

MORPHOLOGY EVOLUTION OF α -Al₂O₃ FROM MILLED γ -Al₂O₃ PRECURSOR WITH NH₄F ADDITIVE

Lingling Zhu¹, Chunhui Sun¹, Sai Li¹, Liugang Chen¹, Guotian Ye¹, Luoqiang Liu¹

¹Zhengzhou University, Zhengzhou, People's Republic of China

llzhu@zzu.edu.cn

ABSTRACT

The morphology evolution of α -Al₂O₃ was investigated by calcination of a commercial γ -Al₂O₃ precursor with NH₄F addition. The study results showed that the morphology of α -Al₂O₃ was significantly improved by the introduction of NH₄F addition, additive content and calcination time. Square-like α -Al₂O₃ powders with primary crystal size of ~200 nm were formed from milled γ -Al₂O₃ precursor with 1 wt.% NH₄F at 1300 °C for 2 hrs. While round cake-like, hexagonal platelets, slender-like and other irregularly shaped α -Al₂O₃ in the size range of 0.2~2 μ m were synthesized from milled γ -Al₂O₃ precursor with 20 wt.% NH₄F addition under the same calcination. Influences of precursor milling treatment and NH₄F addition on the formation of α -Al₂O₃ from γ -Al₂O₃ precursor at 1300 °C were discussed.

Keywords: milled γ -Al₂O₃ precursor; NH₄F additive; α -Al₂O₃; morphology

INTRODUCTION

The alpha alumina (α -Al₂O₃) is one of the most important raw materials widely used in refractory industry, ceramic industry and polishing industry, due to their unique chemical, mechanical and thermal properties [1]. It is well known that the mechanical properties of refractory or ceramics strongly depend on their microstructure, which closely relates with the morphology and size distribution of the α -Al₂O₃ powders [2, 3]. Because of the good flowability, high sintering activity and particle size distributions for maximum packing density, spherical microcrystalline α -Al₂O₃ is one of the most important raw materials used in unshaped refractory [4]. While the plate-like grains are beneficial to improve fracture toughness as plate-like microstructures are helpful to crack bridging form in ceramics matrix [5]. Thus, it can be said that the α -Al₂O₃ powders required for advanced engineering and structural applications need particles having desired morphology.

It has been reported that the many factors [6, 7], such as

precursor, synthesis routes, material variances, milling activation, crystal seed, additives etc., could affect the morphology and particle size of as-prepared α -Al₂O₃. Our previous study has shown that the neck growth of α -Al₂O₃ nuclei formed from commercial precursor could be suppressed by morphology change of milled precursor, and the typical vermicular-alumina formed at high temperatures vanished with the introduction of precursor milling treatment and additives. Further study on the morphology evolution of α -Al₂O₃ micro-powders by using commercial γ -Al₂O₃ precursor with additive as raw material are required.

In this paper, influences of precursor milling treatment, NH₄F additive content and calcination time on the formation of α -Al₂O₃ from milled γ -Al₂O₃ precursor at 1300 °C were discussed. It was found that morphology and the size distribution of α -Al₂O₃ powders formed from 5 hrs milled γ -Al₂O₃ precursor are varied with NH₄F additive content and calcination time. Square-like α -Al₂O₃ powders with primary crystal size of ~200 nm, perfect round cake-like shape α -Al₂O₃ powder in ~1 μ m size range and slight amount of hexagonal platelets or slender-like α -Al₂O₃ in the size range of 0.2~2 μ m emerged in the samples.

EXPERIMENTAL

Commercially available γ -Al₂O₃ micropowders used as raw materials were milled by a batch type planetary mill with zirconia balls. A batch of 30 g of the as-received γ -Al₂O₃ precursor powders were milled for 5 hrs. Ethanol was used as dispersion during the milling treatment of γ -Al₂O₃ precursor; the ball to powder ratio was 15:1 in weight and a rotational speed of 240 r/min was employed in the experiment. The resulting milled precursor powders were oven dried at 80 °C for 24 hrs in an ambient atmosphere.

NH₄F additive (Sinopharm Chemical Reagent Beijing Co., Ltd) used in the experiments are analytically pure. A suit amount of milled γ -Al₂O₃ powders with 1.0 wt.% and 20.0 wt.% additives were grounded manually in an agate mortar for

1 hr, and then the obtained intermixtures with or without NH_4F additive were calcined in air at $1300\text{ }^\circ\text{C}$ for 2 hrs.

