

Synthesis of nano-alumina powder via recrystallization of ammonium alum

(*Síntese de nanopó de alumina via recristalização de alúmen de amônio*)

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Abstract

In the present study, a recrystallization method was implemented to recover alumina powder from ammonium alum crystal. The ammonium alum was completely dissolved in water and treated by ultra-sonication to prevent the agglomeration of the alum crystal. The white precipitate was dried at 150 °C for 6 h, and calcinations at different temperatures were performed for 2 h. The XRD results indicated the crystalline structure of alumina with two main phases: γ -Al₂O₃ and α -Al₂O₃ at 800 and 1200 °C, respectively. The N₂ adsorption/desorption isotherm results indicated that the surface area for the powder in the γ phase, which can be applied in catalysts, was 142.5 m²/g, while, in the α -phase, it was 15.3 m²/g. The morphologies elucidated that the powder particles were widely distributed in the range of ≤ 160 nm at different calcination temperatures and this may be attributed to increments in the particle agglomeration as the calcination temperature increased.

Keywords: alumina, powder, alum, recrystallization method.

Resumo

No presente estudo, um método de recristalização foi implementado para recuperar pó de alumina a partir de cristais de alúmen de amônio. O alúmen de amônio foi completamente dissolvido em água e tratado por ultrassonicação para evitar a aglomeração do cristal de alúmen. O precipitado branco foi seco a 150 °C por 6 h e as calcinações em diferentes temperaturas foram realizadas durante 2 h. Os resultados de DRX indicaram a estrutura cristalina da alumina em duas fases principais: γ -Al₂O₃ e α -Al₂O₃ a 800 e 1200 °C, respectivamente. Os resultados da isoterma de adsorção/dessorção de N₂ indicaram que a área de superfície do pó na fase γ , que pode ser aplicada em catalisadores, foi de 142,5 m²/g, enquanto que na fase α foi de 15,3 m²/g. As morfologias elucidaram que as partículas de pó estavam amplamente distribuídas na faixa de ≤ 160 nm em diferentes temperaturas de calcinação e isso pode ser atribuído a incrementos na aglomeração de partículas à medida que a temperatura de calcinação aumentou.

Palavras-chave: alumina, pó, alúmen, método de recristalização.

INTRODUCTION

Alumina ceramic is one of the most significant materials used for structural ceramic. It has received wide attention due to its properties, such as hardness, oxidation resistance, corrosion resistance, excellent abrasion resistance, and high melting point. It was once used widely in many industrial applications, such as automotive, aerospace, catalytic, microelectronic, and energy applications [1]. It is also practical in many present industries, such as the fine metallurgical, optoelectronic, and electronic industries [2, 3]. Presently, α -Al₂O₃ has numerous uses in traditional and advanced ceramic applications. It is a significant substrate for the development of semiconductors and superconductors via molecular beam [4]. Alumina occurs in two forms: transition or metastable phases. α -Al₂O₃ is the stable phase of alumina, whereas the metastable phases, i.e., chi (χ), eta (η), kappa (κ), theta (θ), delta (δ), and gamma (γ), depend

on the synthesis temperature [5]. The conventional methods for producing α -Al₂O₃ incorporate solid-state, thermally-influenced transformations from the hydrates of aluminum oxide. The amount of and total transformation to the corundum structure depends on the time and temperature of the thermal treatment [5-7]. Bauxite has been typically utilized to the fabrication of alumina via the Bayer method, whilst non-bauxitic treatments, which are more common in many countries, have been used in an effort to strengthen the unconventional methods used for producing alumina. The raw materials used in non-bauxitic treatments include mica, alum, alunite, fly ash, and sillimanite [8, 9]. Ammonium alum is produced by the recovering the alumina from clay, whilst potassium alum is produced via the recovery of alumina from alunite [8]. Ammonium alum [NH₄Al(SO₄)₂·12H₂O], a white crystalline double sulfate of aluminum, is used in fireproofing textiles, porcelain cement, water purification, and natural deodorant [10].

