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Formation of Aluminum Titanate with Small Additions of MgO and SiO_2

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The formation of aluminum titanate was investigated by isothermal treatments of samples obtained from equimolar mixtures of alumina and titania, containing small amounts of silica and magnesia. Results of differential thermal analysis and Rietveld refinements of data collected by X-ray powder diffraction (XRPD) showed that additions of silica in amounts used in this work did not influence the formation of aluminum titanate. However, the presence of magnesia favored the formation of aluminum titanate in two steps, first one by incorporating Mg^{2+} into Al_2TiO_5 lattice during its initial formation, and the second one by accelerating the Al_2TiO_5 formation, contributing to large quantities of this phase. MgO doped samples have also developed a more suitable microstructure for stabilizing of Al_2TiO_5, what make them promising for applications such as thermal barriers, internal combustion engines and support material for catalyst.

Keywords: *aluminum titanate, Rietveld, magnesia, silica*

1. Introduction

Aluminum titanate ceramics (Al_2TiO_5) are promising materials for insulating applications in automotive industry, such as engine components, portliners, manifolds and linings of turbochargers[1,2]. Also, this ceramic is suitable as catalyst carriers for purification of fume produced by cars, containers and tubes for storing or conveying melted steel as well as protective tube for thermocouples. This is because of their low thermal expansion coefficient (0.2 - $1x10^{-6}$ K^{-1}), low Young's modulus, high melting point (~1860ºC), low thermal conductivity (0.9 – 1.5 $Wm^{-1}K^{-1}$) and outstanding thermal shock resistance which can reach up to 500 Wm^{-1} [1-4] .

However, a pronounced anisotropy in thermal expansion coefficient, typical of aluminum titanate, induces severe microcracking during the cooling process that takes to damage mechanical properties of the final sintered material [1,5]. The anisotropic behavior is due to the crystal structure of the Al_2TiO_5 which is isomorphous with pseudobrookite (Fe_2TiO_5), crystallizing in the orthorhombic space group Cmcm, with a theoretical density of 3.70 g/cm^3.

Another problem associated with the formation of Al_2TiO_5 which has limited its application field is the eutetoid-like decomposition to α-Al_2O_3 and TiO_2 (rutile) within temperature range from 900 to 1280ºC[6]. This reaction accompanied by an 11% molar increase contributes to a microcracking process and consequently to deterioration of the ceramic component[7,8].

The referred limitations are usually solved using composites with alumina or mullite, or else additives to stabilize the structure and avoid decomposition reactions[3,7,9,10]. Studies reported that additives can increase the formation of aluminum titanate which leads to thermodynamic stability, as well as an improving in sintering[11]. Although there are some researches about the formation of aluminum titanate doped with different substances[2,12-16], most are related to the presence of large amounts of additives with conflicting results. This encouraged us to investigate the effect of small contents of MgO and SiO_2 on formation of Al_2TiO_5.

Moreover, additives were selected considering the small difference between the size of its cation and aluminum ionic radius (Al^{3+}=0,054nm, Si^{4+}=0,041nm and Mg^{2+}=0,071nm) in order to avoid large distortion in aluminum titanate crystal and damaging the thermal expansion of the material[17].

2. Experimental procedure

The raw materials used in this study were α- Al_2O_3 (A1000 SG, Alcoa), TiO_2 (rutile, Merck), MgO (Sigma-Aldrich, 99.99% trace metals basis) and SiO_2 (fumed silica, Aerosil –Degussa). Titania and alumina powders were separately ground in a ball mill for 16 hours. Afterwards, equimolar mixtures of alumina and titania, containing 0-1.0 wt-% silica or magnesia (as listed in Table 1) were ground in an attritor mill at 250 rpm for 2 hours using isopropanol as liquid medium.

After grinding process, the compositions were dried in a rot evaporator. Samples were submitted to differential thermal analysis (DTA) using air atmosphere to 1400ºC, at

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a heating rate of 10ºC/min, (Netzsch, DSC 404 F3 Pegasus) so that possible reactions involved from 1250 to 1400ºC could be explored.

In order to investigate the reactions taking place in the compositions shown in Table 1, uniaxially (50 MPa) and cold isostatically pressed (200 MPa) pellets were subjected to isothermal treatments at air, being quickly introduced into a tubular furnace which was previously stabilized at 1250, 1300 and 1400ºC, respectively. The pellets were held in respective temperatures for one hour and quenched in water so that a rapid cooling would be ensured to preserve, at room temperature, the aluminum titanate phase which tends to decompose in α-Al_2O_3 and TiO_2 during slow cooling processes. After that, samples were dried at 110° C for 24 hours.

