

Mechanochemical Synthesis of Alumina–Zirconia Nanocomposite Powder Containing Metastable Phases

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Abstract

Alumina–zirconia nanocomposite powder with a particle size around 50 nm was synthesised by mechanochemical activation. Milled powders consisted of CaO and XRD amorphous aluminium and zirconium chloride phases. After annealing the milled powder at 360 °C displacement reactions occurred and ZrO₂ and Al₂O₃ nanoparticles were formed in a CaCl₂ matrix which was removed by washing. DTA, XRD and SEM analysis were applied to characterise the powders. The formation of cubic zirconia and α-alumina were observed at very low temperatures.

Keywords: mechanochemical activation, alumina-zirconia nanocomposite powder, metastable phases

INTRODUCTION

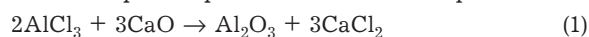
Several methods of preparing alumina/zirconia powders have been reported. The conventional methods involve either dry/wet milling [1] or sol-gel [2–7] technique of alumina/zirconia powders and aluminium/zirconium oxychloride and propoxide precursors, respectively.

However, mechanochemical synthesis is a versatile and simple processing route for the synthesis of ultrafine particles [8–12] and can be used to synthesise alumina/zirconia powders. This technique has already been used for the synthesis of ultrafine zirconia powder [13, 14] from ZrCl₄ and CaO as starting powders which resulted in the formation of cubic ZrO₂ (after washing and heat treatment). Also ultrafine alumina was synthesised by this way resulting in γ-Al₂O₃ which was converted to α-Al₂O₃ at temperatures above 1200 °C [15].

Hence, the objective of the present work is to study the simultaneous synthesis of alumina/15 vol. % zirconia nanocomposite powder by mechanochemical technique from aluminium chloride and zirconium chloride in the presence of calcium oxide to find the differences of the simultaneous synthesis.

EXPERIMENTAL

The starting chemicals used in this study were: CaO (Merck, 97 %), anhydrous AlCl₃ (Merck, ≥98 %) and anhydrous ZrCl₄ (Riedel, 98.5 %). Based on displacement reactions (1) and (2), proper amounts of starting material were used to obtain Al₂O₃/15 vol. % ZrO₂ nanocomposite powder as the final product:



The starting material was milled in a high-energy mill with a speed of 250 rpm under air atmosphere in a sealed polyethylene vial using α-alumina grinding balls. In this paper a ball to powder mass ratio of 25 : 1 with a 24 h milling time was used. To avoid high temperatures during milling, after each 1.5 h of milling a 15 min rest was given but the total milling time was 24 h without considering the resting time. After milling, the powder was annealed in air at 360 °C for 1 h, followed by furnace cooling.

The annealed powder was washed several times under sonication while distilled water was used as the solvent. Subsequent heat treatment of the washed powder was carried out in air at temperatures between 400 and 1300 °C with 1 h holding time at the maximum temperature

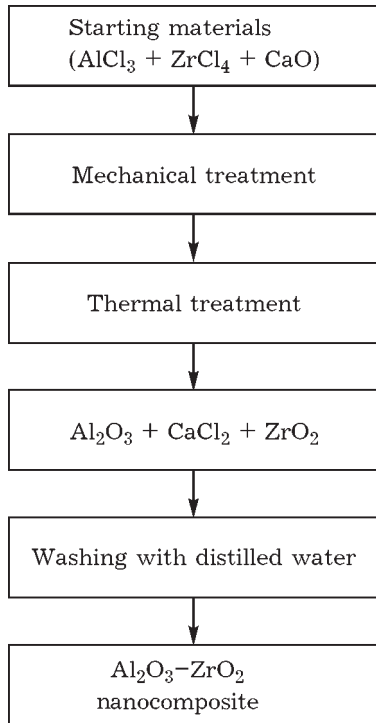


Fig. 1. Typical flow chart of processing technique.

and then it was washed again several times to remove any CaCl₂ obtained during the reaction. After washing we dried the powder at 150 °C in the furnace. Figure 1 shows the typical flow chart of processing the alumina/zirconia nanocomposite powder.

