

The Influence of Temperature on the Properties of ZrW_2O_8

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Abstract

A single-phase ZrW_2O_8 was prepared by the hydrothermal route via decomposition of $ZrW_2O_7(OH_{1.5}Cl_{0.5}) \cdot 2H_2O$ at 843 K. TEM, *in situ* high-temperature XRD and TG-DTA analyses of the ZrW_2O_8 synthesized were performed. The morphology of the material was represented as elongated particles with an intrinsic block structure. The stability fields of ZrW_2O_8 were determined. The ZrW_2O_8 demonstrated a negative thermal expansion behavior from 298 to 1023 K.

Keywords: Zirconium tungstate; Hydrothermal synthesis; Negative thermal expansion coefficient.

1. Introduction

Designing and developing highly-effective materials that remain stable under extreme conditions are among the primary tasks of modern materials science. One potential solution of this problem lies in the development of composite materials with an appropriate matrix and filler. The use of ceramics as a matrix is reasonable as they possess high mechanical strength, hardness and wear resistance while retaining its properties under high temperatures [1–6]. However, ceramics are known to display low toughness making them brittle enough for specific applications. Therefore, the introduction of internal stresses at the filler/matrix interface allows strengthening of the overall composite structure. Such internal stresses can be introduced through a filler that has a negative thermal expansion behavior (NTE) due to the opposite thermal expansion values of the source filler and matrix materials.

There is a class of materials with a negative thermal expansion behavior. More often than not, the contraction of such materials is small, anisotropic and appears in a narrow temperature range. In this respect, zirconium tungstate is a promising material due to a negative isotropic thermal expansion coefficient (CTE) $\alpha = -8.6 \cdot 10^{-6} K^{-1}$ within a wide temperature range from 0 to 1050 K [7].

The unique nature of its thermal behavior is explained by the presence of rigidly connected ZrO_6 octahedrons and WO_4 tetrahedrons in the structure which can rotate relative to one another at an angle of θ with increasing temperature, thereby initiating shrinkage of the material [8]. Variations in the volume concentration of zirconium tungstate would thus enable both to cause internal stresses in ceramic composites, and to make materials with a negative, positive or near zero thermal expansion.

It is known that the method of synthesis has an impact on material behavior under different influences, including an increase in temperature. The hydrothermal method allows for the synthesis of highly-homogeneous powders with small particle size. Zirconium tungstate synthesis using a hydrothermal

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route is based on the decomposition of the precursor $ZrW_2O_7(OH_{1.5}Cl_{0.5}) \cdot 2H_2O$ at relatively low temperatures [9]. At present, there is nevertheless a lack of research on the properties of zirconium tungstate powder obtained using a hydrothermal route when heated. The objective of the work is to investigate the influence of temperature on the properties of ZrW_2O_8 .

2. Materials and experimental procedure

As source components, $Na_2WO_4 \cdot 2H_2O$ (p.a.), $ZrOCl_2 \cdot 8H_2O$ (puriss.) and HCl (puriss.) were used to make the precursor. Aqueous solutions of $Na_2WO_4 \cdot 2H_2O$ (0.5 mol/L), $ZrOCl_2 \cdot 8H_2O$ (0.25 mol/L), HCl (8 mol/L) were thoroughly mixed and moved to a Teflon-lined stainless steel autoclave. The hydrothermal reaction was conducted at 433 K for 36 hours. The product obtained was rinsed repeatedly with distilled water and dried at 383 K. To synthesize a monophasic ZrW_2O_8 powder, the synthesized precursor was annealed at 843 K for an hour in air. The thermal conditions were chosen according to the results reported in [9]. High-temperature *in situ* XRD analyses of the powder were conducted using a Bruker D8 diffractometer with filtered $CuK\alpha$ radiation and conducted at the Borekov Institute of Catalysis SB RAS. Particle form and size analyses were conducted with JEM-2100 transmission electron microscope (TEM). The particle distribution was determined using randomly-cross-section method on TEM photos.

3. Results and discussion

After the overall synthesis, the observations of the morphology of zirconium tungstate using a transmission electron microscopy showed that ZrW_2O_8 powder consisted of elongated particles with an intrinsic blocky structure (Fig. 1). The average block size varied from 20 nm to 50 nm. The distribution of elongated particles by size (longitudinal and lateral) had a unimodal nature. The average lateral size of the elongated particles was from 30 nm to 700 nm, and the average longitudinal size varied from 0.5 μm to 5.0 μm . The EDAX analysis demonstrated that the quantitative atom ratio (O ~ 60 at.%, W ~ 13 at.%, Zr ~ 27 at.% $\pm 2\%$) in the material obtained corresponded to the stoichiometry of ZrW_2O_8 compound (Zr:W = 1:2) [7]. The analysis of reflections observed in the micro-diffraction image indicates the formation of cubic structures.