Pulverized heat-treated pellets were analyzed by X-ray powder diffraction (D5000 Siemens/Brucker diffractometer equipped with copper tube and scintillation detector) in a range from 15 to 100º (2θ) with step of 0.02º (2θ) and 5s/pass. Phases quantitative analysis and computations of lattice parameters were carried out by the Rietveld method using Topas Academic[18] as computer program.

Scanning electron microscopy (Philips XL30 scanning electron microscope) was performed in fractured samples to evaluate the microstructure after the heat treatments.

3. Results and Discussion

Figure 1 shows DTA curves of the studied compositions. There is an endothermic peak between 1300 and 1360°C, which can be associated with the solid state reaction of formation of aluminum titanate. This reaction occurred at lower temperatures when MgO was present, showing that MgO anticipates the formation of Al_2TiO_5 compared to other evaluated compositions. This behavior should be related to a prior reaction with Mg^{2+} ions represented by another endothermic event found at around 1250°C in AT50M and AT100M compositions. Instead, additions of SiO_2 showed no influence on this temperature, since the reactions in compositions with SiO_2 (AT50S and AT100S) overlap with that of the composition without additive (ATP).

X-ray powder diffraction analysis (Figure 2) of isothermally heat-treated samples (1250, 1300 and 1400 for 1 hour)

Table 1. Additives in the equimolar mixture of alumina and titania.

sample	Silica (wt. %)	Magnesia (wt. %)
ATP	-	-
AT25S	0.25	-
AT50S	0.5	-
AT100S	1	-
AT25M	-	0.25
AT50M	-	0.5
AT100M	-	1

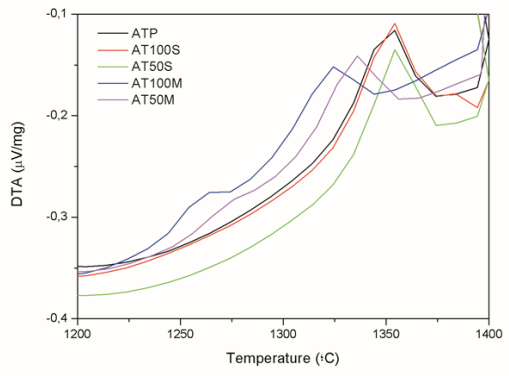

Figure 1. Differential thermal analysis (DTA) curves of samples from 1200 to 1400 °C.

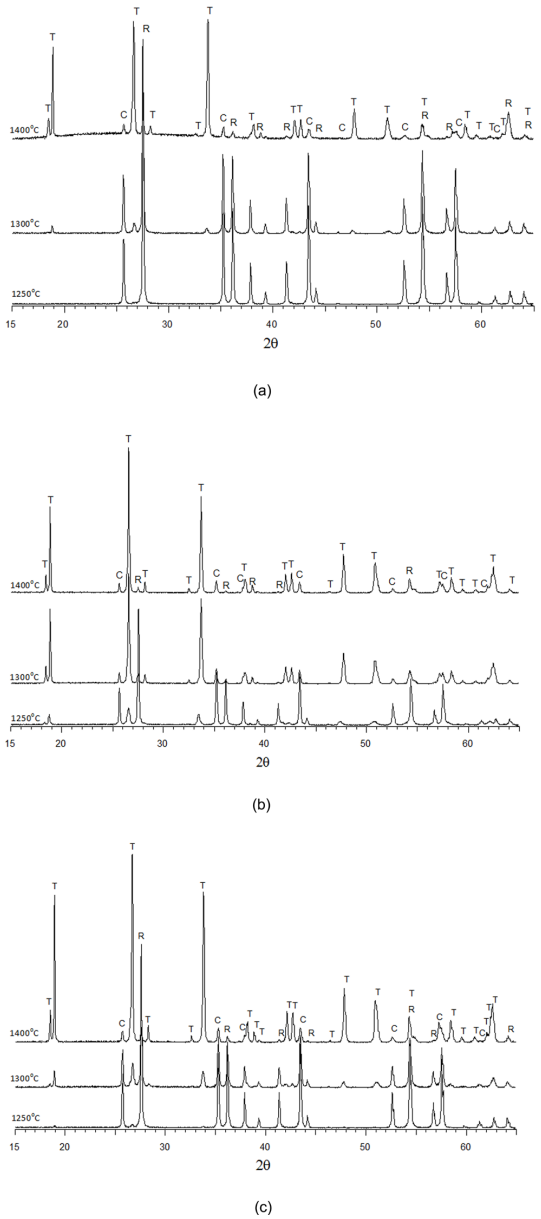

Figure 2. X-ray powder diffraction (XRPD) spectra taken from samples obtained by heat treatments at 1250, 1300 and 1400 for 1 hour. (a) ATP, (b) AT100M and (c) AT100S. T is aluminum titanate, C is α-alumina and R is rutile.

