

PHASE TRANSFORMATIONS IN THE $\text{Al}_2\text{O}_3/\text{TiO}_2$ SYSTEM AND METASTABLE PHASE FORMATION AT LOW TEMPERATURES

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Abstract. In this work we studied the phase formation in the $\text{Al}_2\text{O}_3/\text{TiO}_2$ system using amorphous powders with a high degree of chemical homogeneity and prepared by co-precipitation of inorganic salts. The aluminum tialite (Al_2TiO_5) phase of the $\text{Al}_2\text{O}_3/\text{TiO}_2$ system is of considerable technological interest due mainly to its thermal properties. This phase is thermodynamically stable only at temperatures above 1280 °C; below this value it decomposes into the starting oxides rutile and corundum. The formation of tialite in temperatures below 1280 °C is possible using chemical methods of powder synthesis like co-precipitation. In this work, the gel obtained by co-precipitation of inorganic salts was calcined at different temperatures and dwell times. The formation of metastable tialite under a number of temperature conditions and dwell times below its stable formation temperature was observed. Results showed strong dependence not only on calcination temperature, but also on dwell time. The cooling rate did not significantly alter the conversion or reverse conversion of tialite into rutile and corundum.

1. INTRODUCTION

The name 'metastable phase' is given to the non-equilibrium state of a substance whose properties change reversibly during an observation period. A system is in a metastable state when it is in equilibrium (not changing with time) but is susceptible to fall into lower-energy states with only slight interaction (Fig. 1) [1].

The interest in aluminum titanate ceramics is primarily due to their low volumetric thermal expansion coefficient, similar to molten silica. This macroscopic property is caused by the anisotropic expansion of individual orthorhombic Al_2TiO_5 crystals [2], giving rise to a stable microcracked structure [3] in sinterized polycrystals. In general, Al_2TiO_5 is obtained by the solid state reaction between Al_2O_3 and TiO_2 , which is only thermodynamically possible

at temperatures above 1280 °C [4]. Below this temperature, at a range between 900 and 1280 °C, metastable Al_2TiO_5 undergoes eutectoid decomposition, forming $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 (rutile) [5-9].

Chemical methods such as co-precipitation, sol-gel, hydrothermal and colloid emulsions can efficiently control both the morphology and chemical composition of the materials processed. [10]. Kato *et al.* [7] prepared non-crystalline homogeneous mixtures of titanium and aluminum by chemical precipitation. Thermal treatment showed that the anatase formation takes place before the formation of tialite. Tialite formation occurred at high heating rates around 1250 °C. The difficulty in obtaining tialite was attributed to the formation of rutile and corundum before the formation of Al_2TiO_5 .

However, some authors, using powders obtained by chemical routes, observed the insipient forma-

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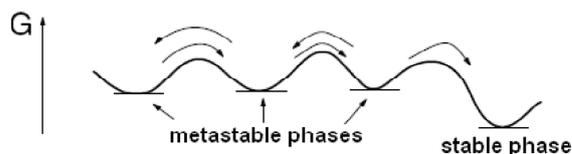


Fig. 1. Illustration of the possible states of minimum energy for a hypothetical material (adapted from Brazhkin [1]).

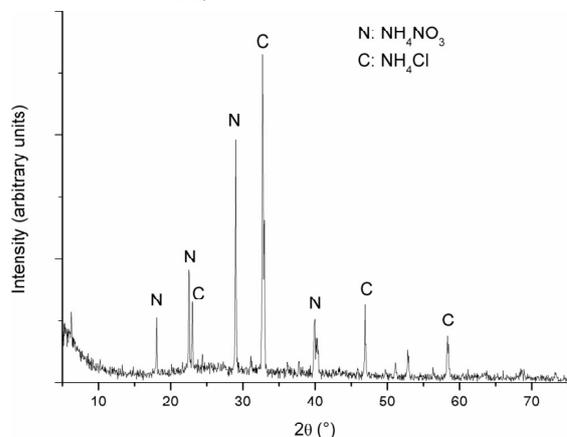


Fig. 2. X-ray diffraction of the gel after drying, revealing the crystalline phases (NH_4NO_3 and NH_4Cl).

tion of tialite at temperatures around 1000 °C. Nagano *et al.* [11] observed the formation of Al_2TiO_5 at 1000 °C and associated this formation to the thermodynamically unstable states of the reagents Al_2O_3 and TiO_2 (anatase). Stancia *et al.* [12] associated the powder synthesis using the sol-gel method with the syntherization technique, which uses an activated electric field that allows heating rates of 150 K/min. Besides, comparing powders obtained by three different methods (co-jellification of alkoxides, co-precipitation of inorganic salts and mixture of individual oxides) they observed the formation of tialite at a temperature of 1100 °C, mainly for the sample obtained by co-jellification that had the highest chemical homogeneity. Using quasi-amorphous powders of $\text{Al}_2\text{O}_3/\text{TiO}_2$ mixture, Camaratta *et al.* [13] obtained tialite by plasma spraying, reinforcing the fact that the tialite formation from $\text{Al}_2\text{O}_3/\text{TiO}_2$ mixtures with a high degree of chemical homogeneity depends on the thermal processing of powders.