Both the phases and crystallinity of the precursors with or without milling, and the phase composition of samples obtained after the calcination were conducted by X-ray diffraction (XRD) using an X-ray diffractometer (X' Pert Pro MPD, Philips, Eindhoven, the Netherlands) with Cuka radiation (40 kV, 40 mA) in the $2\theta=10\text{ }^\circ\text{--}80\text{ }^\circ$ range. The scan was performed at a scan rate of $5\text{ }^\circ/\text{min}$ with the step size of 0.02 ° .

The influence of the milling treatment on the morphology of $\gamma\text{-Al}_2\text{O}_3$ precursor was observed by field-emission scanning electron microscope (SEM, JSM-7500F, JEOL, Tokyo, Japan) at an accelerating voltage of 15 kV. The samples were sputtering-coated with gold before placed on stubs for the SEM analysis, and Secondary electron SEM images were selected. While field-emission scanning electron microscope pictures of $\alpha\text{-Al}_2\text{O}_3$ samples synthesized at $1300\text{ }^\circ\text{C}$ were taken using Ultra-55 Scanning Electron Microscope (SEM, ZEISS, Oberkochen, Germany) at an accelerating voltage of 10 kV.

RESULTS AND DISCUSSION

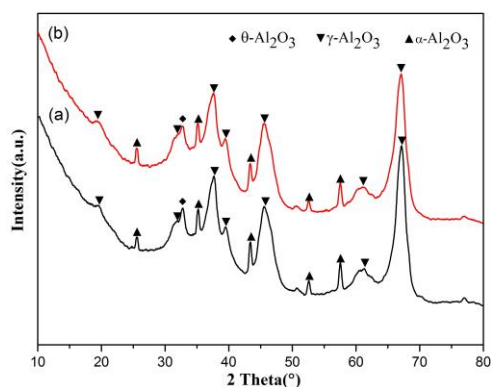


Fig. 1 XRD patterns of commercial $\gamma\text{-Al}_2\text{O}_3$ samples with and without milling treatment. (a) without milling treatment, (b) milling for 5 hrs.

The influence of milling treatment on the phase composition and crystallinity of precursor is shown in Fig. 1. XRD pattern of unmilled precursor shown in Fig. 1(a) indicates that the commercial precursor used in the experiments are composed of $\gamma\text{-Al}_2\text{O}_3$ (JCPDS File No: 10-0425) accompanying with the presence of little transition phase $\theta\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$. It's clear that the milled precursor has identical phase composition with the unmilled precursor by comparing Fig. 1 (a) and (b). Strong peaks centered at 12.59 ° ; 31.45 ° ; 37.59 ° ; 39.42 ° ; 45.63 ° ; 60.98 ° and 67.10 ° are attributed to (111), (220), (311), (222), (400), (511) and (440) crystal planes of $\gamma\text{-Al}_2\text{O}_3$ respectively; the peak at 32.75 ° are resulted from $\theta\text{-Al}_2\text{O}_3$ and peaks at 35.28 ° ; 43.39 ° ; 52.58 ° and 57.62 ° are correspond to

$\alpha\text{-Al}_2\text{O}_3$. However, the diffraction peaks of $\gamma\text{-Al}_2\text{O}_3$ centered at 31.45 ° and 60.98 ° are weakened and broadened as the precursor were milled for 5 hrs, which are corresponded to (400) and (511) crystal planes of $\gamma\text{-Al}_2\text{O}_3$ respectively. Those above results indicate that the crystallinity of $\gamma\text{-Al}_2\text{O}_3$ precursor has been slightly decreased by increasing the milling treatment to 5 hrs.

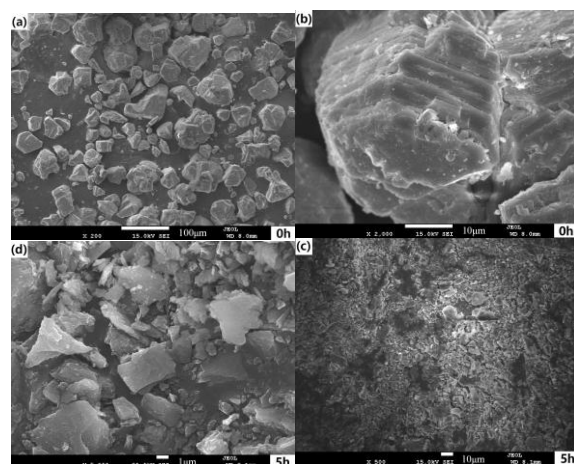


Fig. 2 SEM photographs of commercial $\gamma\text{-Al}_2\text{O}_3$ samples with and without milling treatment. (a) and (b) without milling treatment, (c) and (d) milling for 5 hrs.

