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REACTION SINTERING OF Al_2TiO_5**

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Influence of powder precursors on reaction sintering of Al_2TiO_5

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Abstract

Al_2TiO_5 has been obtained by reaction sintering of precursor powders synthesized by three powder processing methods. A field activated sintering technique has been used for the process, with 100 °C/min heating rate and short holding plateaus (minutes) at the maximum temperature. SEM, XRD, and density measurements were performed after sintering.

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1. Introduction

Development in the ceramic materials field has required continuous efforts to improve precursor preparation methods to yield better final products. When choosing a certain preparation method, one has always to balance the advantages and drawbacks of each precursor powder for purity, reactivity, composition control, particle size and economic aspects [1].

Its low thermal expansion properties, high thermal shock resistance and high melting point make aluminum titanate (tialite) an interesting ceramic material [2]. It has been traditionally obtained by conventional comminution of crystalline powders that are fired at temperatures above 1300 °C [3–7]. The advantages of this method are low cost and non-aggregation of powders, but it also has some drawbacks, because of the low purity, homogeneity and large particle size [1,2]. Solution methods, such as sol–gel processes have led to aluminum titanate at temperatures under 1000 °C [8–12].

Among solution methods, ion flotation, or precipitate flotation (co-precipitation) and its variants (adsorption colloid flotation, electrocoagulation-flotation) [13–15] for ceramic precursor synthesis, present some advantages,

such as: simplicity, economic cost, high separation efficiency (>95%) and by-product recycling.

One of the intrinsic problems with aluminum titanate is that its anisotropic thermal expansion on the three axes leads to high internal stresses and microcracking. It has been proved that a reduced grain size (0.5–1 μm) helped reduce the microcracking problem [16–21].

The use of high heating rates (typically 100–600 °C/min) in the field assisted sintering technique (FAST), with an electrical field applied have proved to have beneficial effects on synthesis and densification of this material [22].

The present work reports the results got by FAST sintering of three types of powders: (a) co-gelified alumina–titania powders, (b) mechanical mixtures of alumina and titania individual sol–gel powders, and (c) alumina–titania powders synthesized by co-precipitation.

2. Experimental

Sol–gel synthesis of co-gelified alumina–titania mixtures has been conducted from aluminum and titanium alkoxides and has been described in detail elsewhere [23]. The resultant synthesis product powder has been heat treated at 450 °C to remove water and organics and labeled as powder a. Also, individual alumina and

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titania powders have been separately obtained by a similar sol–gel process, from individual aluminum and titanium alkoxides [23]. They have been mechanically mixed in a 1:1 mole ratio in ethyl alcohol, then dried and annealed at 450 °C for 2 h to remove water and organics and the mixture is labeled as powder b in this work.

A co-precipitation procedure (dissolved air flotation variant—DAF) was applied for poly-component systems of M_1 – M_2 –LA ($M_1 = \text{Al(III)}$, $M_2 = \text{Ti(IV)}$) and LA = laurylamine ($\text{C}_{12}\text{H}_{25}\text{NH}_2$) starting from dilute aqueous chloride systems (10^{-3} – 10^{-2} M). A mixture of hydroxyl species and hydroxyl amine species could be separated, that is $[\text{TiO}(\text{OH})_2\{\text{Al}(\text{OH})_3\}_2\text{H}_2\text{O}]$ and $[\text{TiO}_2(\text{OH})_6\text{Al}_2(\text{LA})_2]$, after applying the flotation method for different collector/metallic ion molar ratios. A detailed description of the experimental procedure for synthesizing the alumina–titania mixture by flotation is given elsewhere [13]. The resultant co-precipitated powder was also dried and annealed at 450 °C to remove water and organics (powder c).

Powders a, b and c were densified by FAST at maximum temperatures of 1100, 1200, and 1300 °C. The same sintering conditions, including a heating rate of 100 °C/min, and a holding time of 10 min at the maximum temperature were used for all three powders. The loose powders have been loaded and pre-pressed in a graphite punch-die set-up, which was used to hold the sample in the sintering device. The FAST experiments were done with a Spark Plasma Sintering machine (Sumitomo, Japan), working in a 3 Pa vacuum atmosphere. An electric current was applied to the punch-die assembly as a pulsed voltage (up to 6 V) and in 12/2 ms on/off cycles, with mechanical pressure of 45 MPa. The electric current heats up the graphite punch-die set by Joule heating, and heat is then transferred to the sample. The XRD analysis of the sintered ceramic samples was performed using a Scintag diffractometer XDS 200 with Cu-K α radiation ($\lambda = 1.54184$ Å).