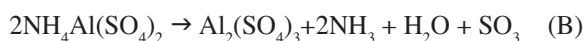
There are some studies that have considered the synthesis of alumina from alum, but most of them have utilized direct heat treatments involving different temperatures or

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precipitation methods to obtain pure alumina powder, but the powder obtained in these cases has had large particle sizes with low surface area and has been in need of more chemical materials [11, 12]. The underlying purpose of the present study is to facilitate the recovery of ammonium alum and produce a large quantity of high-purity alumina powder with an easy and brief cycle chemical technique.

MATERIAL AND METHODS

Alumina powder was prepared using ammonium alum crystal as the raw material. The ammonium alum suspension was prepared by dissolving 87 g of alum in 100 mL of distilled water at 70 °C, then treating it with ultrasonication for 2 h until fully dissolved. After 2 h under a cooling process, white, flake-shaped precipitates were formed, which were then filtered and washed in deionized water several times. The powder produced was dried at 150 °C and calcined at 800 °C to obtain γ -alumina, then finally transformed to α - Al_2O_3 at 1200 °C. The following equation shows the recrystallization reactions [6, 13]:



The X-ray diffractometer (XRD 6000, Shimadzu, Japan) was used to identify the phases of the alumina powder at room temperature using $\text{CuK}\alpha$ radiation ($\lambda=1.5405 \text{ \AA}$) and a scanning range from 20° to 70°. The scanning rate used was 5 °/min, and the applied power was 40 kV/30 mA. Infrared (FTIR) spectra of samples were recorded (Shimadzu 1800, Japan) to evaluate the molecular structure of the functional group in the inorganic materials. The N_2 adsorption/desorption isotherms were obtained via a QSURF surface area analyzer. Prior to performing the test, the samples were degassed at 200 °C under vacuum inside the apparatus. The isotherms were measured at the temperature of liquid nitrogen (77 K) in order to identify their surface areas. Field emission scanning electron microscopy (FE-SEM, Zeiss, LEO 1530) was carried out in order to identify the morphologies of the as-synthesized powder particles. In order to confirm the purity of the resultant powder, the energy dispersive spectrometer (EDS, Bruker) was utilized. Observations concerning the morphologies and sizes of the particles were carried out via transmission electron microscopy (TEM, Jeol, JEM-ARM 200F).

RESULTS AND DISCUSSION

Fig. 1 displays the XRD results for the alumina powder prepared via the recrystallization of alum. It was clearly observed that the diffraction patterns increased slightly when examining the degrees of sharpness of the peaks with increasing the calcination temperature. In addition, in the

diffraction pattern of the alumina powder before heating boehmite phase showed very broad peaks, which indicated that the crystallinity of the alumina powder was low (amorphous). The other diffraction pattern in the γ -alumina phase showed the same trends; they were narrow compared with the pattern of the alumina before calcination due to the increase in the crystallinity of the alumina powder. The increase in calcination temperature led to a transformation from γ to α alumina [14, 15]. The stable phase (corundum) appeared after calcination at 1200 °C. The obtained diffraction data matched fully with JCPDS files 10-0173 and 50-0741, which confirmed the presence of γ and α - Al_2O_3 ,