show the evolution of the formation of aluminum titanate. Quantitative analysis with Rietveld refinements confirms the efficiency of MgO additions to Al_2TiO_5 formation. Plots of Al_2TiO_5, Al_2O_3 and TiO_2 contents in function to amount of additive (MgO or SiO_2) and temperature of isothermal heat treatment (Figure 3), indicates that Al_2TiO_5 phase was formed in all investigated samples, except in pure sample (ATP) and in that with 0.25 wt-% SiO_2 (AT25S), both treated at 1250°C. Although this temperature did not favor the formation of Al_2TiO_5, MgO already proved to be an effective additive for obtaining the studied ceramic.

The greater efficiency of MgO with respect to SiO_2 is quite pronounced when the heat treatment was performed at 1300°C (see Figures 3a and 3b). Just as an example, the sample containing 1 wt-% MgO reached 81.72 wt-% Al_2TiO_5, while other doped with 1 wt-% SiO_2 promoted formation of 22.26 wt-% Al_2TiO_5. It means a difference of three times in amount of formed Al_2TiO_5.

At 1400°C, despite the addition of MgO has promoted formation of Al_2TiO_5 in higher amounts than the addition of SiO_2, the influence of additive concentration is very slight. In other words, the effect of temperature exceeded that of additives when the heat treatment proceeded at 1400°C.

The effect of MgO additions on formation of Al_2TiO_5 most likely involves the endothermic reaction detected in the DTA curves (Figure 1) for MgO doped samples (AT50M and AT100M). This reaction can be associated with the altered values found for the Al_2TiO_5 lattice parameters of MgO doped samples treated at 1250°C (Table 2). Ishitsuka et al.[19] studying Al_2TiO_5 synthesized with $Mg(OH)_2$, observed changes in lattice parameters of Al_2TiO_5 phase assigned to formation of solid solutions of $Al_{2(1-x)}Mg_xTi_{1+x}O_5$, at low temperatures. Some works related the presence of a transitional phase during the formation of Al_2TiO_5, however conflicting opinions yet are discussing in view of the presence of this phase, as well as its composition and effect on the formation of Al_2TiO_5[12,14,20].

Altered values found for the Al_2TiO_5 lattice parameters of MgO doped samples treated at 1250°C (Table 2) suggest that aluminum titanate is formed in two steps, just characterized by the endothermic reactions. In the first step, Mg^{2+} should be incorporated into Al_2TiO_5 lattice during its formation, producing a solid solution that behaved as a nucleating agent to accelerate the second stage of Al_2TiO_5 formation. It is means that the efficiency of the additive is related to the Mg^{2+} incorporation into the structure of Al_2TiO_5.

