Investigation on Preparation of Al$_{0.52}$Zr$_{0.48}$O$_{1.74}$ by Microwave Pyrolysis

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Abstract. ZTA composite powder was prepared by muffle furnace heating and microwave heating respectively. The effect of pyrolysis on the preparation of ZTA composite powder was investigated. Zirconium chloride ($\text{ZrOCl}_2 \cdot (8\text{H}_2\text{O})$), aluminium sulfate and ammonia were used as raw materials. Heating temperatures were at 600°C, 700°C, 800°C, 900°C, 1000°C for 20 min respectively. XRD and SEM were carried out to characterize samples. Results showed that microwave heating completed the preparation of ZTA composite powder at an excellent lower temperature (600°C) with an optimum size (211 nm). It is mainly due to the rapid coupling between microwave and materials. The different of crystal phase of the samples by muffle furnace heating and microwave heating is mainly due to the selective response between microwave and ZTA composite materials. Microwave plasma is the main factor leading to grain refinement of ZTA ceramic powder.

1. Introduction
Alumina-zirconia (ZTA) composite powder is getting more extensively attention in bio-ceramics and spray materials due to their excellent mechanical and chemical properties [1-3]. As we all know, excellent ceramic products lie to high performance powder. However, alumina-zirconia (ZTA) composite powder is generally prepared by mixing zirconia and alumina in industry, and its poor performance can’t meet the requirements of advanced ceramics [4-6]. How to get uniform ZTA composite powder has become a hot topic for scholars. Aragón-Duarte M C [7] illustrated the relationship between the mechanical properties of ZTA, AZT, 3Y-TZP and 8Y-CSZ and explored the better performance of $\text{Al}_2\text{O}_3$ and $\text{ZrO}_2$ composite. Naga S M et al [8] prepared SrAl$_2$O$_{19}$ enforced ZTA particles by solid-state reaction and found that the SrAl$_2$O$_{19}$ was beneficial to distribution of ZTA particles to improve the sintering properties of ZTA particles. Microwave heating is the dielectric
loss caused by the coupling of materials and microwaves, which is converted into uniform thermal energy in materials. Without uniform heating, non-thermal effects are found when some materials are heated by microwave, phase transition and decreasing synthesis temperature of the materials, and so on [9-11]. Microwave heating is an efficient way to prepare nano-ceramic powder [12-14]. Pian Xiaoxuan [15] prepared ZrO₂ bulk samples by microwave heating and found that samples by microwave heating have showed a better performance than conventional sintered samples. Wei Shengnan et al [16] synthesized SiC at a temperature with 1100°C through seed crystal induction. Unfortunately, less paper was found in microwave heating prepared ZTA composite powder. In this work, muffle furnace heating and microwave heating were carried out to prepare ZTA composite powder. The effect of heating methods on the preparation and performance of ZTA composite powder was investigated.

2. Materials and methods

2.1. Materials preparation

Zirconium oxychloride octahydrate (ZrOCl₂·(8H₂O), analytically pure), yttrium nitrate hexahydrate (Y(NO₃)₃·6H₂O, analytically pure) and aluminum sulfate (Al₂(SO₄)₃, analytically pure) used as zirconium source, yttrium source and aluminum source. Ammonia (analytically pure, 25%) used as precipitant, and PEG2000 (analytically pure) used as dispersant.

Zirconium with 3%mol yttrium hydroxide (3Y-Zr(OH)₄) and aluminum hydroxide (Al(OH)₃) were prepared by simultaneous cross-jet method, and muffle furnace heating and microwave heating were used to prepare the ZTA composite powder.

2.2. Methods

3Y-Zr(OH)₄&Al(OH)₃ were prepared by simultaneous cross-jet method. Al₂(SO₄)₃·18H₂O (566.24g), Y(NO)₃·6H₂O (8.62g) and (ZrOCl₂)·8H₂O (46.89g) were dissolved in deionized water with 0.1mol/L solution as solution A. Ammonia was diluted to 0.1mol/L as solution B. Solution A and solution B were separately transferred to the material pools A and B, and atomization was carried out by a pressure pump and an atomizing nozzle. The ammonia and the reaction mass were thoroughly reacted in the air with very small droplets, where the reaction time was 1 h. The prepared gel was washed three times with distilled water and ethanol in an ultrasonic cleaner, and the supernatant solution was titrated with a silver nitrate solution until no precipitation occurred. The product was separated by a vacuum filter to obtain a hydroxide precursor gel.

