EFFECT OF FLUORINE AND CHLORINE IONS ON THE REACTION SINTERING OF MECHANICALLY ACTIVATED ZIRCON-ALUMINA MIXTURE

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The aim of this work was to study the effect of fluorine and chlorine ions on the formation of mullite during the reaction sintering of mechanically activated zircon-alumina powder mixture. The results showed that mechanical activation of zircon-alumina powder mixture for 20 h led to grain refinement and partial amorphization. In the presence of fluorine and chlorine ions, complete formation of mullite in the mechanically activated sample occurred after 2 h of reaction sintering at 1300°C and 1400°C, respectively. In the sample lacking fluorine and chlorine ions, mullitization was not completed even after 2 h of reaction sintering at 1400°C. It was concluded that presence of fluorine and chlorine ions enhance the dissociation of zircon and formation of mullite during the reaction sintering of mechanically activated zircon-alumina mixture.

INTRODUCTION

Mullite-zirconia composites have good resistance to thermal shock, chemical inertness, high melting point, high strength and fracture toughness, good wear resistance and low chemical attack-corrosion by siliceous and metallic melts. These properties made them candidates for applications require high strength, toughness, wear resistance and thermal-shock resistance [1-3]. Various processing routes can be used to produce mullite-zirconia composites. Reaction sintering of zircon-alumina mixture is a simple and inexpensive method to produce mullite-zirconia composites with enhanced mechanical properties. However, reaction sintering needs high processing temperatures to reach complete mullitization [4]. One of the methods that has been used to lower the temperature of chemical reactions is mechanical activation [5]. This process is an effective method to increase the contact area and the interaction of the reactants and enhance the kinetic of reactions during the subsequent thermal treatment [6]. In recent years, fluorine and chlorine ions have been used to enhance the fabrication of forsterite during the annealing of mechanically activated powders [7, 8].

The aim of the present study was to investigate effects of fluorine and chlorine ions on the dissociation of zircon and formation of mullite during the reaction sintering of mechanically activated zircon-alumina mixture.