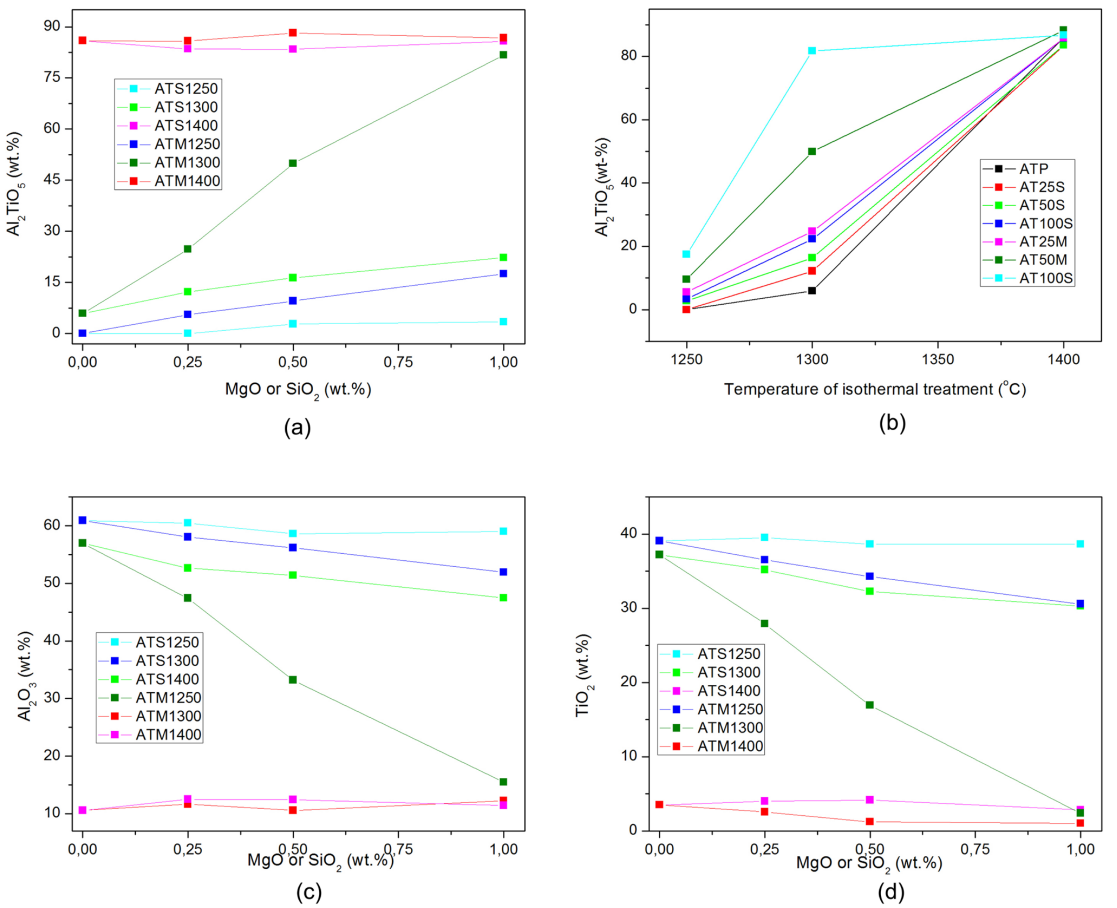

Figure 3. Al_2TiO_5 (a and b), Al_2O_3 (c) and TiO_2 (d) contents calculated by the Rietveld method as a function of the additive content and heat treatment temperature. ATS is the abbreviation for SiO_2 doped samples; ATM is the abbreviation for MgO doped samples; 1250, 1300 and 1400 are the heat treatment temperatures (°C).

Besides, Al_2O_3 and rutile phases were detected in the samples (Figures 2 and 3), indicating that the solid state reaction for formation of Al_2TiO_5 could not be concluded in any conditions used here. Although high amounts of Al_2TiO_5 have been formed during heat treatments at 1400°C, Al_2O_3 and TiO_2 were also found as residual phases.

The quantitative phase analysis clearly demonstrates that larger amounts of alumina remained as residual phase in all samples (Figure 3c), indicating that rutile is preferably consumed to form Al_2TiO_5. These results reveal that an equimolar mixture of Al_2O_3 and TiO_2 does not contribute to complete the formation of Al_2TiO_5 by means of solid state reaction.

Figure 4 shows micrographs of samples with fractured surfaces. By this figure, it is observed that both additions result in inhibition of grain growth of Al_2TiO_5, and MgO additions are more efficient in this action compared to SiO_2 additions. This suggests that MgO is also more efficient in stabilization of Al_2TiO_5 phase and consequently for reducing of microcracks. This because the phenomena are related to grain size, i.e., Al_2TiO_5 becomes stable at room temperature, below a critical grain size. Also, below a certain critical grain size (which is not necessarily the same), the stresses caused during cooling become insufficient for formation of microcracks[21-23]. This fact controls thermal and mechanical properties of the material[22,24,25].

Table 2. Al_2TiO_5 lattice parameters obtained by Rietveld refinements.

Identification	a (Å)	b (Å)	c (Å)	Cell vol. (Å^3)
AT25M-1250°C	3.59462(55)	9.5020(23)	9.7300(24)	332.340(13)
AT25M-1300°C	3.58728(18)	9.45799(56)	9.68367(61)	328.552(33)
AT25M-1400°C	3.588785(85)	9.44434(21)	9.65933(21)	327.390(13)
AT50M-1250°C	3.60200(37)	9.5054(15)	9.7299(16)	333.138(82)
AT50M-1300°C	3.58971(13)	9.45307(38)	9.66753(42)	328.056(23)
AT50M-1400°C	3.589806(86)	9.44414(22)	9.65758(23)	327.417(13)
AT100M-1250°C	3.59642(28)	9.5156(10)	9.7300(11)	332.982(58)
AT100M-1300°C	3.59229(11)	9.44913(29)	9.66158(31)	327.953(18)
AT100M-1400°C	3.592480(75)	9.44984(21)	9.66067(21)	327.964(12)