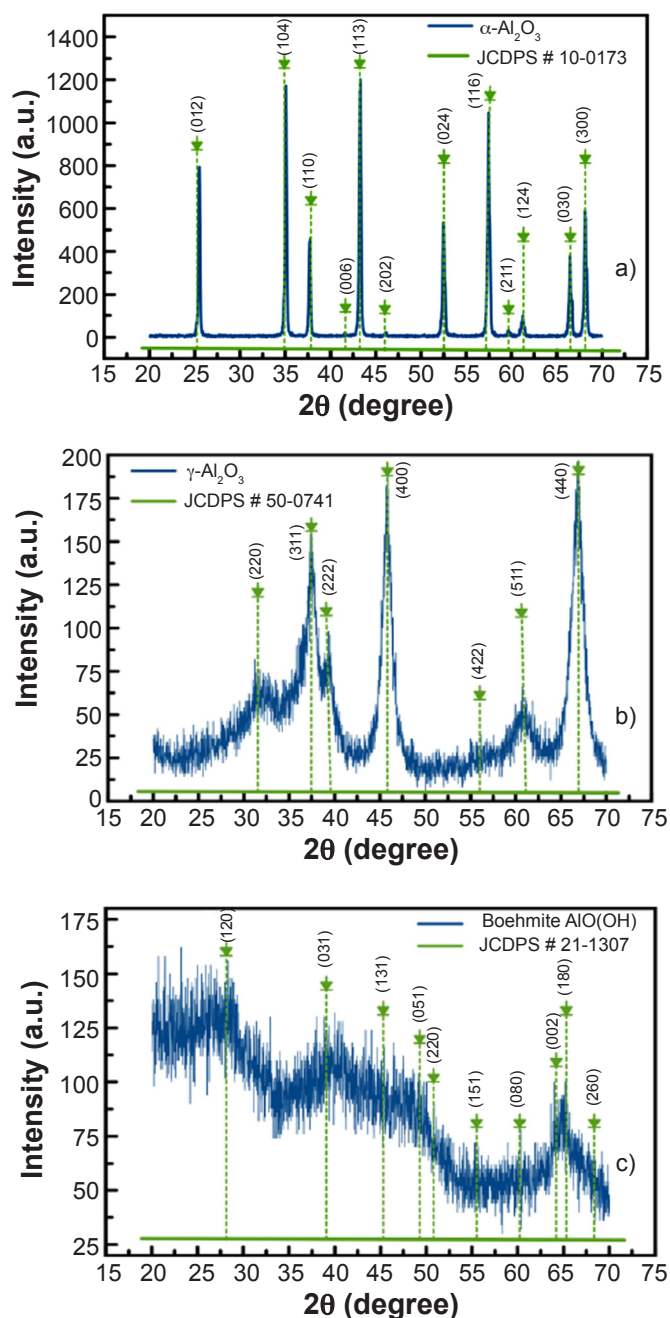


Figure 1: XRD patterns of: a) α - Al_2O_3 ; b) γ - Al_2O_3 ; and c) boehmite. [Figura 1: Padrões de DRX de: a) α - Al_2O_3 ; b) γ - Al_2O_3 ; e c) boehmita.]

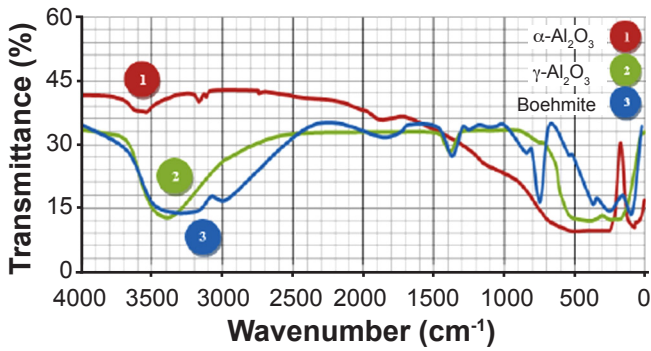


Figure 2: FTIR spectra of the prepared alumina powder calcined at different temperatures.

[Figura 2: Espectros de FTIR do pó de alumina calcinado em diferentes temperaturas.]

Table I - Bond attributions of alumina powder.

[Tabela I - Atribuições de ligações do pó de alumina.]