The grain size and general microstructure of the sintered ceramic samples were evaluated from the fracture surface of the samples, by scanning electron microscopy, performed with a field emission gun scanning electron microscope type Phillips XL FEG/SFEG.

3. Results

Fig. 1 presents the XRD of ceramic samples processed by FAST sintering at 1100 °C of powders a, b and c. It can be seen from these patterns that powder a led to almost complete formation of aluminum titanate at 1100 °C. The results suggested that a low quantity of aluminum titanate formed at 1100 °C when powder b was reaction-sintered. The aluminum titanate lines are much stronger in the XRD spectrum for the sample sintered from powder c than from powder b, at 1100 °C.

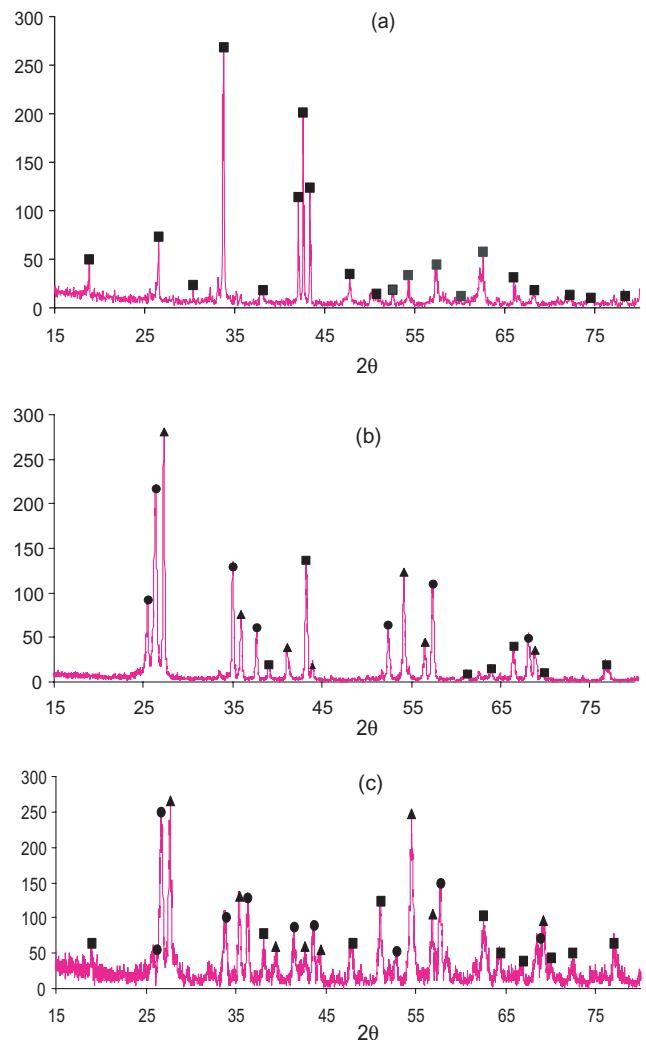


Fig. 1. XRD spectra for the alumina–titania samples sintered at 1100 °C from: (a) powder a; (b) powder b; (c) powder c. (■)– Al_2TiO_5 , (▲)– TiO_2 , (●)– Al_2O_3 .

The results of the XRD analysis performed on samples a, b and c, which were sintered at 1200 °C, showed complete crystallization of aluminum titanate from precursor a, and only a small quantity of alumina and titania remained unreacted for the sample sintered from powder c. The amount of aluminum titanate formed from powder b at 1200 °C was still fairly low, as determined by XRD. As shown by XRD on other samples, all the powders (a, b and c) undergo a complete transformation to Al_2TiO_5 at 1300 °C.

Representative SEM micrographs of the samples sintered at 1100 °C samples (Fig. 2) show fracture surfaces of the powders a (Fig. 2(a)), and c (Fig. 2(b)). The Al_2TiO_5 theoretical density is 3.7 g/cm³. Table 1 shows the results of the grain size analysis (SEM on fracture surfaces), together with the density measurements results (Archimedes method) performed on all the sintered samples.