EXPERIMENTAL

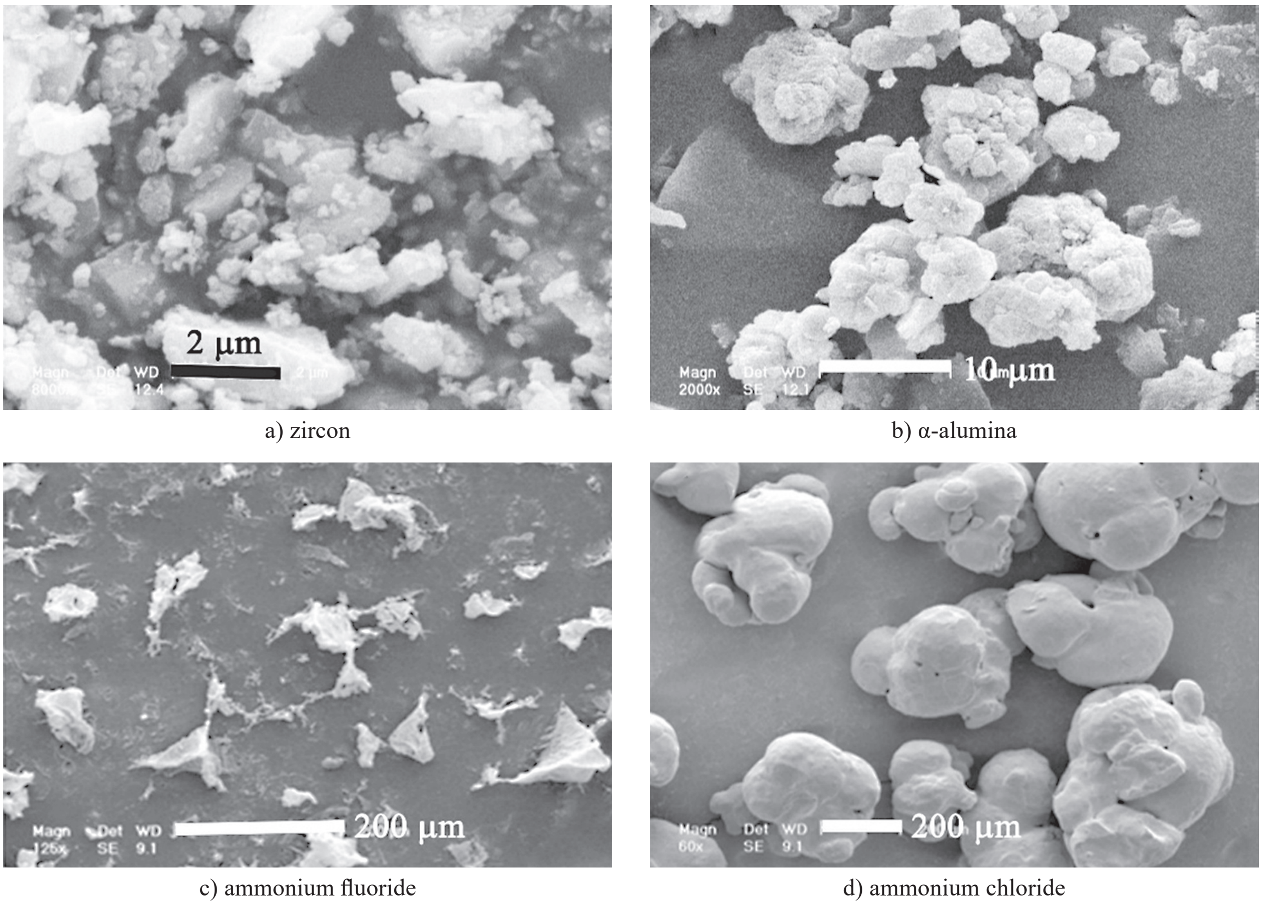
Zircon ($ZrSiO_4$, 99 % purity, Accer), alumina (α-Al_2O_3, 99 % purity, Merck), ammonium fluoride (NH_4F, 98 % purity, Merck), and ammonium chloride (NH_4Cl, 98 % purity, Merck) powders were used as starting materials. Figure 1 shows the morphology of initial powders. In order to investigate the effect of fluorine and chlorine ions on the formation of mullite-zirconia composite, three mixtures were prepared. First, a mixture of alumina and zircon with molar ratio of 3:2 (stoichiometric) were milled in a planetary ball mill (Fritsch P7 type) under ambient conditions for 20 h. Another mixture with the same composition was milled under the same conditions for 19 h. Then, 3 g of NH_4F and NH_4Cl were separately added to the milled powders and milled for another 1 h, so that the total time of mechanical activation for the three mixtures was 20 h. The milling media consisted of five zirconia balls each with a diameter of 20 mm confined in a 120 ml zirconia vial. The rotation speed was 500 rpm and a ball-powder-mass ratio of 10:1 was employed. The as-milled powders were then cold-pressed at 600 MPa into pellets of 10 mm in diameter and sintered at 1200°C, 1300°C and 1400°C for 2 h in an electrical furnace. Phase transformation during the milling and the subsequent reaction sintering was investigated by X-ray diffraction (XRD) in a Philips XPERT MPD diffractometer using filtered Cu Kα radiation (λ = 0.15406 nm). The XRD patterns were recorded in the 2q range of 10 - 70° (step size 0.05°, time per step 1 s). The morphology of powder particles was studied by scanning electron microscopy (SEM) using a Philips XL30 at an accelerating voltage of 30 kV.

