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Short communication

# Effect of $ZrO_2$ on phase transformation of $Al_2O_3$

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**Abstract**

This study investigates the effect of $ZrO_2$ on phase transformation of alumina. Alumina and alumina–zirconia composite powders were produced by the precipitation method from aluminum sulfate and zirconium sulfate precursors. Precipitates obtained at 15 °C were dried at 80 °C for 72 h, and then calcinated at four different temperatures; 1000 °C, 1100 °C, 1200 °C and 1300 °C for 1 h. Powders calcinated at 1300 °C were pressed uniaxially and sintered at 1600 °C for 1 h. XRD and DSC analyses showed that the presence of zirconia retarded the transformation to α-alumina. SEM studies on the powders calcinated at 1300 °C revealed that both alumina and alumina–zirconia particles were 100–300 nm in size and of near spherical shape. Zirconia additions inhibited abnormal grain growth of alumina and provided homogeneous, equaxied grain structure.
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*Keywords:* Alumina; Alumina–zirconia composite; Phase transformation; Precipitation

## 1. Introduction

Alumina is one of the most widely used engineering ceramic materials due to its high elastic modulus, high wear resistance and chemical corrosion resistance, high-temperature stability and strength [1]. The drawback of common alumina (α-type phase) is its relatively poor mechanical properties, such as flexural strength (∼380 MPa) and fracture toughness (about 3.5 $MPam^{1/2}$). It is well known that the mechanical properties of alumina ceramics can be considerably increased by the incorporation of fine zirconia particles. The toughening mechanisms associated with zirconia toughened alumina (ZTA) are mainly based on the stress-induced tetragonal → monoclinic martensitic transformation and microcracks [2,3]. The uniform dispersion of zirconia particles in the alumina matrix can be controlled by homogeneous powder synthesis techniques. A series of powder processing techniques have been investigated to synthesize homogenous powder mixture. The precipitation and the sol–gel methods are the easiest and commercialized chemical synthesis routes for producing zirconia doped nanoparticles [4,5]. In the present work, the precipitation method has been used to prepare alumina and alumina–zirconia composite powders and the effect of zirconia addition on phase transformation of alumina is examined. The original aspect of the present study is to produce alumina and alumina–zirconia composite powders from aluminum and zirconium sulfate salts on which very few work are available in the open literature.

## 2. Experimental details

Alumina and alumina with 10 wt.% zirconia powders were produced by the precipitation method. Pure $Al_2O_3$ powders were produced from $Al_2(SO_4)_3$ salt and $Al_2O_3 + 10$ wt.% $ZrO_2$ composite powders were processed from $Al_2(SO_4)_3$ salt and aqueous solution of $Zr(SO_4)_2$ salt. For alumina powder production, aluminum sulfate salt was dissolved in hot distilled water and then it was cooled down to 15 °C. $NH_4OH$ was added into the metal salt solution for precipitation at pH 10. Precipitate was calcinated at four different temperatures,i.e. 1000 °C, 1100 °C, 1200 °C and 1300 °C for 1 h and dried at 80 °C for 72 h. $Al_2O_3 + 10$ wt.% $ZrO_2$ composite powder was obtained in the same way as alumina powder production. In this method, aluminum sulfate salt was first dissolved in hot water and then aqueous zirconium sulfate salt was added into the cooled aluminum salt solution with continuous stirring. The production route of powders is given in Fig. 1 for the two types of powders.

X-ray phase analysis of calcinated and dried powders was performed by using CuKα radiation with a wavelength of 1.5418 Å over a $2\theta$ range of 10–90°. Thermal gravimetric (TG)