The micrographs of $\gamma\text{-Al}_2\text{O}_3$ precursor with and without milling are shown in Fig. 2. As shown in Fig. 3(a), $\gamma\text{-Al}_2\text{O}_3$ precursor sample before milling are irregular agglomerates in the size range of $20\text{--}100\text{ }\mu\text{m}$. Those irregular aggregates are composed of many small grains with smooth surface, as shown in Fig. 2(b). Furthermore, there are lots of cracks and interspaces among $\gamma\text{-Al}_2\text{O}_3$ precursor particles (shown in Fig. 2(b)), some crushed pieces in a $\leq 1\text{ }\mu\text{m}$ size range are coexisted on the grain surface or interspace among precursor grains.

SEM micrographs shown in Fig. 2(c) and (d) are 5 hrs milled $\gamma\text{-Al}_2\text{O}_3$ precursor. By comparing with unmilled $\gamma\text{-Al}_2\text{O}_3$ precursor, the morphological features of precursor sample milled for 5 hrs have significantly changed by planetary milling treatment. Those large irregular agglomerates were broken into small irregularly pieces by milling for 5 hrs. Except a small amount of $5\text{--}10\text{ }\mu\text{m}$ pieces, most pieces are in a $1\text{--}5\text{ }\mu\text{m}$ size range; furthermore, many refined particles are far lower than $\leq 1\text{ }\mu\text{m}$ as shown in Fig. 2 (b). Those above results clearly demonstrate that the milling treatment lead to significant refinement in microstructure and particle size distribution of $\gamma\text{-Al}_2\text{O}_3$ precursor.

Fig. 3 shows the XRD patterns of samples obtained from milled $\gamma\text{-Al}_2\text{O}_3$ precursor with NH_4F additive by calcination. The peaks centered at 25.56 ° ; 35.14 ° ; 37.78 ° ; 43.34 ° ; 52.594 ° ; 57.54 ° ; 61.28 ° ; 66.52 ° ; 68.20 ° and 76.90 ° in the XRD pattern

shown in Fig. 3 (a), (b) and (c) are attributed to (012), (104), (110), (113), (024), (116), (018), (214), (300) and (1010) crystal planes of α -Al₂O₃ respectively. The above results revealed that γ -Al₂O₃ and θ -Al₂O₃ phases in the milled precursor samples were fully converted to α -Al₂O₃ at 1300 °C resulting in single-phase α -Al₂O₃ samples by calcination.

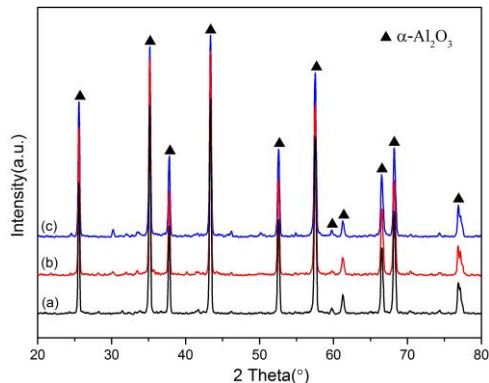


Fig. 3 XRD patterns of α -Al₂O₃ samples obtained from milled γ -Al₂O₃ with or without NH₄F by calcination (a) milled γ -Al₂O₃ without NH₄F, calcined at 1300 °C for 2 hrs; (b) milled γ -Al₂O₃ with 1 wt.% NH₄F; (c) milled γ -Al₂O₃ with 20 wt.% NH₄F calcined at 1300 °C for 2 hrs.