RESULTS AND DISCUSSION

Phase transformation

Figure 2 shows the XRD patterns of different samples after mechanical activation for 20 h and subsequent reaction sintering at various temperatures for 2 h. For the zircon-alumina mixture (Figure 2a), broad peaks corresponded to zircon and alumina were presented in the as-milled condition, indicating grain refinement and even partial amorphization during the milling [9]. After reaction sintering at 1200°C for 2 h, the intensity of zircon and alumina peaks increased because of the crystallization of amorphous phase and grain growth. Moreover, peaks corresponded to mullite and tetragonal zirconia were also appeared in the XRD pattern, indicating partial dissociation of zircon and formation of mullite. After reaction sintering at 1300°C, the intensity of zircon peaks reduced and peaks corresponded to monoclinic zirconia were also appeared in the XRD pattern. By increasing the reaction sintering temperature to 1400°C, zircon peaks completely vanished and the intensity of monoclinic zirconia peaks increased. This is due to the complete dissociation of zircon to zirconia and amorphous silica. Presence of alumina peaks and low intensity of mullite peaks indicated that formation of mullite was not completed even after reaction sintering at 1400°C for 2 h.

In the XRD pattern of as-milled zircon-alumina-ammonium fluoride mixture, one broad peak corresponded to $(NH_4)_3ZrF_7$ along with those of zircon and alumina were observed. Presence of the $(NH_4)_3ZrF_7$ peak can be attributed to the reaction between zircon and ammonium fluoride. After reaction sintering at 1200°C for 2 h, the intensity of zircon peaks significantly reduced and alumina peaks disappeared completely. Meanwhile, peaks corresponded to monoclinic zirconia, mullite and silica were appeared in the XRD pattern, suggesting dissociation of zircon and formation of mullite. The intensity of mullite and monoclinic zirconia peaks were higher than those observed in the zircon-alumina mixture after milling and subsequent reaction sintering at 1200°C. This shows that the dissociation of zircon and formation of mullite were enhanced by the presence of fluorine ion. It should be mentioned that $(NH_4)_3ZrF_7$ decomposes by heating [10], and therefore its peak disappeared after reaction sintering at 1200°C.



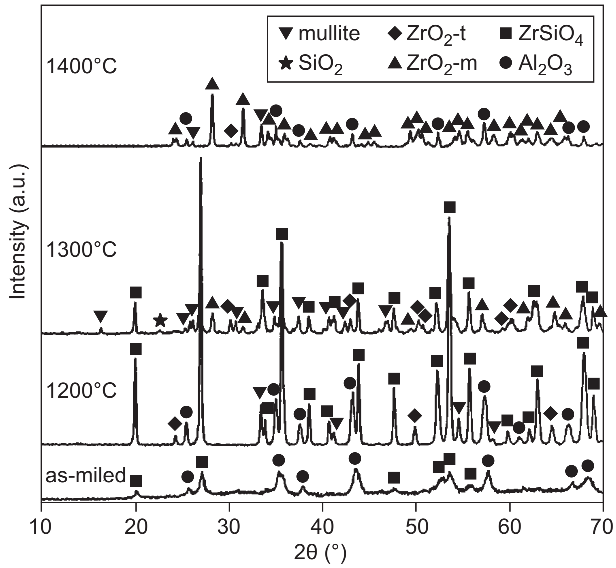
a) zircon b) α-alumina c) ammonium fluoride d) ammonium chloride

Figure 1. Morphology of initial powders; a) zircon, b) α-alumina, c) ammonium fluoride, d) ammonium chloride.

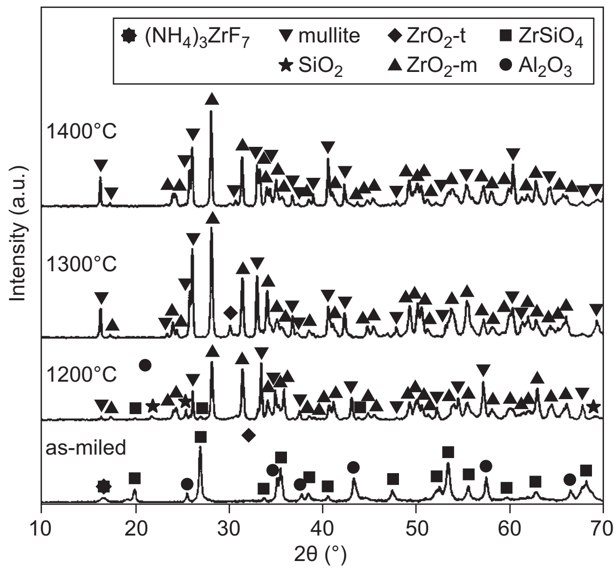
By increasing the reaction sintering temperature to 1300°C, zircon peaks completely disappeared and the intensity of mullite and zirconia peaks increased. These evidences showed that formation of mullite-zirconia composite was completed at this temperature. Increasing the reaction sintering temperature to 1400°C had no significant effect on phase composition and structure.

