported only in [5] and there is no information about its thermal expansion behavior. Apparently during the cooling process cubic zirconium tungstate decomposes to t - ZrW_2O_8 , ZrO_2 and WO_3 . Thus the decomposition of ZrW_2O_8 to the oxides may proceed through intermediate t - ZrW_2O_8 phase.

It was established experimentally that the thermal expansion coefficient of the sintered Al_2O_3 - 20 wt.% ZrO_2 ceramic without addition of ZrW_2O_8 was $9.7 \cdot 10^{-6} \text{ C}^{-1}$. CTE value calculated using the mixture rule: $\alpha = \sum a_i V_i$, here a_i are thermal expansion coefficients for each component and V_i are the volume concentrations. Using the experimental data for Al_2O_3 ($\alpha = 9.7 \cdot 10^{-6} \text{ C}^{-1}$) and ZrO_2 ($\alpha = 11 \cdot 10^{-6} \text{ C}^{-1}$) CTE of the ceramic composite was calculated - $\alpha = 10.1 \cdot 10^{-6} \text{ C}^{-1}$. The experimental data are in a good agreement with calculated values of CTE for Al_2O_3 - 20 wt.% ZrO_2 ceramic composite.

The relative elongation – temperature relationship for (Al_2O_3 - 20 wt.% ZrO_2) - 10 wt.% ZrW_2O_8 ceramic composite is presented in Figure 6. This relationship can be divided into 2 areas with different slope to the horizontal axis. In this case thermal expansion coefficient is the slope of approximation line to the x axis. The CTE of (Al_2O_3 - 20 wt.% ZrO_2) - 10 wt.% ZrW_2O_8 ceramic composite was

$9 \cdot 10^{-6} \text{ C}^{-1}$. The temperature of deviation from linear law on the double logarithmic plot was $210 \pm 5 \text{ }^\circ\text{C}$.

The CTE value calculated using the mixture rule was $7.8 \cdot 10^{-6} \text{ C}^{-1}$. The reasons for the slope change and mismatch between experimental and calculated data can be phase transitions, internal stresses, formed as a result of thermal expansion mismatch of the components. All this can make a significant contribution to the thermal expansion of the material. To understand completely the thermal behavior of $(\text{Al}_2\text{O}_3 - 20 \text{ wt.}\% \text{ ZrO}_2) - \text{ZrW}_2\text{O}_8$ additional studies are required.

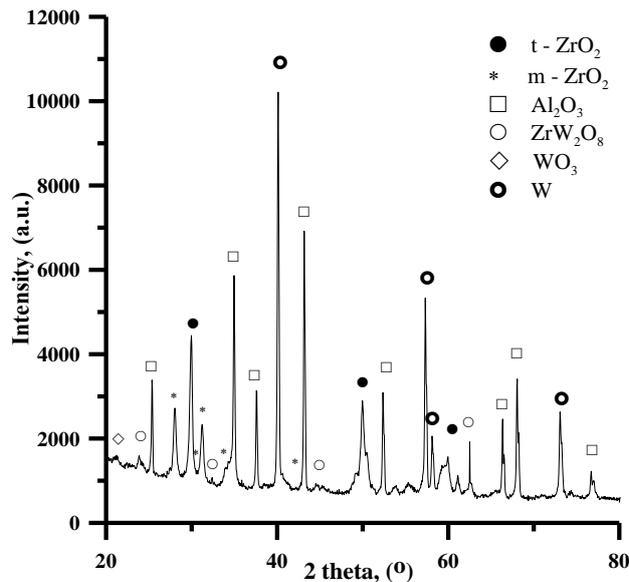


Figure 5. XRD pattern of $(\text{Al}_2\text{O}_3 - 20 \text{ wt.}\% \text{ ZrO}_2) - 10 \text{ wt}\% \text{ ZrW}_2\text{O}_8$.

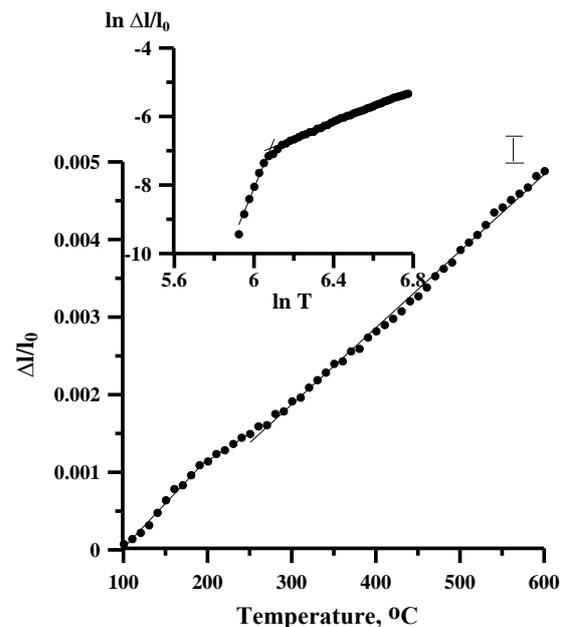


Figure 6. Relative elongation–temperature dependence of $(\text{Al}_2\text{O}_3 - 20 \text{ wt.}\% \text{ ZrO}_2) - 10 \text{ wt}\% \text{ ZrW}_2\text{O}_8$.

4. Conclusion

The morphology of the zirconium tungstate powder obtained by hydrothermal method is represented with elongated particles with mean transverse size $0.2 \text{ } \mu\text{m}$.

Zirconium tungstate remains kinetically stable up to $540 \text{ }^\circ\text{C}$. After that further increase of temperature up to $850 \text{ }^\circ\text{C}$ causes decomposition into constituent oxides through rearrangement of atoms in crystal structure of ZrW_2O_8 intended to form sublattices of zirconium and tungsten oxides.

Phase transition from low-temperature α - to high-temperature β - ZrW_2O_8 modification at $200 \text{ }^\circ\text{C}$ is accompanied by change of CTE of the material from $-9.4 \cdot 10^{-6} \text{ C}^{-1}$ for α - ZrW_2O_8 to $-3.8 \cdot 10^{-6} \text{ C}^{-1}$ for β - ZrW_2O_8 .

Phase composition of the ceramic composite was represented with corundum, monoclinic ZrO_2 and two modifications of ZrW_2O_8 – cubic and tetragonal. According to dilatometric studies the CTE of $(\text{Al}_2\text{O}_3 - 20 \text{ wt.}\% \text{ ZrO}_2) - \text{ZrW}_2\text{O}_8$ ceramic composite was $\alpha = 9 \cdot 10^{-6} \text{ C}^{-1}$. The difference between experimentally obtained data and calculations can be determined by several factors including phase transitions, formation of internal stresses due to thermal expansion mismatch.

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