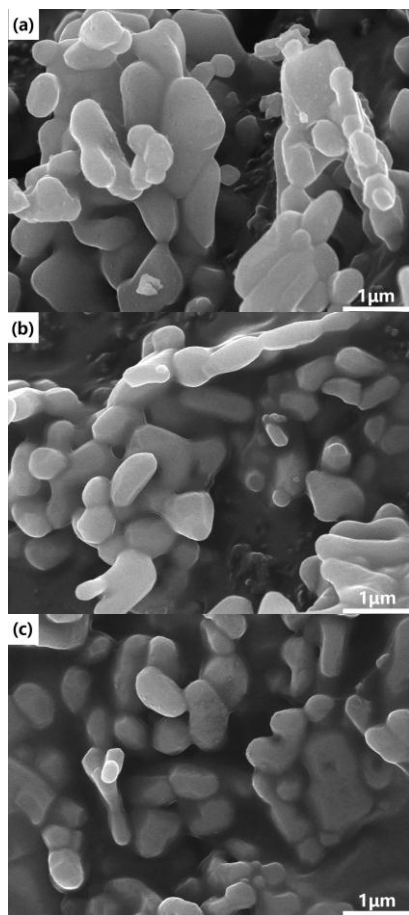


Fig. 4 SEM photographs of α -Al₂O₃ samples obtained from milled γ -Al₂O₃ precursor without NH₄F additives calcined at 1300 °C for 2 hrs.

The micrographs of α -Al₂O₃ samples calcined at 1300 °C for 2 hrs are shown in Fig. 4. As shown in Fig. 4(a), (b) and (c),

α -Al₂O₃ powders from milled γ -Al₂O₃ precursor fired at 1300 °C mainly follows by the solid phase mass transfer mechanism, contacted α -Al₂O₃ gains coalesce with each other and the as-synthesized α -Al₂O₃ powders still keep the shape of milled γ -Al₂O₃ agglomerates.

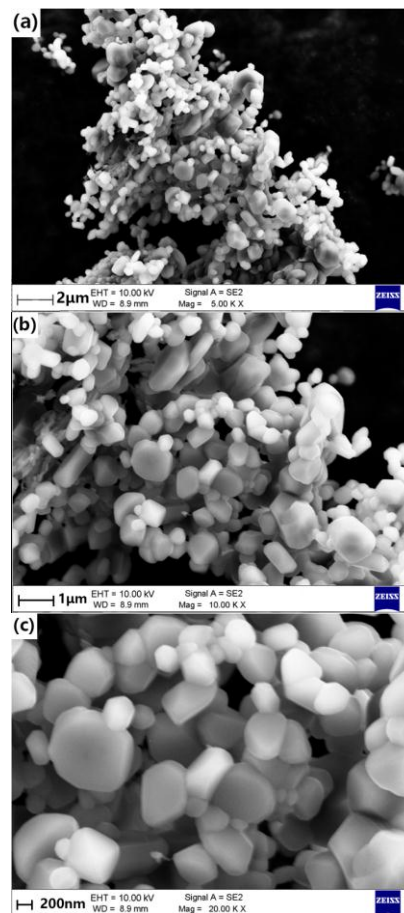


Fig. 5 SEM photographs of α -Al₂O₃ samples obtained from milled γ -Al₂O₃ precursor with 1 wt.% NH₄F additives calcined at 1300 °C for 2 hrs.

The micrographs of α -Al₂O₃ samples from γ -Al₂O₃ precursor with 1 wt.% NH₄F additive calcined at 1300 °C for 2 hrs are shown in Fig. 5(a), (b) and (c). As shown in Fig. 5, the synthesized α -Al₂O₃ powders are mostly square-like α -Al₂O₃ particles with an average primary crystal size of ~200 nm; meanwhile partially polygon-like α -Al₂O₃ particles with an average primary crystal size of 400~600 nm appear. The above results indicate that typically worm-like structure formed by neck growth of α -Al₂O₃ gains at high temperature was suppressed by the coefficient of the 5 hrs milling treatment and the introduction of 1 wt.% NH₄F additive, resulting in the greatly morphology modification of as-formed α -Al₂O₃ powders.

The micrographs of α -Al₂O₃ samples obtained from milled γ -Al₂O₃ precursor with 20 wt.% NH₄F addition are shown Fig. 6. As shown in Fig. 6(a), (b) and (c), round cake-like,

hexagonal platelets, slender-like and other irregularly shaped α -Al₂O₃ powders in the size range of 0.2~2 μ m were synthesized from milled γ -Al₂O₃ precursor with 20 wt.% NH₄F addition by calcination at 1300 °C for 2 hrs. Furthermore, it's clear to see those small grains in the size range of ~200 nm are embedded in those 1~2 μ m sized α -Al₂O₃ particles, indicating that the growth of α -Al₂O₃ particles is attributed to the consumption of small particles. Meanwhile, both the diameter and the thickness of α -Al₂O₃ particles are significantly improved with the increase of NH₄F additive content from 1 wt.% to 20 wt.%. The above results reveal that the growth rate of α -Al₂O₃ different crystal plane has been modified by the increased gas intermediate compound, including AlOF, AlO₂⁻¹ etc., produced from the reaction of Al₂O₃ precursor and NH₄F addition at high temperature.