Figure 2c shows the XRD patterns of the zircon-alumina-ammonium chloride mixture after 20 h of milling and subsequent reaction sintering at different temperatures for 2 h. In the as-milled condition, zircon, alumina and ammonium chloride phases were present. After reaction sintering at 1200°C, alumina and ammonium chloride peaks disappeared and the intensity of zircon peaks significantly reduced. Meanwhile, peaks corresponded to monoclinic and tetragonal zirconia, silica and mullite appeared in the XRD pattern, suggesting dissociation of zircon and formation of mullite. By increasing the reaction sintering temperature to 1300°C, the intensity of zircon peaks further decreased and that for monoclinic zirconia and mullite increased. After reaction sintering at 1400°C, only mullite and zirconia phases were present, indicating complete formation of mullite-zirconia composite.

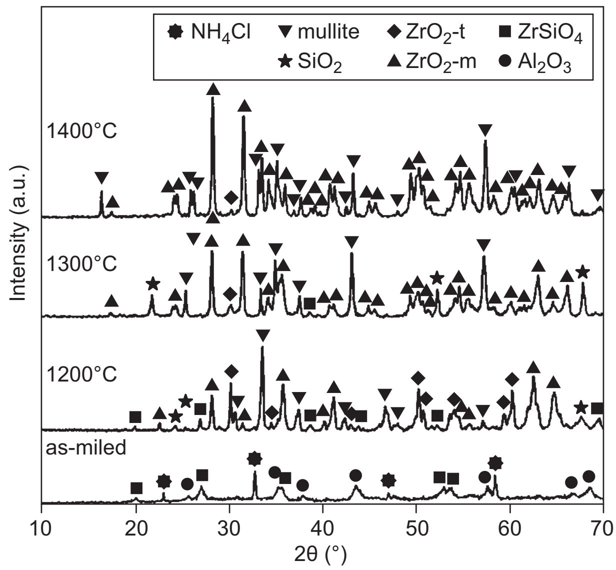
It is observed that the presence of ammonium fluoride and ammonium chloride reduce the temperature for the dissociation of zircon and formation of mullite. For the zircon-alumina mixture milled for 20 h, complete dissociation of zircon was observed after reaction sintering at 1400°C, while mullite formation was not completed. In the presence of ammonium fluoride, the temperature for the complete dissociation of zircon and formation of mullite was 1300°C. In the sample contained ammonium chloride, both complete dissociation of zircon and formation of mullite were observed after reaction sintering at 1400°C. In the un-milled zircon-alumina mixture, complete formation of mullite-zirconia composite was observed in the temperatures higher than 1600°C [11-13]. Here, mechanical activation with the presence of fluorine and chlorine ions decreased the temperature for complete formation of mullite-zirconia composite by ~300°C. It seems that presence of ammonium fluoride and ammonium chloride promotes the dissociation of zircon through formation of intermediate compounds. Because the dissociation of zircon is a very difficult step in the formation of mullite from zircon-alumina mixture [11], mullite formation also enhances and mullite-zirconia composite is obtained at lower temperatures. It should be noted that further study is needed to determine the effect of fluorine and chlorine ions on the mechanism of mullite formation.