Peak position (cm ⁻¹)	Band	Ref.
594, 447	Al-O bending vibration	[13]
640	Stretching vibration of Al-O band	[14]
3300-3510	Stretching vibration of O-H band	[15]
2866, 2924	Stretching vibration of C-H band	[13]

respectively [16]. Fig. 2 shows the infrared spectra of pure alumina powder prepared at 1200 °C for 2 h. The main absorption peaks shown in Fig. 2 and listed in Table I were located at ~594 and ~447 cm⁻¹, which referred to the Al-O bending vibration of the Al-OH groups. In addition, 640 cm⁻¹ peak represented the stretching vibration of the Al-O band and identified the typical absorption band of α-Al₂O₃, ~3300-3510 cm⁻¹ represented the broadening vibration of the O-H bands, and the stretching vibrations of the C-H band were located at ~2866 and ~2924 cm⁻¹ [17-19].

Fig. 3 displays the FE-SEM micrographs of pure alumina powder calcined at 800 and 1200 °C with a heating rate of 5 °C/min and soaking time of 2 h. The SEM images illustrate the influence of the calcination temperature on the

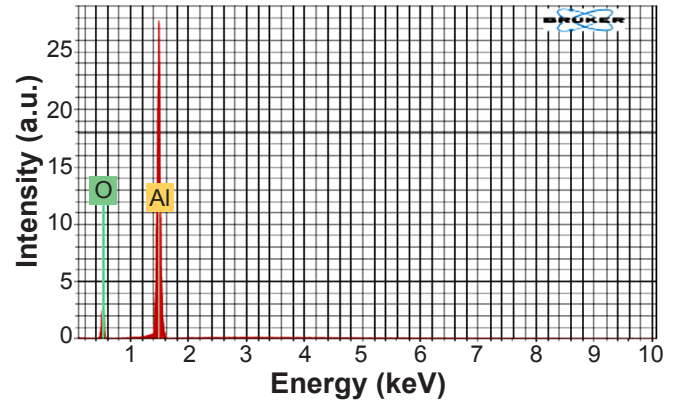


Figure 4: EDS spectrum for Al₂O₃ powder calcined at 1200 °C.

[Figura 4: Espectro de EDS do pó de Al₂O₃ calcinado a 1200 °C.]

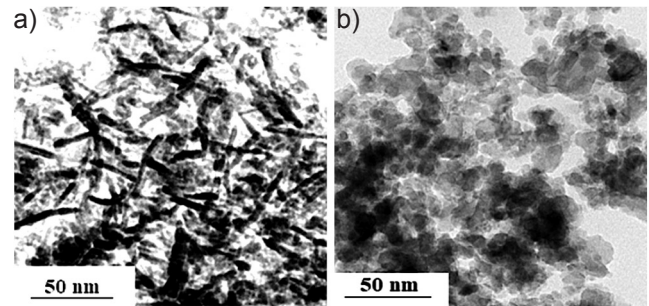


Figure 5: TEM micrographs of Al₂O₃ powder calcined at different temperatures: a) γ-Al₂O₃ at 800 °C; and b) α-Al₂O₃ at 1200 °C.

[Figura 5: Micrografias de MET do pó de Al₂O₃ calcinado em diferentes temperaturas: a) γ-Al₂O₃ a 800 °C; e b) α-Al₂O₃ a 1200 °C.]

morphology of γ and α-alumina prepared powders. It can be seen that when the calcination temperature rose from 800 to 1200 °C, the morphology of the alumina powder changed from practically spherical to vermiciform in shape and the particles were extremely arranged and attached to each other, leading to an increase in particle size. The alumina powder size increased from 70 to 160 nm due to the coalescence and the densification of the preliminary particles [12]. Fig. 4 illustrates the EDS results for alumina powder prepared at 1200 °C for 2 h. The analysis showed clearly the existence

