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Nanostructured aluminium titanate (Al_2TiO_5) particles and nanofibers: Synthesis and mechanism of microstructural evolution

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ABSTRACT

In this study, aluminium titanate (AT) particles and nanofibers were synthesized through citrate sol gel and sol gel-assisted electrospinning methods in both nanostructured powder and nanofiber forms. The results of X-ray diffraction analysis, field-emission scanning electron microscopy and differential thermal analysis showed that the synthetic products benefit a nanostructured nature with a grain size less than 70 nm. The optimal values for time and temperature at which a roughly pure AT is attained were determined as 2 h and 900 °C, respectively. It was found that the sol gel precursor bears an amorphous structure till 700 °C and begins to be crystallized to alumina, anatase and AT at higher temperatures. Moreover, AT tends to decompose into rutile and alumina at temperatures higher than 900 °C and its degradation rate reaches a maximum at temperatures near to 1100 °C. In this synthesis, citric acid was used as a chelating agent for Al^{3+} and Ti^{4+} ions and it was shown that a low citric acid-to-metal cation ratio leads to larger numbers of nuclei during crystallization and smaller grain size. Finally, a model was suggested to describe the microstructural evolution of AT compound based on a nucleation and growth regime.

1. Introduction

Aluminium titanate (AT) and their compounds are characterized as refractory materials bearing a high melting point as high as 1860 °C, low thermal expansion and high thermal insulation [1–3]. These superior properties make AT-based ceramics an interesting candidate material being potentially advantageous for the fabrication of filters in hot gas clean-up applications, soot traps for diesel engines and refractory for automotive and non-ferrous metallurgical industries [1,4]. On the other hand, AT fibers and their nanoporous structures have the potential to be used as industrial filters for purification of drinking water, since these structures are useful to remove natural turbidity and pathogenic micro-organisms such as protozoa, bacteria and Cryptosporidium in particular [5].

Nevertheless, there exist two counterproductive shortcomings restricting the industrial applications of AT-based ceramics as follows:

(i) The average crystallographic thermal expansion of AT is slightly higher than that of its parent phase, i.e. alumina. This property is allegedly reported to result in high compressive residual stresses on the AT grains and consequently, a great deal of microcracks in the sintered bodies during cooling from sintering temperature [6–9].
(ii) AT compound is thermodynamically unstable at high temperatures whose range is highly controversial and decomposes into its parent phases i.e. alumina and anatase [10–12]. However, in accordance with the general agreement, thermal degradation of AT is a eutectoid reaction occurring in the temperature range 800–1280 °C [13]. The relevant reaction is as follows:

$$\beta\text{-}Al_2TiO_5 \rightarrow Al_2O_3 + TiO_2. \tag{1}$$

To date, some experimental and semi-empirical examinations are conducted to consider the effective parameters controlling the thermal decomposition of AT and its thermokinetic conditions [9,14]. Among the reported results in literature, some main points are as follows:

(i) The maximal rate of AT degradation appears at 1100 °C [14,15].
(ii) The possible mechanisms of AT decomposition are poorly understood until now, but experimental examinations verify that the reaction kinetics abides by a nucleation and growth regime [14,15] based on the Johnson–Mehl–Avrami equation $\ln(1-\alpha) = -kt^n$ [16]. However, no significant microstructure features have been reported to validate this mechanism [17].
(iii) The density of α-Al_2O_3 and rutile-TiO_2 is 3.99 and 4.25 g/cm^3, respectively. Hence, reaction (1) is accompanied by ~11% volume contraction, which causes serious problems during sintering [18].

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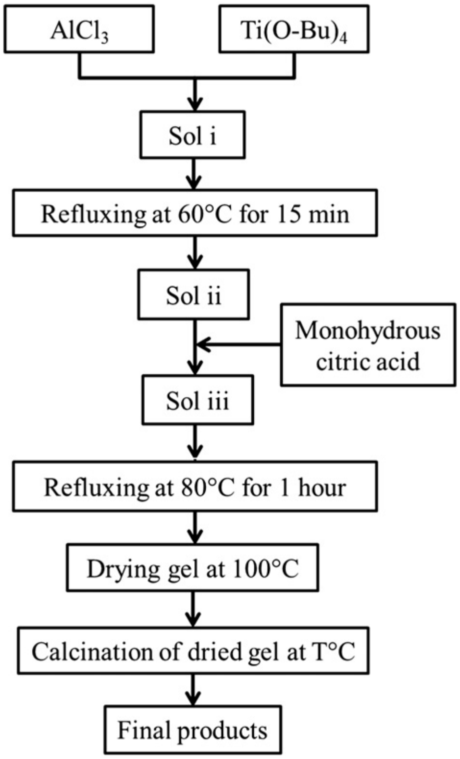

Fig. 1. Schematic flow chart for synthesis procedure of nanostructured aluminium titanate.

Table 1
The chemical composition of used solutions in sol gel process.