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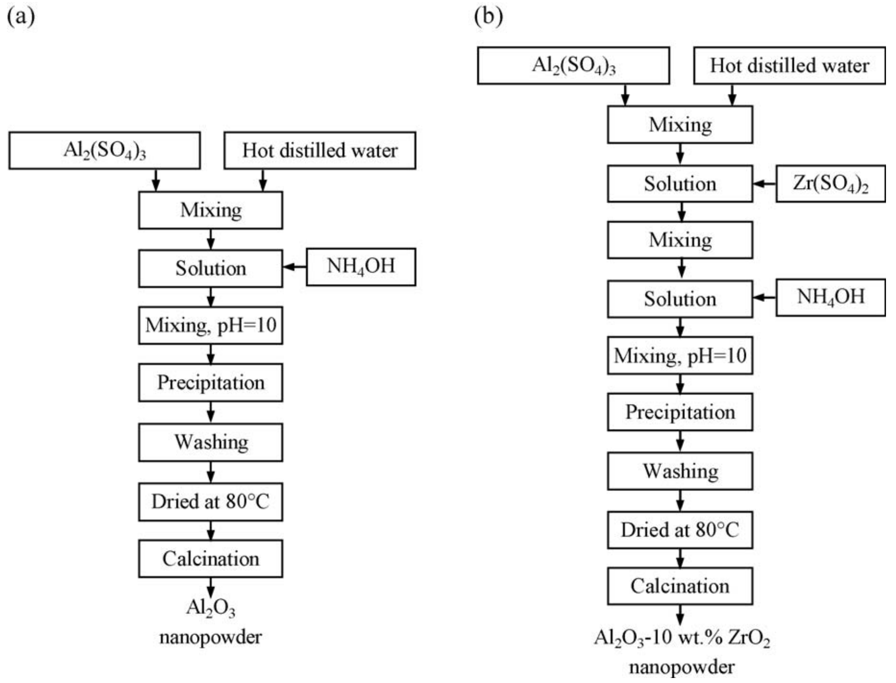

Fig. 1. Flow chart for production of (a) alumina and (b) alumina with zirconia powders.

and differential scanning calorimetric (DSC) measurements of dried powders were performed in a temperature range of 20–1400 °C with a scanning rate of 10 °C/min. Powders morphology and particle sizes were studied by means of scanning electron microscopy (SEM) and energy dispersive spectroscopic analysis (EDS).

The powders, calcinated at 1300 °C for 1 h, were uniaxially compacted at 170 MPa and then sintered at 1600 °C for 1 h with a heating rate of 5 °C/min. Sintered samples were prepared by classical metallographic method, etched thermally at 1450 °C for 1 h and examined by SEM.

## 3. Results and discussion

### 3.1. Thermal analysis studies

The results of thermal analysis performed on dried hydrated powders by means of TG and DSC are given in Fig. 2. The DSC and TG curves for both of the hydrated powders are similar. Three noticeable reactions appeared in DSC curves, the first two being endothermic and the other exothermic. From the room temperature up to 100–110 °C weight loss is 10% in the powder with hydrated aluminum and 7% for aluminum–zirconium. During this time, dehydration took place in other words physical water was removed from the body. Second weight loss starts at about 200 °C and continues up to 370 °C. The second DSC peak was observed in this region indicating that dehydroxylation [4] (dissociation of hydrates) took place. The weight losses for hydrated aluminum and for aluminum–zirconium are 20% and 23% respectively. Above 1020 °C, weight losses were not observed. In hydrated aluminum and aluminum–zirconium powders, exothermic reaction took place at 1280 °C and 1380 °C, respectively. Exothermic reaction reveals the formation of α-alumina and it is clear that $ZrO_2$ retards the phase transformation.

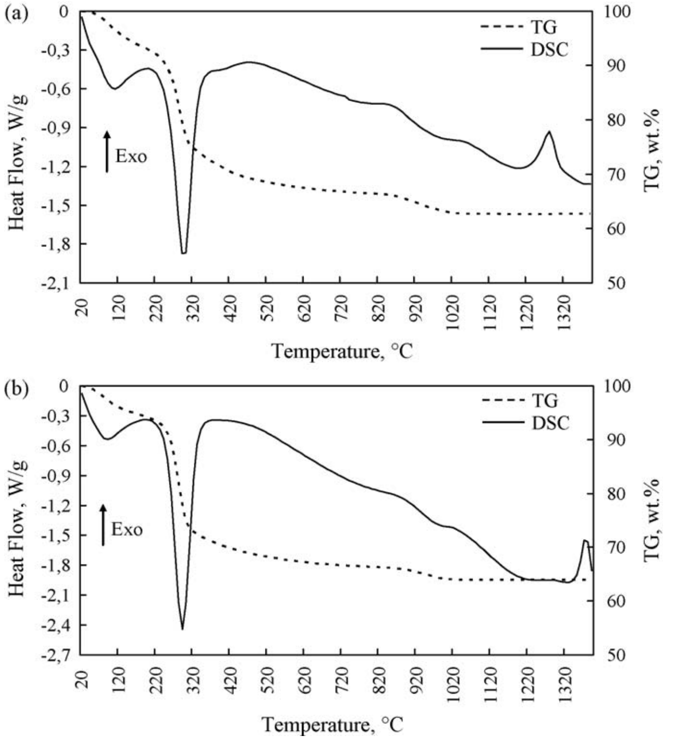

Fig. 2. DSC and TG analysis for (a) aluminum hydrate and (b) aluminum + -zirconium hydrate precipitated form sulfate salts.