RESULTS AND DISCUSSION

The difference in the thermal behavior was studied by performing differential thermal

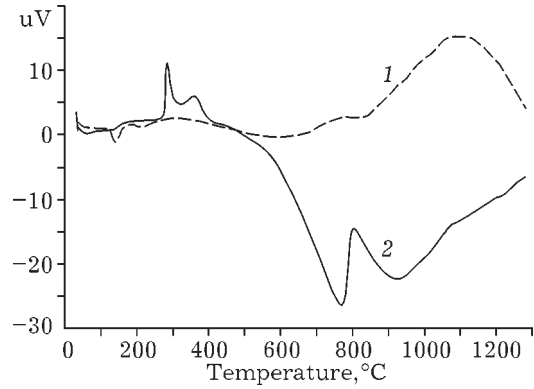


Fig. 2. Differential thermal analysis: unmilled starting material (1) and milled powder (2).

analysis (DTA) experiment. The differential thermal analysis was conducted in air at a heating rate of 10 °C/min using a Perkin-Elmer (the USA) instrument. The results of this study for the unmilled and milled powders are shown in Fig. 2. As can be seen for the displacement reactions to happen in the unmilled powder the temperature needs to reach around 1100 °C. This is because the particles are separate and it is hard for them to diffuse and react with each other. But in the milled samples the displacement reactions occur at lower temperatures which is due to the cold welding and fracturing that happen by the milling treatment. Cold welding and fracturing produce a number of crystal defects such as dislocations, vacancies, grain boundaries *etc.* providing short-circuit diffusion paths. In our specimen, displacement reactions started at 360 °C. As mentioned earlier, the displacement reactions will result in Al₂O₃ and ZrO₂ particles within a CaCl₂ salt matrix.

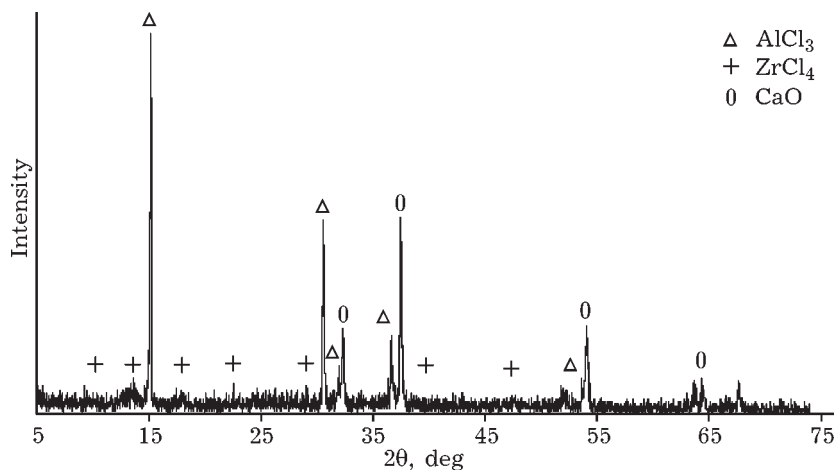


Fig. 3. X-ray diffraction pattern of starting materials.

To study the samples in more detail, XRD analysis was applied. X-ray powder diffraction patterns were obtained using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range $5\text{--}80^\circ$. Figure 3 shows the XRD pattern for starting materials which indicates the presence of CaO , AlCl_3 and ZrCl_4 phases.

In Fig. 4 (curve 1) the milled powder indicates that we only have CaO peaks, although it has broadened due to the reduction in particle size and probably amorphisation. Figure 4 (curve 2) shows the as-milled powder which has been annealed at 360°C , it can be seen that we have only CaCl_2 peaks which is a result of displacement reactions.

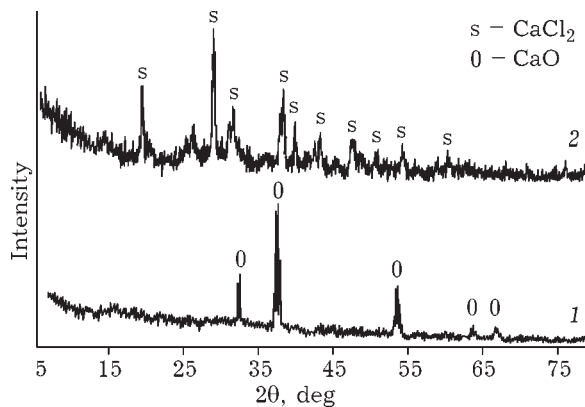


Fig. 4. X-ray diffraction pattern of the as-milled (1) and the annealed as-milled (2) powder.

