

## Synthesis of Aluminium Titanate Powder by Sol-Gel Technology

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**Keywords:** Aluminum titanate, sol-gel technology, X-ray diffraction.

**Abstract.** The ceramic raw materials, aluminum titanate ( $\beta$ -  $\text{AlTiO}_5$ ), were prepared by the sol-gel method. To produce aluminum titanate powder, aluminum and titanium alcoxides were used as precursors with the addition of hydrochloric acid aiming to produce a translucent gel to minimize the precipitate formation. The most translucent gel obtained showed, by thermal treatment, a typical structural evolution: the direct crystallization of the aluminum titanate phase at 900°C. In this temperature the aluminum titanate phase was detected after 3 hours treatment. With 900 °C for 5 hours treatment, the phase becomes well crystallized without any change in its characteristics within 10 hours treatment. At 1400°C occurred the formation of aluminum titanate in all prepared samples. The sol-gel method minimized a residual  $\alpha$ -alumina and rutile phases when compared with one obtained by conventional method of oxide admixtures.

### Introduction

Aluminum titanate or tialite is a synthetic member of multiple oxide family type pseudobrookite,  $\text{Fe}_2\text{TiO}_5$  that owns the general form  $\text{X}_2\text{YO}_5$ . The crystal structure of aluminium titanate is orthorhombic with bordered targeted to spatial group Cmc<sub>2</sub>m (1). It is a synthetic ceramic material obtained from the reaction in solid state of powder of aluminium oxide,  $\square$ - $\text{Al}_2\text{O}_3$  (corundum), titanium oxide,  $\text{TiO}_2$  (anatase or rutile) in equivalent molar quantities. This is a conventional method of synthesis. Other techniques of preparation include: chemical deposal of steam [2, 3], burning [4], sun-gel [5] and pyrohydrolyse in gas phase [6].

The synthesis reaction occurs over 1300°C according to reaction (1). But its formation is, in fact, a complex process, strongly dependent on the weather and temperature. It occurs in the interface  $\text{Al}_2\text{O}_3/\text{Al}_2\text{TiO}_3$  with the titanium ion dispersing itself through  $\text{Al}_2\text{TiO}_3$  layer [7].



The most important physical and mechanical properties of aluminum titanate are summarized on Table 1 [8]. Additionally, we may mention a feature that has provoked a great industrial interest that is the lowest wetting of this material comparing to non-ferrous metals [42]. It is detached on table 1 the extreme an isotropic property thermal expansion of linear rates of each crystal that provoke the formation of microcracks. These microcracks occur when the aluminum titanate is cooled since manufacturing temperature (burning temperature) and a complex system of internal tensions is developed in the polycrystalline material due to the different behavior of thermal expansion of each crystal in the different crystallographic directions. In this work, it has been focused the first step of ceramic process, the raw material preparation, using the sol-gel process in the aluminum titanate synthesis,  $\text{Al}_2\text{TiO}_3$ , using aluminum and titanium alcoxides as precursor. The interest in the synthesis of aluminum titanate, a synthetic ceramic, derivate primarily from its thermal

properties since that this material owns a dischargeable thermal expansion rate and a high melting point. But, the deficiencies of this ceramic restrain its applications in the industry. Thus, a lot of synthesis methods of aluminum titanate were presented on the literature aiming to minimize or to eliminate these deficiencies. Among these methods we detach the sol-gel method. As reference to the obtained product via sol-gel also is synthesized the aluminum titanate under traditional route: the moisture of aluminum and titanium oxides.

Table 1 – Physical and mechanical properties of aluminum titanate [8].

Density (g/cm <sup>3</sup> )	3.7
Thermal conductivity (W/mK)	1.1 (600°C) 2.0 (1000°C) 3.0 (1200°C)
Thermal Expansion Rate of polycrystalline material	1,5 - 1,7 (20 - 1000 °C) 4,4 (20 - 1450 °C)
Thermal Expansion Rate of crystal (10 <sup>-6</sup> K <sup>-1</sup> ) (20 -1000°C)	Shaft a: -3.0 Shaft b: +11.8 Shaft c: +21.8
Mechanical resistance (Mpa)	10 – 30
Poisson Number	0.29 – 0.30
Young Module (Gpa)	13 – 15
Specific Heat (kJ/kgK)	1.2 (1400°C)
Thermal Shock Resistance	Very good
Melting point (°C)	1860

Aluminum titanate is considered a promising material for refractory applications. This interest is due to its low thermal expanded rate if compared to the melted silica and its high melting point [9]. The thermal expanded rate joint to the presence of microcrack causes an excellent resistance to the thermal shock in cyclic situations [7].