### 3.2. XRD studies

Bayerite $Al(OH)_3$ was detected in the XRD pattern of dried powders in Fig. 3. After drying aluminum–zirconium hydrate,

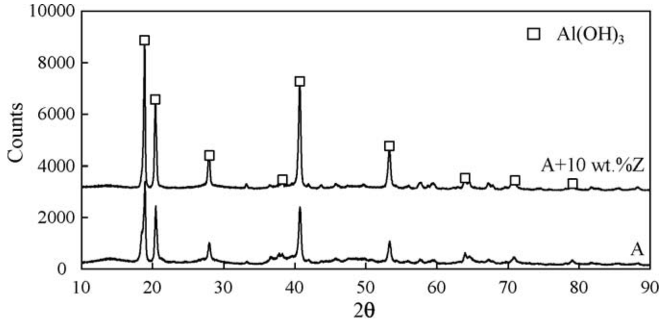

Fig. 3. XRD patterns of hydrated powders following drying (A: hydrated aluminum powder, A + 10 wt.% Z: hydrated aluminum + 10 wt.% zirconium powder).

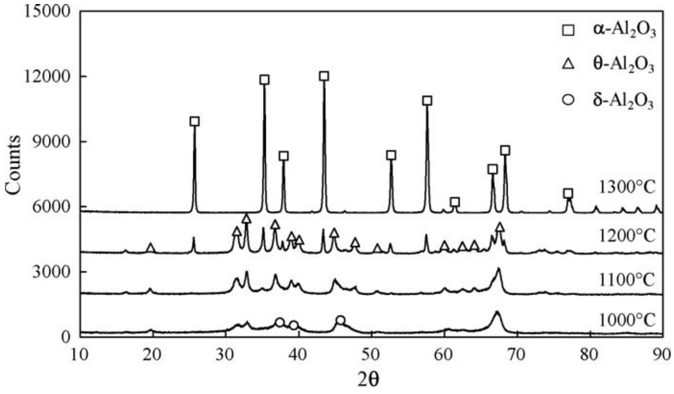

Fig. 4. XRD patterns of alumina powder produced from aluminum salt after calcination at different temperatures.

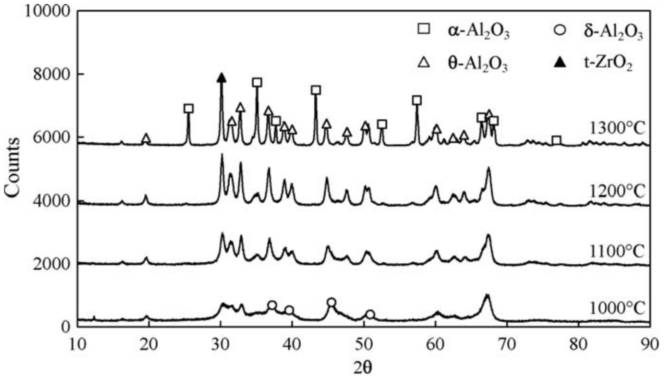

Fig. 5. XRD patterns of alumina + 10 wt.% ZrO$_2$ powder produced from aluminum + zirconium salt after calcination at different temperatures.

zirconium containing phase was not detected in XRD pattern. However, the presence of zirconium element was confirmed by EDS analysis. This result can be related to the amorphous form of zirconium constituent after drying process.