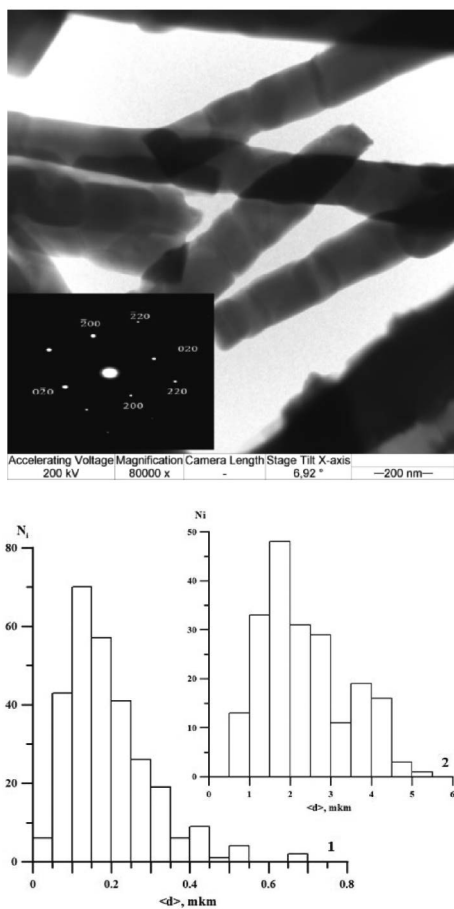


Fig. 1. TEM picture, microdiffraction, particle distribution by lateral (1) and longitudinal (2) ZrW_2O_8 sizes
 1. ábra A ZrW_2O_8 TEM felvétel, mikrodiffrakció és szemcseméret-eloszlás oldalirányban (1) és hosszirányban (2)

The investigations of phase transformation in a material at increasing temperature were performed *in situ*. The results of high-temperature *in situ* XRD observations are presented in Fig. 2. When ZrW_2O_8 is heated from room temperature to 423 K, a gradual decrease in the reflection intensity is observed in XRD pattern from surfaces (1 1 1), (2 2 1) and (3 1 0) up to its complete disappearance at temperatures beyond 473 K. According to [7, 9, 10], the disappearance of such peaks results from the transition from a low-temperature $\alpha - ZrW_2O_8$

($P2_13$) to a high-temperature modification $\beta - ZrW_2O_8$ ($Pa3$) induced by an increase in symmetry of a space group. An increase to 873 K leads to the appearance of weak diffraction lines corresponding to tungsten oxide and zirconium oxide. A further increase in temperature to 1023 K led to an increase in the peak intensity of WO_3 , the appearance of ZrO_2 lines and a decrease in ZrW_2O_8 reflections.

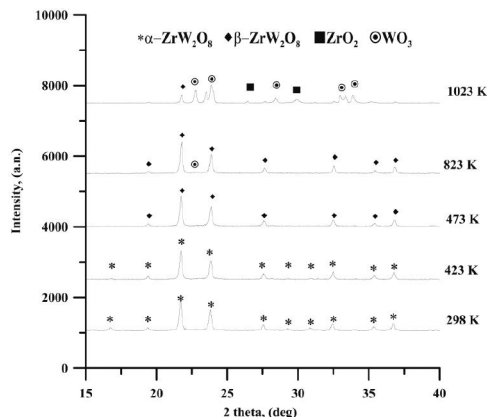


Fig. 2. The *in situ* high-temperature XRD pattern of ZrW_2O_8
 2. ábra A ZrW_2O_8 kerámia magas hőmérsékletű *in-situ* röntgen-diffraktogramjai

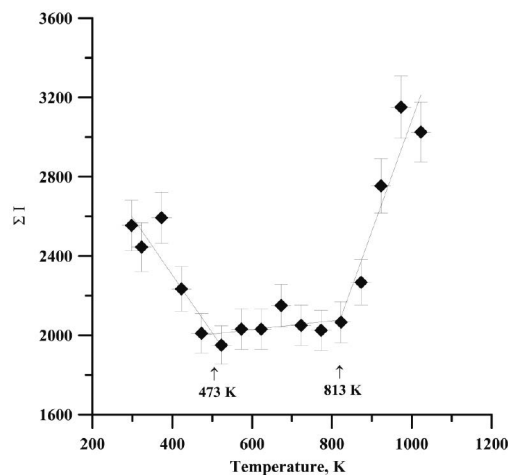


Fig. 3. The dependence between the temperature and the total intensity (ΣI) of all X-ray reflexes
 3. ábra A valamennyi röntgen reflexió teljes intenzitása a hőmérséklet függvényében