Solution	Chemical composition
Solution 1	4 g $AlCl_3$–35 ml ethanol
Solution 2	4 g $AlCl_3$–35 ml ethanol–5.2 g $Ti(O\text{-}Bu)_4$
Solution 3	4 g $AlCl_3$–35 ml ethanol–5.2 g $Ti(O\text{-}Bu)_4$–1.5 g anhydrous citric acid

(iv) There are some factors influencing the thermal degradation of AT. Among them, additives, grain size, atmosphere, pressing and sintering procedure are the most important ones [14]. As a case study, Low et al. showed that the rate of AT degradation in air is slower than that in vacuum. Atmospheres of low-oxygen partial pressure such as vacuum or argon encourage the thermal instability via oxygen nonstoichiometry changes in AT [14,16].

(v) Grain size in AT-based ceramics can affect their mechanical properties. It is indicated that these properties are enhanced with a decrease in grain size. Therefore, a nanograined AT is favorite for those applications requiring superior mechanical properties [3].

(vi) It is found that the chemical stability of AT-based compounds is enhanced by doping some oxide additives forming solid solutions in the crystalline structure of AT. The recent researches are focused on SiO_2, MgO, Fe_2O_3 and ZrO_2 [19–21].

To date, a lot of concerted efforts have been taken to synthesize nano-sized AT particles via low-temperature methods instead of prolonged high-temperature sintering of oxide compounds such as Al_2O_3 and TiO_2. Sobhani et al. synthesized AT nanoparticles via a sol gel process by aluminium chloride and titanium tetrabutoxide (TTIP). They showed that the average particle size of synthesized AT powder is less than 100 nm but AT nanoparticles are agglomerated like cabbage shape [22]. Andrianainarivelo et al. successfully synthesized Al_2TiO_5 at low temperatures, over 600 °C without the formation of TiO_2 or Al_2O_3 intermediate phases through a nonhydrolytic sol–gel process [23]. Nagano et al. produced the precursors of Al_2TiO_5 powders by homogeneous precipitation or coprecipitation and showed that sintering of pure Al_2TiO_5 precursors gives a fine-grained structure at 1300 °C, while leading to large-grained and cracked microstructures at 1400–1500 °C [3].

In this study, the citrate sol gel and sol gel-assisted electrospinning are employed to synthesize the nanostructured particles and nanofibers of pure Al_2TiO_5. It is shown that both of synthesized particles and nanofibers bear a nanostructured nature with a grain size much less than 100 nm.

2. Experimental procedure

2.1. Synthesis of nanostructured AT particles

The starting materials used to synthesize nano-grained AT particles were aluminium chloride ($AlCl_3$), anhydrous citric acid ($C_6H_8O_7$), TTIP ($C_{16}H_{36}O_4Ti$) and absolute ethanol (C_2H_6O). All raw materials were provided by Merck company. Fig. 1 presents a schematic flow chart of all steps taken during the sol gel synthesis. During this process, aluminium chloride and TTIP were used at a stoichiometric molar ratio. $AlCl_3$ was dissolved in 35 ml ethanol as a solvent and called solution 1. TTIP was added to solution 1 drop wise under constant flow of nitrogen gas and stirring at ambient temperature to form solution 2. Then, solution 2 was heat treated at 60 °C for 15 min and 1.5 g anhydrous citric acid was added to it as solution 3. The precise chemical compositions of the used solutions are summarized in Table 1. Consequently, a homogenous solution of honey-like color was formed. This solution was refluxed at 80 °C under continuous stirring for 1 h. After the reflux, a colorless gel of high homogeneity and transparency was formed. This transparent gel was dried overnight at 100 °C in an oven and was grinded into powders by which a uniform distribution of the honey-colored particles was reached. This powder was calcined at different temperatures of 700, 800, 850, 900, 950, 1000 and 1050 °C for 2 and 15 h in order to form the crystalline phase of AT and to monitor the thermal transformations of various phases attributed kinetic and thermodynamic conditions. 15 h as a primary approximation is elected to guarantee the extreme limit

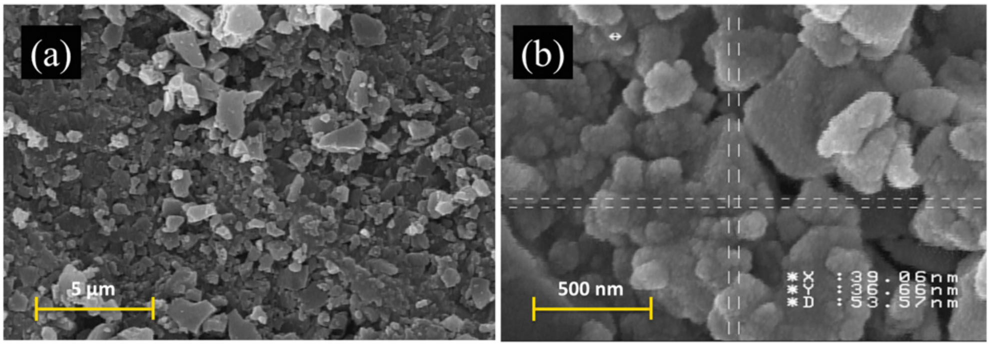

Fig. 2. Field-emission scanning electron microscopy images of dried gel in different magnifications of (a) 6000× and (b) 60,000×.