The high cost of aluminium titanate cause some difficult in its industry uses. The research and development of this material use precursor and additives of controlled nature in order to become better the mechanical properties and to inhibit the eutectic reaction. Both of them promote a very significant improvement in these properties but make its use prohibited. It is not a surprise that the use of this material would be face to the advanced ceramic areas.

### Experimental Procedure

It is noticed that there are few metal compounds that are properly water soluble and that would be used in the sol-gel process. Also, the use of metal salts as precursors in the production of mixed oxide via sol-gel does not allow reacting a good homogeneity in the atomic scale easily when compared to the use of alcoxides [10, 11]. In the specific case of production of aluminium titanate, the unique salt according to the technical point of view that would be used in this route of precursors would be the TiCl<sub>4</sub>. Although, the supplying of this chemical product is retracted by the Brazilian Army, besides of its use be discouraged due to its property of absorbing the air humidity and to produce a dense white and persistent smoke that is irritant to eyes and to the respiratory system. Thus, in this work it was decided to use alcoxides as precursors in the aluminium titanate synthesis. Although, in general, the metallic alcoxides present a strong reactivity with water and this is favorable to the hydrolysis reaction, causing a direct precipitation of the metallic hydroxide. They

were used as received the aluminum sec- A butoxide alcoxide ( $C_{12}H_{27}O_3Al$  – Merck) and titanium sec-butoxide ( $C_{16}H_{36}O_4Ti$ –Alfa). Another chemical products used were isopropyl alcohol, HCl and  $NH_4OH$  (25%) solutions, all of them under analytic grade and distilled water. Into glove box, under a nitrogenous atmosphere, 43.92 g of titanium sec-butoxide and 63.57 g of aluminium sec-butoxide were removed to a glass with three ends with 1L volumetric capacity. Thus, the molar reaction of  $Al^{+3}$ :  $Ti^{+4}$  had been adjusted to 2:1.

After then, yet under nitrogenous atmosphere in the three-ended balloon, shaker homogenized these alcoxides with Teflon® blade and glass tem during 30 minutes. The moisture of alcoxides was almost viscous and presented a yellow transparent coloring. After this time, it was added 100 ml of isopropyl alcohol to solve the moisture of alcoxides and the shaking was continued for two hours more. After this, the balloon atmosphere was not kept inert; it was added under constant shaking 30 ml of 0.5 M of HCl and 1.7 M of  $H_2O$  solution in isopropilico alcohol solution. The time of addition took two hours and the shaking was continued for 15 minutes more. This solution was removed and stored in a closed beaker covered with PVC paper.

A greatest part of the above precursor solution was removed to a beaker and it was tested under the following way: it was dropped slowly the solution of  $NH_4OH$  (25%) in the precursor solution under shaking, causing the formation of white precipitate when the drops reached the precursor solution.

The precipitate and the non-reacted solution were restrained in the beaker for 7 days, closed by a PVC paper. The quantity of precipitate increased in this period due to the PVC paper is semi-permeable to the air humidity and this one reacts to the precursor solution. The precipitate was separated and dried under atmosphere temperature until the day after when it was placed in heater under  $100^\circ C$  for 48 hours.

### Results and Discussion

The table 2 shows us the used solutions and the feature of obtained gel in the respective assays. The assay that used the major quantity of acid – the sample AT-5, was the one, which better promoted the formation of transparent gel. The assays of samples AT-1, AT-2 and AT-3 produced gel, firm these results would be compared with the notes, which were done in preceding works in the production of titanium via sun-gel using the addition of nitric acid or hydrochloric acid [12,13,14]. In these studies, the quantity of strong acid used in relation to the precursors showed to have an important influence in the features of gel. In these ones, the lack or a few acid had provoked the precipitation.

Table 2 – Used Solutions and the features of obtained gels in the respective assays.