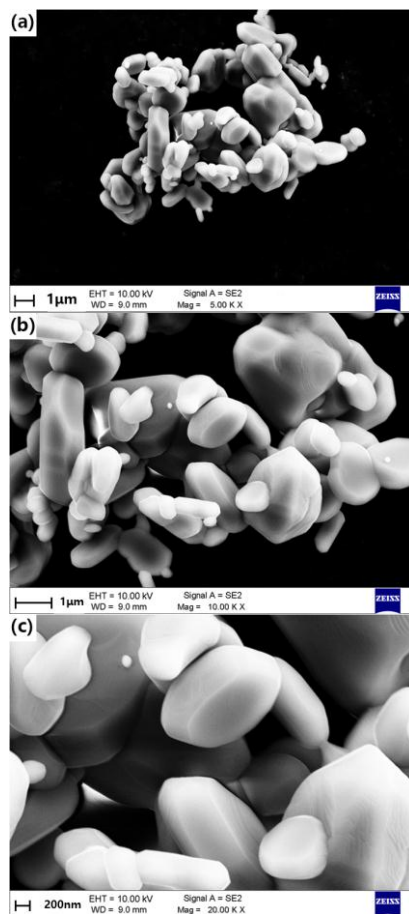


Fig. 6 SEM photographs of α -Al₂O₃ samples obtained from milled γ -Al₂O₃ precursor with 20 wt.% NH₄F additives calcined at 1300 °C for 2 hrs.

CONCLUSIONS

The microstructure and the particle size distribution of α -Al₂O₃ were highly dependent to the morphology of γ -Al₂O₃ precursor, NH₄F addition and additive content. By the introduction of precursor milling treatment and NH₄F addition,

the neck growth of α -Al₂O₃ nuclei formed from milled precursor has been efficiently suppressed by the morphological changes of γ -Al₂O₃ precursor and the formation of gas intermediate compound, such as AlOF, AlO₂⁻¹ etc, produced from the reaction of Al₂O₃ precursor and NH₄F addition at high temperature. Square-like α -Al₂O₃ powders with ~200 nm in size were formed from 5 hrs milled γ -Al₂O₃ precursor with 1 wt.% NH₄F at 1300 °C for 2 hrs. Multi-morphology α -Al₂O₃ in the size range of 0.2~2 μ m, including round cake-like, hexagonal platelets, slender-like and other irregularly shape, emerged in the sample with the increase of 20 wt.% NH₄F addition under the same calcination.

ACKNOWLEDGEMENTS

The authors acknowledge National Natural Science Foundation of China (Contract No. U1504526, 51372230) and Outstanding Young Talent Research Fund of Zhengzhou University (No. 1421320048) for financial support.

REFERENCES

- [1] Miao YX, Shi L, Cai LN, Li WC. Alumina hollow microspheres supported gold catalysts for low-temperature CO oxidation: effect of the pretreatment atmospheres on the catalytic activity and stability. *Gold Bulletin*. 2014;47(4):275-282.
- [2] Binner JGP, Mcdermott AM. Rheological characterization of ammonium polyacrylate dispersed, concentrated alumina suspensions. *Ceram Int*. 2006;32(7):803-810.
- [3] Otroj S, Daghighi A. Microstructure and phase evolution of alumina-spinel self-flowing refractory castables containing nano-alumina particles. *Ceram. Int*. 2011;37(3):1003-1009.
- [4] Sarkar R. Effect of alumina fines on high alumina self-flow low cement castables. *Refractories Worldforum*. 2014; 6(1):73-78.
- [5] Lu HX, Sun HW, Li GX, Chen CP, Yang DL, Hu X, Microstructure and mechanical properties of Al₂O₃-MgB₂ composites. *Ceram. Int*. 2005;31(1):105-108.
- [6] Riello D, Zetterström C, Parr C, Brailio M, Gallo J, Pandolfelli V. AlF₃ mechanism and its influence on the calcined alumina properties. *Proceedings of 14th Biennial Worldwide Congress; 2015 Sep 15-18; Unitecr 2015, Vienna, Austria, Proceeding 69*.
- [7] Su XH, Li SQ, Li JG. Effect of potassium sulfate on the low-temperature formation of alpha alumina platelets from bayerite. *J. Am. Ceram. Soc*. 2010;93(7):1904-1908.