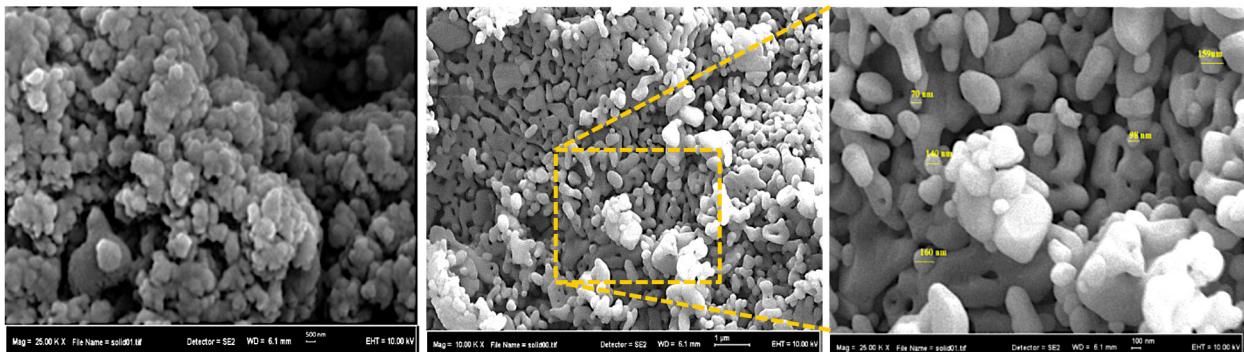


Figure 3: SEM micrographs of Al₂O₃ powder calcined at different temperatures: a) 800 °C; and b,c) 1200 °C.

[Figura 3: Micrografias de MEV do pó de Al₂O₃ calcinado em diferentes temperaturas: a) 800 °C; e b,c) 1200 °C.]

of Al and O. It was found that the α -alumina was chemically pure (no detectable impurities), and this finding was in good agreement with the XRD pattern. Fig. 5 shows the TEM micrographs of α -Al₂O₃ powder after different calcination temperatures. According to Fig. 5a, the γ -alumina particles had a needle-like morphology; however, Fig. 5b illustrates the uniform distribution of the particle size in α -Al₂O₃, with an average size of <50 nm. The morphology of the produced powder is vital to the nanocrystalline structure of α -Al₂O₃, in which small particles tend to eventually form the surface of the powder, inducing a spherical-like morphology [20]. On the other hand, the flake morphology refers mainly to the minimum contact points, which help diffusion take places for other possible reactions; therefore, the phase transformation occurs as the grain growths. In spite of this, the stacking orientation and timing of the flake layers are preserved during the calcination and consequently result in the formation of γ -Al₂O₃ with a rod-like morphology [21, 22].

Table II lists the surface area results for the alumina powder calcined at different temperatures. It can be seen that the γ -Al₂O₃ had a greater surface area than the α -Al₂O₃. This result was due to the increase in the calcination temperature, which led to the agglomeration of the α -Al₂O₃ particles and prevented the N₂ gas molecules from moving freely between the particles [23].

Table II - Surface area of prepared alumina powders.
[Tabela II - Área superficial dos pós de alumina preparados.]

Sample	Calcination temperature	BET surface area (m ² /g)
1	800 °C (γ -Al ₂ O ₃)	142.5
2	1200 °C (α -Al ₂ O ₃)	15.3

CONCLUSIONS

In this work, nano-sized alumina ceramic powders have been prepared successfully with a shortened cycle route using recrystallization of ammonium alum. The use of recrystallization of ammonium alum method proved to be very effective for the synthesis of alumina ceramic powder. XRD analyses identified γ -Al₂O₃ phase at 800 °C, and α -Al₂O₃ was completely formed at 1200 °C. The preparation of the alumina precursor as recrystallization of ammonium alum that has been treated by ultra-sonication had a significant effect on the resulting alumina particle shape and in the formed alumina phases. The SEM and TEM micrographs showed the microstructures of the synthesized alumina powders, which had regular and nearly spherical-like structure at 1200 °C and needle shape at 800 °C, with diameters ranging from 70 to 160 nm. The N₂ adsorption/desorption (BET) surface area for the synthesized powder of γ -Al₂O₃ was 142.5 m²/g, while it was 15.3 m²/g for α -Al₂O₃. The difference in surface area between the two phases was

attributed mainly to the increase in agglomeration, which led to an increase in the α -Al₂O₃ particle sizes.

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