Assays	AT-1	AT-2	At-3	AT-4	AT-5
Used Solutions in the gel synthesis	Precursor + $H_2O$	Precursor + HCl 1.0 M	AT-4 Solution + HCl 1.0 M	Precursor + $NH_4OH$	Precursor + HCl 2.4 M + $H_2O$
Obtained gel features	Firm gelatinous precipitate	Firm gelatinous precipitate	Firm gelatinous precipitate	Precipitate	Firm and translucent gel

The progressive increasing of acid promoted the production of a more translucent gel until it became transparent. The excess of acid determined the reduction of gel stability with the formation of precipitates in its net and make the gel turbid during the aging.

The Fig.1A and 1B show the obtained images on electronic sweeping microscopy of samples AT-1 and AT-3, respectively, and they show us these milled xerogels and its particles. Enlarged details of surface of these particles are showed in the images of Fig. 1C and 1D, respectively.

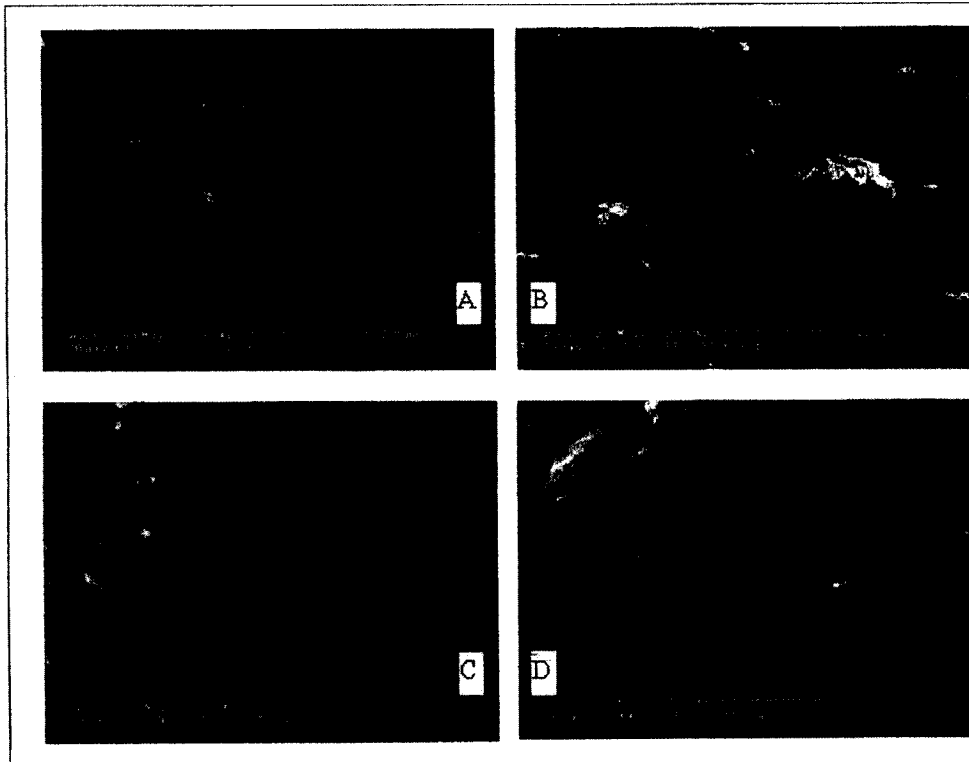


Fig. 1 – SEM micrographs of samples AT-1 (Fig. A and C) and AT-3 (Fig. B and D).

The Fig. 2 shows us the differential thermal analysis of all samples.

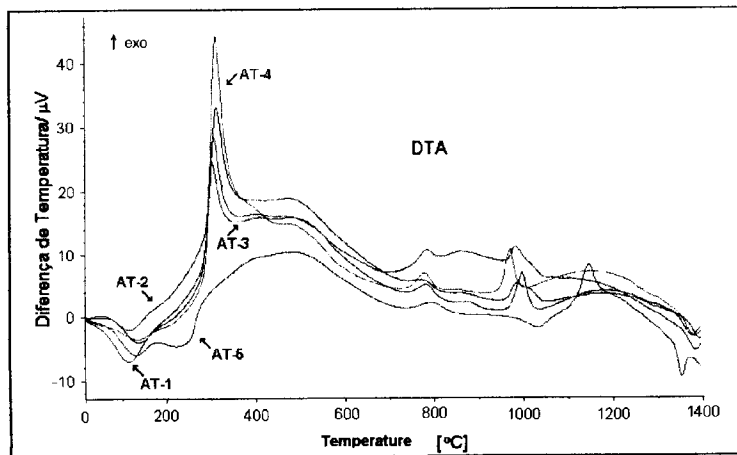


Fig. 2 – Differential Thermal Analysis (DTA) of samples AT.