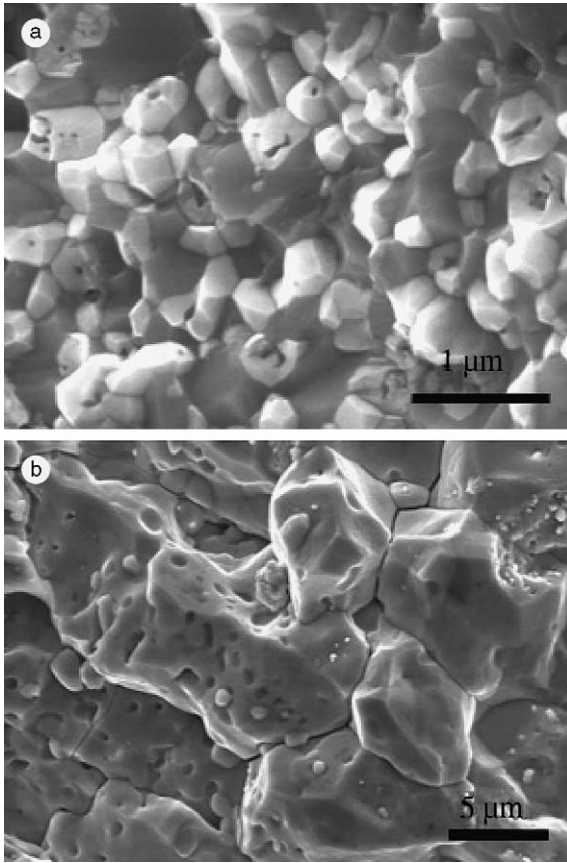


Fig. 2. SEM images of the fracture surface of alumina–titania composites sintered at 1100 °C from (a) powder a and (b) powder c.

Table 1
Grain size and density of the samples sintered by FAST method at 1100 and 1200 °C

Powder	Initial grain size	Density and grain size			
		1100 °C		1200 °C	
		ρ (g/cm ³)	GS (μm)	ρ (g/cm ³)	GS (μm)
a	50 nm	3.65	0.5	3.63	1
b	50 nm	3.0	0.5	2.96	1
c	2 μm	3.55	8.0	3.50	30

4. Discussion

Fine grain size in aluminum titanate has been proved to be critical in reducing the microcracking present during aluminum titanate formation. The literature reports that there is a critical grain size of 0.5–1 μm for microcracks to occur in Al₂TiO₅ ceramics [24–27].

Rapid heating rates (100–600 °C/min for FAST sintering) favor densification rather than grain growth in systems where the driving force for densification is lower than for grain growth, as in the case of ZnO or α-Al₂O₃

[28,29]. For our Al₂O₃/TiO₂ samples, the non-densifying mechanisms (surface diffusion and evaporation condensation) prevail below 800 °C, which, as indicated by dilatometry measurements, is the onset of densification. A relatively rapid heating rate quickly passes the temperature regime where surface diffusion dominates, taking the system to higher temperatures, where densification occurs. Also, the short holding time at the maximum temperature (10 min) in contrast with the hours range used in conventional sintering, helps preventing an exaggerated grain growth.

The small particle size of the sol–gel powders a and b (50 nm) was expected to provide an advantage for the densification behavior, because of larger surface energy, which would enhance the neck formation in the initial sintering stage. The results show that the mechanical mixing of sol–gel oxides (powder b) leads to low density aluminum titanate, despite the small particle size, 50 nm, of the starting powder. The densification process is enhanced for samples a and c. The highest final density was achieved for the field sintering of powder a, which combines the advantage of a small particle size (50 nm) with the high homogeneity offered by molecular mixing. The XRD results show complete formation of the Al₂TiO₅ phase at 1100 °C by field sintering of powder a. Aluminum titanate forms by the additive reaction between alumina and titania at temperatures above 1280 °C [7]. Al₂TiO₅ is usually unstable and decomposes below this temperature [2]. The formation temperature of Al₂TiO₅ has been lowered under 1280 °C by using the sol–gel powder a and the electrical field application during sintering.

The results show that reacting together aluminum and titanium precursors by the sol–gel method (powder a) allows formation, under field assisted processing, of dense, fully transformed, aluminum titanate materials at temperatures lower than 1280 °C. The mechanical mixture of sol–gel powders (powder b) does not provide enough reaction sites to enable the reaction sintering to take place at low temperatures.

5. Conclusions

The influence of precursor powder on the reaction-sintering of aluminum titanate (Al₂TiO₅) ceramic materials has been investigated. Sol–gel derived powders synthesized by co-gelation in the same solution, mechanical mixtures of individual sol–gel oxides and co-precipitated powders have been compared.

Sintering precursor powder made by co-gelation that has nanometer size particles, under an applied electric field, lowered the formation temperature of Al₂TiO₅ and achieved high density and minimum grain coarsening of the final ceramic material.

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