Hydroxide precursor gel was pyrolyzed by microwave heating and muffle furnace heating respectively. Firstly, hydroxide precursor gel was transferred into an alumina crucible, and then the crucible was transferred into a microwave oven containing a mullite fiber as thermal insulation structure for heating. Heating temperatures were 600°C, 700°C, 800°C, 900°C and 1000°C respectively, with the holding time 20min. The heating rate of microwave was 60°C/min, and then heating rate of muffle furnace was 5°C/min. Muffle furnace heating can’t reach the heating rate of microwave heating. In order to ensure the effect of muffle furnace heating, the heating rate of muffle furnace was 5°C/min.

2.3. Sample characterization techniques

The phases in samples were characterized by SmartLab 3 X-ray diffractometer (XRD). Morphologies of samples were observed by JSM-7001F field-emission scanning electron microscopy (FE-SEM). The size of the samples was carried out by nanoparticle size analyser.

3. Results and discussion

3.1. XRD analysis

Figure 1 shows XRD patterns of ZTA composite powder with a range of temperatures from 600°C to 1000°C by muffle furnace and raw materials. As shown in Figure 2, Al₀.₅₂Zr₀.₄₈O₁.₇₄, γ-Al₂O₃ and α-
Al$_2$O$_3$ were detected in all samples and $\alpha$-Al$_2$O$_3$ was the main phase of samples. A rising trend was found in $\alpha$-alumina phase, as the heating temperature increasing. When the sintering temperature was 800°C, two weak peaks at 30.2° and 67.0° corresponding to the typical diffraction peaks of Al$_{0.52}$Zr$_{0.48}$O$_{1.74}$ were observed in the patterns. The diffraction spectrum peak at 25.48° corresponding to the typical diffraction peaks of Al$_2$O$_3$ indicated that the alumina grows mainly along the crystal plane(111). The upward trend of the diffraction peak of 25.48° corresponding to the Al$_2$O$_3$(111) crystal plane of means that the degree of completion of the ZTA composite powder rises with the increasing of the heating temperature. When the heating temperature was 1000°C, no other diffraction peak was found, which indicating that the ZTA composite powder couldn’t be completely completed at this heating temperature.

**Figure 1.** XRD patterns of ZTA composite powder with muffle furnace heating.

XRD patterns of ZTA composite powder by microwave heating with a range of temperatures from 600°C to 1000°C and raw materials as shown in Figure 2. Compared with Figure 1, ZTA composite powder prepared by microwave heating shows higher and sharper in diffraction peaks. Al$_{0.52}$Zr$_{0.48}$O$_{1.74}$, $\gamma$-Al$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ were detected in all samples and Al$_{0.52}$Zr$_{0.48}$O$_{1.74}$ was the main phase of samples. Sharp diffraction peaks were found at the heating temperature of 600°C. Rising trends were found in Al$_{0.52}$Zr$_{0.48}$O$_{1.74}$ and $\alpha$-Al$_2$O$_3$ phases, as the heating temperature increasing. The diffraction peak of $\gamma$-Al$_2$O$_3$ phase didn’t change heavily with a range of heating temperatures from 600°C to 1000°C.

Compared with muffle furnace heating, ZTA composite powder by microwave heating had been completed crystallization at the temperature of 600°C. The microwave heating method significantly reduces the crystallization temperature of the sample. The microwave heating method converted the order of the ZTA composite powder from the conventional pyrolysis of $\alpha$-Al$_2$O$_3$ preferential crystallization into the Al$_{0.52}$Zr$_{0.48}$O$_{1.74}$ preferential crystallization in microwave pyrolysis. This maybe mainly due to microwave non-thermal effects. The zirconium ions in the hydroxide of ZTA composite powder can respond to microwave at a lower temperature. It became a hot spot for crystallizing as nucleate, and completed the crystallization of the Al$_{0.52}$Zr$_{0.48}$O$_{1.74}$ phase. When the heating temperature was 800°C, two weak peaks at 30.2° and 67.0° corresponding to the typical diffraction peaks of Al$_{0.52}$Zr$_{0.48}$O$_{1.74}$ were observed in the patterns. The diffraction spectrum peak at 25.48° corresponding to the typical diffraction peaks of $\alpha$-Al$_2$O$_3$ indicated that the alumina grows along the crystal plane(111). The upward trend of the diffraction peak of 25.48° corresponding to the Al$_2$O$_3$(111) crystal plane illustrated the increasing in crystallinity of alumina.
3.2. SEM analysis
The morphology of the ZTA composite by the muffle furnace heating are shown in Fig 3. Samples cannot be completely prepared in all heating temperatures from 600°C to 1000°C. When the heating temperature was 1000°C (Figure 3e), samples appeared to be obvious agglomeration particles. In Figure 3a, many areas of the hydroxide precursors cannot pyrolyzed at 600°C due to the insufficient heating temperature. In Figure 3c, when the temperature was 800°C, the particles shows the clear graininess and its size is smaller than sample heated with 600°C and 700°C. Sintering driving force of ZTA composite rises sharply with the rising of the temperature. When the heating temperature was 600°C, because the atomic kinetic energy of hydroxide precursors is not enough to cross lattice potential energy, many large areas of precursors cannot be pyrolyzed, and only few pyrolysis particles appeared at the interface of the precursors. Thus, many large plates of amorphous structural surfaces are adhered with a few crystallized alumina particles. More crystallized particles were found in
samples owed to pyrolysis driving force by the increasing of heating temperature. When the pyrolysis temperature reached 900°C (Figure 3d), the partially crystallized fine particles began to bond under the drive of the surface energy, so some agglomeration particles were found. When the heating temperature was higher (1000°C), the ZTA composites powder has obvious grain aggregation, which can be found in Figure 3e.