From differential thermal analysis we note that the water and solvent evaporations occurred between 100°C and 170°C in all cases, except with sample AT-5 that occurred additionally a second smooth endothermic pick between 170° and 250°C and it is attributed to the continuous elimination of molecules attached in the polymeric net strongly united. Between 250°C and 550°C occurred the burning of organic residual compounds provoking in all analysis a complex exothermic peak that included an intense peak near to 300°C, except at AT-5 that showed a graduated and smooth curve in all this step of temperature. This different behavior of AT-5 is also attributed to the polymeric net strongly united of xerogel. The HCl is eliminated between 100°C and 600°C.

The results of X-ray diffratograms of all samples are showed on table 3. Note that only the xerogel AT-5 had an expressive difference on the phases analysis on the calcination program. As we see on Table 2, the addition of HCl on the control of reactions affected substantially the gel features only when it was used an appropriated quantity. As shown, it was obtained a gel and respective xerogel with a considerable homogeneity that promoted the formation of aluminium titanate at 900°C, under eutectic temperature. Despite of it, the presence of anatase phase in these calcinations suggests that the xerogel AT-5 is not so homogeneous, it means, there is heterogeneity located due to probable formation of precipitates when it was noted the gel became lightly turbid during the aging process. As mentioned before, it was used during preceding search strong acid to control titanium alcoxides reactions in the preparation of titanium gel [14]. In this study, the use of strong acid in determined rate of concentration controlled all hydrolysis and condensation reactions and allowed the formation of a translucent polymeric and, consequently, homogeneous gel. Despite of it, the presence of anatase phase in these calcinations suggests that the xerogel AT-5 is not so homogeneous, it means, there is heterogeneity located due to probable formation of precipitates when it was noted the gel became lightly turbid during the aging process. As mentioned before, it was used during preceding search strong acid to control titanium alcoxides reactions in the preparation of titanium gel [14]. In this study, the use of strong acid in determined rate of concentration controlled all hydrolysis and condensation reaction and allowed the formation of a translucent polymeric and, consequently, homogeneous gel. Under this rate it occurred the formation of gelatinous precipitates in the gel net. In the case of AT-5 probably the concentration of acid used was out of optimum rate to the reactions yet evolving the titanium alcoxide but not the aluminum alcoxide. It may cause gelatinous precipitates of titanium and, consequently heterogeneity under microscopic level, which is detected by the X ray diffraction analysis.

Table 3 – Summary of showed phases by the X-ray diffraction of samples AT.

(°C)	AT-1	AT-2	AT-3	AT-4	AT-5
500	□ - alumine	□ - alumine	□ - alumine	□ - alumine	Amorphous and anatase traces
700	□ - alumina	□ - alumina	□ - alumina	□ - alumina	Anatase and □ - alumine
900	Rutile and □ - alumina	Rutile and □ - alumina	Rutile and □ - alumina	Rutile and □ - alumina	Tialite and Anatase
1100	Rutile and □ - alumina	Rutile and □ - alumina	Rutile and □ - alumina	Rutile and □ - alumina	Rutile and □ - alumina
1400	Tialite and □ - alumina / rutile traces	Tialite and □ - alumina / rutile traces	Tialite and □ - alumina / rutile traces	Tialite and □ - alumina / rutile traces	Tialite and □ - alumina / rutile traces

### Conclusions

Sol-gel method ceramic materials prepared it, aluminium titanate, at bench level, providing considerable dominium with this chemical route. The use of hydrochloric acid in an appropriated concentration in the assay AT-5 controlled the hydrolysis and condensation reactions of alcoxides and brought the formation of a translucent gel, decreasing the formation of precipitates and promoting the homogeneity of material. With the thermal treatment at 900°C of sample AT-5 it occurred the direct formation of titanate phase of metastable aluminum together with the anatase phase. Other samples presented corundum and rutile phases to the same thermal treatment. The procedures and concentrations used in the sample AT-5 preparation assay were resulted in an appropriated material to obtained a pure aluminum titanate.

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## **Advanced Powder Technology III**

doi:10.4028/www.scientific.net/MSF.416-418

## **Synthesis of Aluminium Titanate Powder by Sol-Gel Technology**

doi:10.4028/www.scientific.net/MSF.416-418.519