As the TG curves indicate the calcination process at the temperature of 1000 °C did not result in any weight loss. Therefore, the samples were calcinated at 1100 °C, 1200 °C and 1300 °C for 1 h. XRD patterns of calcinated powders are shown in Figs. 4 and 5. Depending on calcination temperatures the phases formed and verified by XRD analysis on pure alumina and alumina–zirconia composite, are given in Table 1. After calcination at 1000 °C δ- and θ-alumina phases were formed within the powders synthesis from aluminum sulfate salt. δ-alumina disappeared with increasing calcination temperature up to 1100 °C and θ-alumina was formed at this temperature. At 1200 °C θ-alumina as well as α-alumina were also detected. After calcination at 1300 °C, all powders transformed into α-alumina trivial whose fraction increases with the process temperature. Phase transformations in the crystallization sequence are [6]: bayerite → boehmite → γ-alumina → δ-alumina → θ-alumina → α-alumina. Boehmite and γ-alumina were not found in the present study because of the relatively high calcination temperatures. After calcination, the phases formed in hydrated aluminum–zirconium powders are similar to the phases formed in hydrated alumina powders. Also, it was observed that powders with zirconia require higher calcination temperatures or prolonged time for the formation of thermodynamically stable α-alumina. Furthermore, in alumina–zirconia composite powders, zirconia phase retained its tetragonal form at all calcination temperatures. This can be attributed to the higher elastic modulus of alumina [7].

### 3.3. SEM studies

SEM micrographs and EDS analysis of alumina and alumina–zirconia composite powders calcinated at 1300 °C are given in Fig. 6. The particle size of calcinated powders ranges from 100 nm to 300 nm. The particles are of near spherical shape. EDS analysis shows that powders contain Al, Zr and O elements without any impurities.

Table 1
Depending on process and calcination temperatures the phases formed and theirs percentages.

| Process | Calcination temperature (°C) | Phases | Phase (%) | | | |
|---|---|---|---|---|---|---|
| | | | δ | θ | α | t-ZrO$_2$ |
| Precipitation | 1000 | δ/θ | 42.85 | 57.15 | – | – |
| | 1100 | θ | 100 | – | – | – |
| | 1200 | θ/α | – | 65 | 35 | – |
| | 1300 | α | 100 | – | – | – |
| Co-precipitation | 1000 | δ/θ/t-ZrO$_2$ | 40 | 50 | – | 10 |
| | 1100 | θ/δ/t-ZrO$_2$ | 12.5 | 75 | 6.25 | 6.25 |
| | 1200 | θ/α/δ/t-ZrO$_2$ | 5.55 | 77.78 | 11.11 | 5.55 |
| | 1300 | θ/α/t-ZrO$_2$ | – | 59.1 | 36.36 | 4.54 |