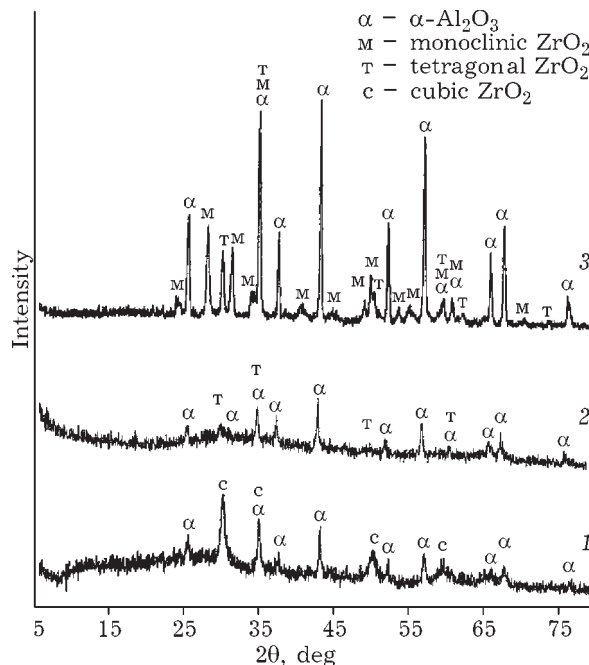


Fig. 5. X-ray diffraction patterns of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanopowders heat treated at 400°C (1), 700°C (2), and 1300°C (3).

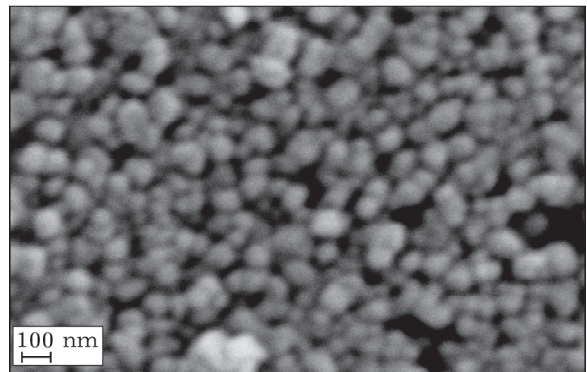
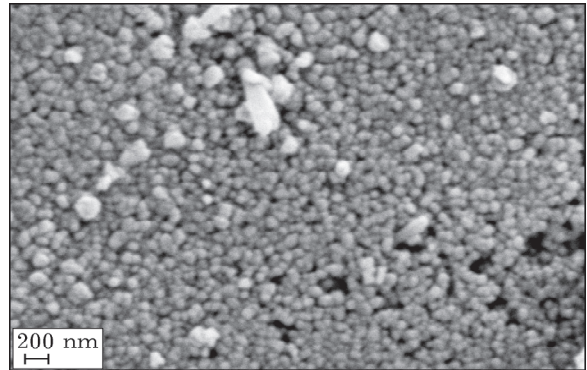


Fig. 6. SEM images of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanopowders calcined at 400°C .

After washing and drying the annealed powder at 150°C the powder was heat treated at 400°C which resulted in cubic zirconia and $\alpha\text{-Al}_2\text{O}_3$ phases as shown in Fig. 5 (curve 1). At increasing heat treatment temperature, α -alumina is stable while the low-temperature metastable cubic zirconia gradually converts to the low-temperature metastable tetragonal polymorph at 700°C and this polymorph partially converts to the monoclinic one at temperatures higher than 900°C .

Figure 6 shows SEM images of the produced $\text{Al}_2\text{O}_3/15 \text{ vol. } \%$ ZrO_2 nanocomposite powder. To our knowledge, the formation of $\alpha\text{-Al}_2\text{O}_3$ by this technique at this low temperature has not been reported in the literature and the exact reason is under review.

CONCLUSION

1. $\text{Al}_2\text{O}_3/15 \text{ vol. } \%$ ZrO_2 nanocomposite powder with a particle size around 50 nm was synthesized by mechanochemical activation.
2. $\alpha\text{-Al}_2\text{O}_3$ was obtained at 400°C and it was stable at temperatures higher than 1300°C .

3. Low-temperature metastable cubic ZrO₂ was formed at 400 °C and it was stable till 700 °C.

4. Low-temperature metastable tetragonal zirconia was obtained at 700 °C and was stable to temperatures around 1300 °C although it was partially converted to the monoclinic polymorph.

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