The morphology of the ZTA composite by the microwave heating are shown in Fig 4. Samples completely prepared in all heating temperatures from 600°C to 1000°C. The size of the ZTA composite powder rises slightly with the increasing of heating temperature. When the pyrolysis temperature was 1000°C (Figure 4e), agglomerate particles were found in samples. When the heating temperature were 600°C and 700°C, the hydroxide precursor pyrolysis process had been completed, and the ZTA composite powder particle size is fine, as shown in Figure 4a and Figure 4b. When the heating temperature was 800°C, the particle size of ZTA composite powder was about 350 nm, the ZTA composite powder appears agglomeration as shown in Figure 4c. When the heating temperature was at 1000°C, the agglomeration of sample was heavily aggravated and the particle size increased significantly to 430nm.

![Figure 4. Morphology of ZTA composite powder with microwave heating: (a) 600°C; (b) 700°C; (c) 800°C; (d) 900°C; (e) 1000°C.](image)

![Figure 5. Sizes of ZTA composites powder.](image)
3.3. Size analysis

As shown in Figure 5, the size of ZTA composite by microwave heating are obviously finer than muffle furnace heating. With the increasing of heating temperature, the size of ZTA composites increased by both muffle furnace heating and microwave heating. The size of ZTA composite powder by muffle furnace heating showed a higher increase, which was observed by morphology, XRD patterns and nanosizer analysis. The main reason for the finer particle size of the ZTA composite obtained by microwave heating is due to the integral heating of the microwave heating and the surface purification of the microwave heating. The uniform thermal field brought about by microwave integrity heating allows the ZTA composite particles to grow more uniformly. The pure interface of the ZTA composite powder carried out by surface cleaning of the microwave hinders the abnormal growth of the ZTA composite particles. The uniform internal thermal field by the microwave integral heating greatly reduced the heat conduction process. Therefore, the morphology and size of ZTA composite powder obtained by the microwave heating was fine and uniform. The microwave plasma effect can aggravate the gas reaction on the surface of the material, facilitate the volatilization of impurities with a low melting point on the surface of the material, and purify the interface of the material. And it can effectively suppress the adverse the effect of low melting point impurities on the particle size of the ZTA composite powder. Therefore, the ZTA composite powder obtained by microwave heating shows a better application in many fields.

4. Conclusions

ZTA composite powder was prepared by simultaneous cross-jet method technology and muffle furnace heating and microwave heating technology at a range of temperatures from 600°C to 1000°C. However, muffle furnace heating cannot complete preparation and crystallization even at the temperature of 1000°C. ZTA composite powder prepared by microwave heating is finer than that prepared by muffle furnace heating under the same conditions. Due to different reaction processes, Al0.52Zr0.48O1.74 phase was obtained by microwave heating, while the t-ZrO2 and Al2O3 phases were obtained by muffle furnace heating. The rapid coupling, selective response and microwave plasma purification of microwaves are the main reasons for the performance of ZTA composite powder by microwave heating.

Acknowledgement

This work was sponsored by the National Natural Science Foundation of China (NSFC) (51172113 and 51772277). National Key R&D Program of China (2017YFB0304000). The authors would say thanks for the support.

The authors declare that they have no conflict of interest.

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