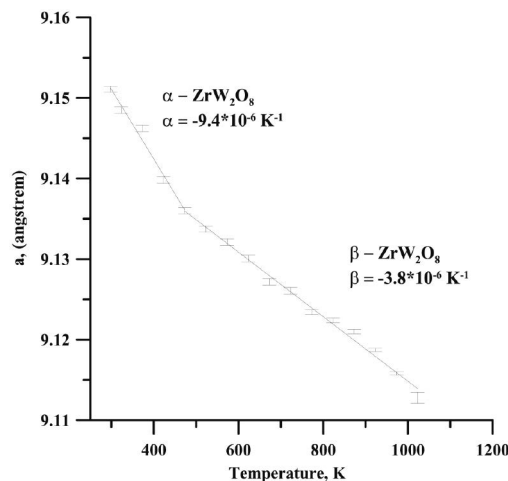


Fig. 4. The dependence between the temperature and the cubic lattice parameter of ZrW_2O_8
 4. ábra A ZrW_2O_8 kerámia köbös rácsparaméterének változása a hőmérséklet függvényében

The dependence of the total intensity (ΣI) of all X-ray reflections on temperature, based on the results of XRD analysis, is shown in Fig. 3. The curve can be unambiguously divided into 3 stages. As the temperature increases to 473 K, the total intensity decreases (stage 1). As the temperature increases from 473 K to 823 K (stage 2), the values of ΣI vary within the margins of experimental error. A further increase in temperature to 1023 K (stage 3), results in an increase in the total reflex intensity. The inflexion points where the slopes changed corresponded to 473 K and 823 K. According to the X-ray diffraction data, the decline in the total intensity in stage 1 was initiated by an $\alpha \rightarrow \beta$ transition and, as a consequence, by the disappearance of some reflections. At stage 2, there is only a high-temperature β -ZrW₂O₈. The increase in the total intensity at stage 3 can be explained by a pre-transitional phenomenon for forming new structures. Atoms in the zirconium tungstate structure begin to rearrange themselves in order to form sublattices of tungsten and zirconium oxides. Presumably, this movement of atoms precedes the decomposition of zirconium tungstate. It is known [7, 9, 10, 11] that zirconium tungstate loses its thermodynamic stability and decomposition into ZrO₂ and WO₃ occur at temperatures above 1050 K. According to the XRD analyses, weak lines of WO₃ and ZrO₂ were observed on diffraction patterns above 873 K. The intensity of the lines grew as the temperature is increased to 1023 K (Fig. 3).

The dependence of the cubic lattice parameter of ZrW₂O₈ on temperature is shown in Fig. 4. As seen in the graph, the lattice parameter decreased with an increase in temperature from 298 K to 1023 K, indicating a negative thermal expansion. Two segments with different slopes in relation to the x-axis can be outlined in the dependence. Changes in CTE occur at 473 K, which corresponds to the $\alpha - \beta$ transition. For each segment, the coefficient of thermal expansion was calculated at the following values of temperature: $\alpha = -9.4 \cdot 10^{-6} \text{ K}^{-1}$ from 298 K to 473 K, $\alpha = -3.8 \cdot 10^{-6} \text{ K}^{-1}$ from 473 K to 1023 K.

4. Conclusion

This paper studied the influence of temperature on the properties of zirconium tungstate powder obtained using a hydrothermal route. It shows that 800 K is the limit until which zirconium tungstate retains its crystal structure. A subsequent increase in temperature is accompanied by changes in ZrW₂O₈ structure induced by the appearance of WO₃ and ZrO₂ phase nuclei which precedes the decomposition of ZrW₂O₈ into two constituent oxides at temperatures above 1000 K. The phase transition from the low-temperature (α) to high-temperature (β) modification of cubic zirconium tungstate occurs at 200°C. The coefficients of thermal expansion of zirconium tungstate powder obtained using a hydrothermal route were: $-9.6 \cdot 10^{-6} \text{ K}^{-1}$ for α -ZrW₂O₈ and $-3.8 \cdot 10^{-6} \text{ K}^{-1}$ for β -ZrW₂O₈.

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A hőmérséklet hatása a ZrW₂O₈ kerámiák tulajdonságaira

A tanulmány nagytisztaságú ZrW₂O₈ kerámia vizsgálatával foglalkozik. Az egyfázisú ZrW₂O₈ kerámia, hidrotermális úton a ZrW₂O₇(OH_{1.5},Cl_{0.5})•2H₂O, 843 K-en történő hőbontásával került előállításra. A cirkónium-wolframátot TEM, TG-DTA valamint magas hőmérsékletű in-situ XRD vizsgálattal jellemezték. Az anyag morfológiáját tekintve saját blokkstruktúrával rendelkező jellegetes megnyúlt szemcsékből áll. Meghatározásra került a kerámia stabilitási intervalluma valamint a hőtágulási együtthatója, mely a 298-1023 K közötti tartományon negatív előjelű.

Kulcsszavak: cirkónium-wolframát; hidrotermális szintézis; negatív hőtágulási együttható