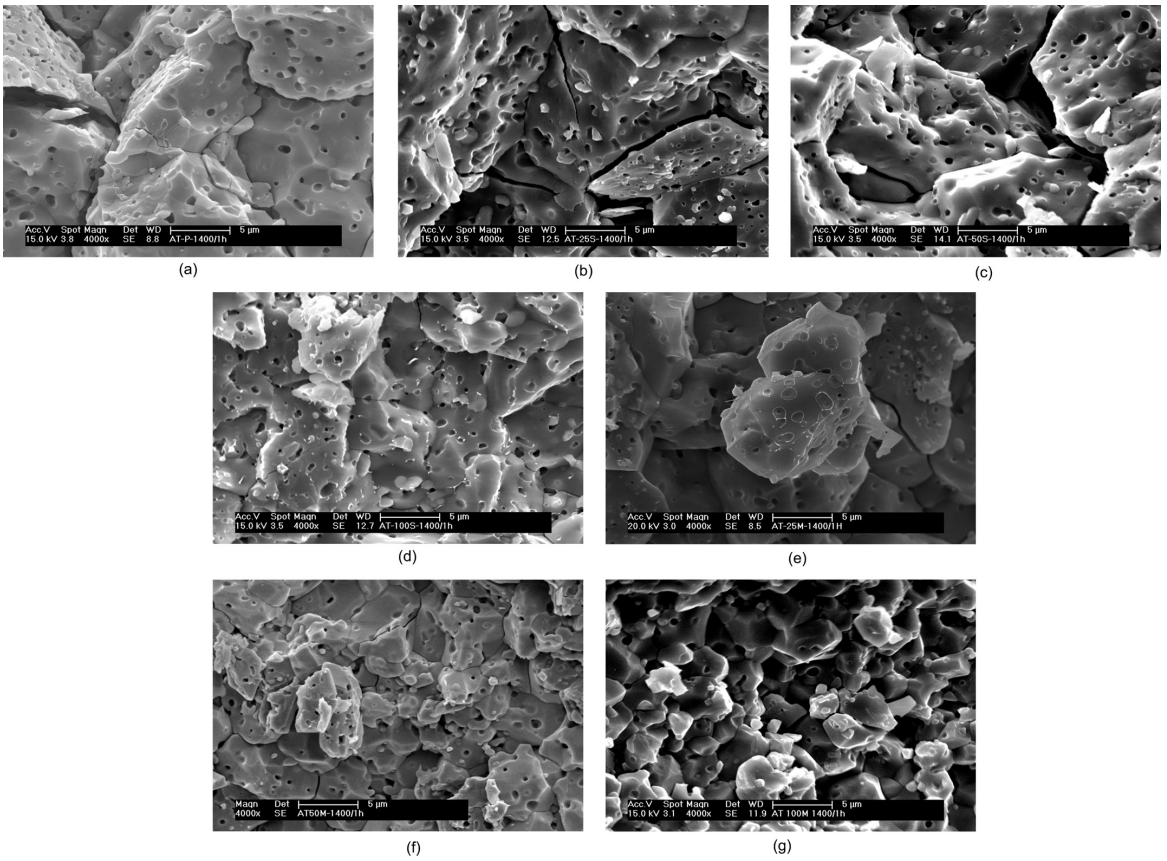

Figure 4. Scanning electron micrographs of the fracture surface of the samples treated at 1400°C for 1 hour. (a) ATP, (b) AT25S (c), AT50S, (d) AT100S, (e) AT25M, (f) AT50M and (g) AT100M.

4. Conclusions

Additions of MgO provided prior formation of Al_2TiO_5 owing to a further endothermic reaction detected at low temperature. The presence of two endothermic reactions in MgO doped samples as well as results of XRPD and Rietveld refinement led to conclude that the formation of Al_2TiO_5 occurred in two stages. The first stage was associated with formation of an aluminum titanate solid solution containing Mg^{2+}, and the second reaction was related to actual formation of Al_2TiO_5. Also, small contents of MgO shown to be promising in the stabilization of Al_2TiO_5, whereas they promoted the development of a microstructure consisting of small grains.

In contrast, additions of silica do not promote expressive results related to the formation of Al_2TiO_5.

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