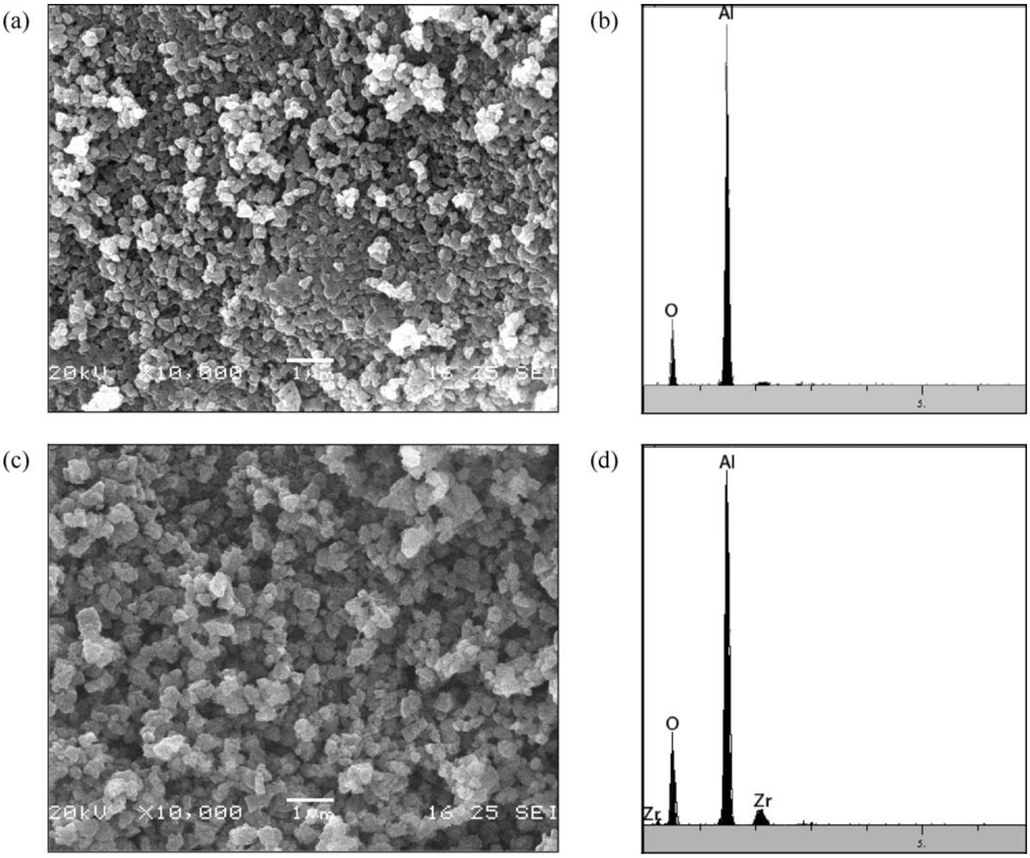

Fig. 6. SEM and corresponding EDS analysis of powders produced by precipitation calcined at 1300 °C (a) $Al_2O_3$ and (b) EDS analysis of alumina, (c) $Al_2O_3 + 10$ wt.% $ZrO_2$ and (d) EDS analysis of alumina zirconia mixture.

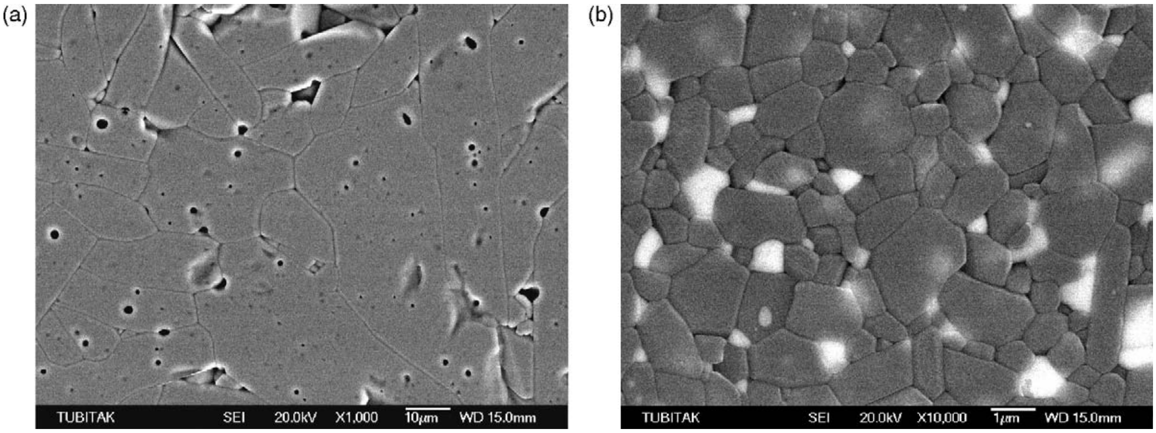

Fig. 7. SEM micrograph of (a) alumina and (b) alumina–zirconia sintered at 1600 °C.

Fig. 7 shows micrographs of alumina and alumina–zirconia composite sintered at 1600 °C for 1 h. In Fig. 7, white areas reflect zirconia phase and gray areas indicate alumina phase. Pure alumina sample has a microstructure with coarse and anisotropically grown grains, 30–40 μm in size. In alumina–zirconia composite, the structure consists of equiaxed fine grains of typically 2 μm in size and with zirconia precipitates uniformly dispersed in the alumina matrix. Zirconia particles are generally located at grain boundaries of alumina particles. It is clear that zirconia inhibited abnormal grain growth of alumina as cited in the literature [2,8].

## 4. Conclusions

$Al_2O_3$ and $Al_2O_3 + 10$ wt.% $ZrO_2$ powders have been synthesized from aluminum and zirconium sulfate salts through the precipitation method. The results obtained from this study are listed below:

1. Thermal and XRD analyses revealed that the addition of $ZrO_2$ retarded the phase transformation to α-alumina.
2. The crystallized fraction of α-alumina increases with process temperature for both test materials but the increment in pure alumina powder is higher than for alumina–zirconia composite powder.
3. XRD analyses show zirconia phase to be tetragonal at all calcination temperatures.
4. In sintered alumina–zirconia samples, zirconia addition inhibited abnormal grain growth of alumina matrix.

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