a) zircon-alumina



b) zircon-alumina-ammonium fluoride

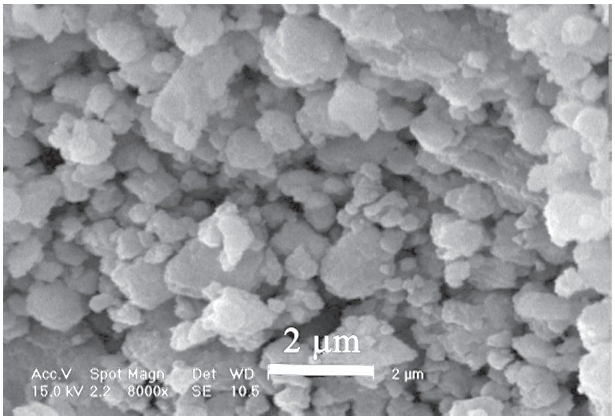


c) zircon-alumina-ammonium chloride

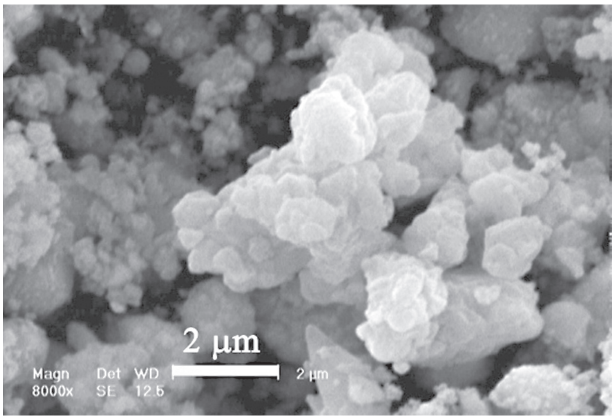
Figure 2. XRD patterns of samples after 20 h of mechanical milling and reaction sintering at different temperatures for 2 h; a) zircon-alumina, (b) zircon-alumina-ammonium fluoride, (c) zircon-alumina- ammonium chloride.

Powder morphology

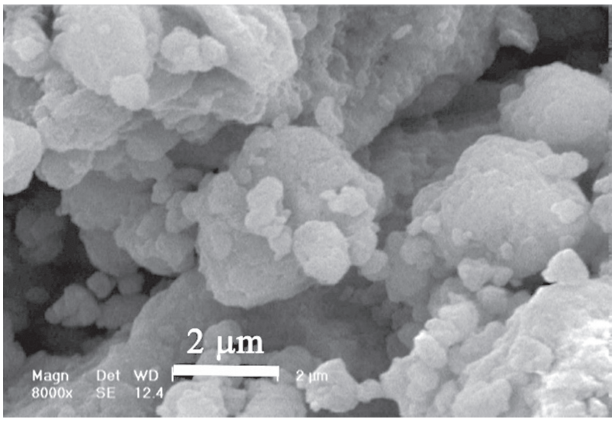
Figure 3 shows the SEM micrographs of the 20 h ball-milled powders. As can be seen, in the presence of ammonium fluoride and ammonium chloride, larger particles and agglomerates were obtained. Mechanical alloying involves repeated fracturing and cold welding of powder particles which determine final particle size [9]. Presence of ammonium fluoride and ammonium chloride enhanced the cold welding and agglomeration of powder particles and therefore larger particles and agglomerates were formed.



a) zircon-alumina



b) zircon-alumina-ammonium fluoride



c) zircon-alumina-ammonium chloride

Figure 3. SEM micrograph of the 20 h ball-milled powders; a) zircon-alumina, b) zircon-alumina-ammonium fluoride, c) zircon-alumina-ammonium chloride.

CONCLUSIONS

In the present study, effects of fluorine and chlorine ions on the formation of mullite-zirconia composite during the reaction sintering of 20 h milled zircon-alumina powder mixture were investigated. The following conclusions were drawn:

- Mechanical alloying of zircon-alumina powders for 20 h led to grain refinement and even partial amorphization.
- During the mechanical milling of zircon-alumina-ammonium fluoride mixture, $(NH_4)_3ZrF_7$ compound formed.
- In the as-milled zircon-alumina mixture, complete dissociation of zircon was observed after 2 h of reaction sintering at 1400°C, whereas mullite formation was not completed.
- In the presence of fluorine ion, complete dissociation of zircon and formation of mullite occurred after reaction sintering at 1300°C for 2 h.
- In the presence of chlorine ion, dissociation of zircon and formation of mullite were completed after 2 h of reaction sintering at 1400°C.

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