Despite the high chemical homogeneity obtained with sol-gel-prepared powders, in most of the studies using the $\text{Al}_2\text{O}_3/\text{TiO}_2$ mixture, the formation of tialite is preceded by the formation of rutile and corundum at temperatures below 1280 °C. It is presumed that the dwell time of powders from the $\text{Al}_2\text{O}_3/\text{TiO}_2$ mixture at low temperatures, albeit near 1280

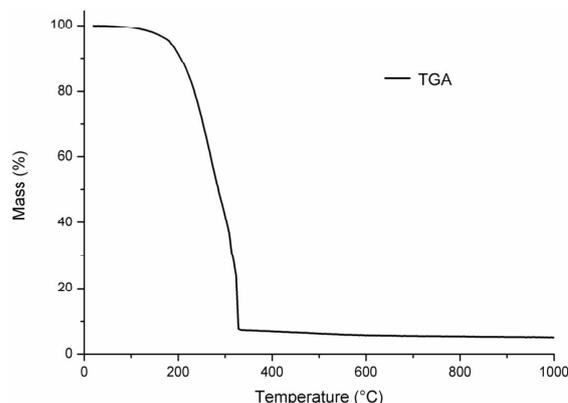
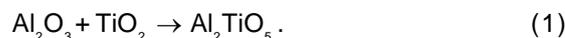


Fig. 3. TGA of the dried gel.

°C, offsets the tialite formation because at these temperatures there is a strong diffusion in the opposite direction of the reaction (1).



Therefore, this work investigated the formation of the metastable tialite phase at temperatures between 900 °C and 1100 °C. The formation and decomposition of the tialite phase is strongly dependent on the dwell time.

2. MATERIALS AND METHODS

To obtain the powders from the $\text{Al}_2\text{O}_3/\text{TiO}_5$ mixture using the co-precipitation method, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (aluminum nitrate nonahydrate) and TiCl_4 (titanium tetrachloride) were used as sources of Al and Ti,

Table 1. Names and calcination conditions of all the samples.

	Temperature	Dwell	Cooling
6006hL	600 °C	6 h	Slow
90030L	900 °C	30 min.	Slow
9006hL	900 °C	6 h	Slow
95030L	900 °C	30 min.	Slow
95030R	950 °C	30 min.	Fast
9506hL	950 °C	6 h	Slow
100030L	1000 °C	30 min.	Slow
100030R	1000 °C	30 min.	Fast
10006hL	1000 °C	6 h	Slow
105030L	1050 °C	30 min.	Slow
10506hL	1050 °C	6 h	Slow
110030L	1100 °C	30 min.	Slow
11006hL	1100 °C	6 h	Slow

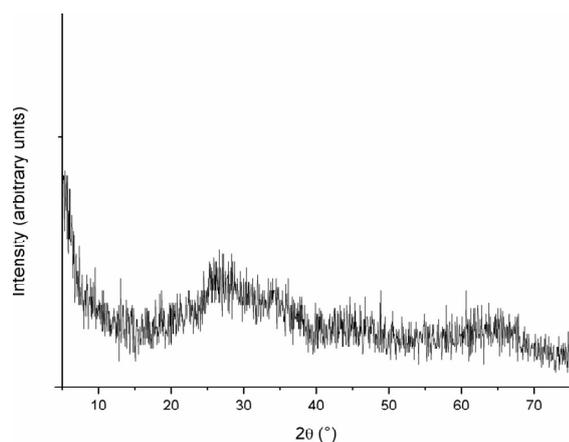


Fig. 4. X-ray diffraction of powder calcined at 600 °C with dwell time of 6 hours did not show the presence of crystalline phases.

respectively. The solvent was ethylene glycol. We used 3 ml of TiCl_4 , 20.469 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 100 ml of ethylene glycol p.a. (proanalysis grade), forming a 0.82M solution, obeying stoichiometry of 2 Al for 1 Ti.

Coprecipitation was done by increasing the pH of the solution through the addition of base $\text{NH}_4(\text{OH})$ p.a. until gel formation. The gel was dried in an infrared chamber under controlled maximum temperature up to 40 °C. Thermogravimetric analysis (TGA) was conducted to identify the evaporation temperatures of the by-products of the sol-gel process. X-ray diffraction was used to determine the phases present before and after the calcination processes.

Calcinations were done in a muffle furnace in alumina crucibles. A heating rate of 150 °/h was pre-defined and the maximum temperature, dwell time, as well as the cooling conditions were varied. Temperatures of 950 °C and 1000 °C with 30-min dwell time were selected to determine the influence of the cooling rate. In these cases samples cooled inside the furnace were compared with those removed from the furnace after the dwell temperature and exposed to the air for abrupt cooling. Table 1 shows calcination conditions of all the samples.

3. RESULTS AND DISCUSSION

After being dried under infrared radiation, the gel showed the formation of ammonium nitrate (NH_4NO_3) and ammonium chloride (NH_4Cl) (Fig. 2). These phases decomposed in the calcination process, leaving only the oxides of interest. TGA showed the complete volatilization of these phases up to around 340 °C (Fig. 3).

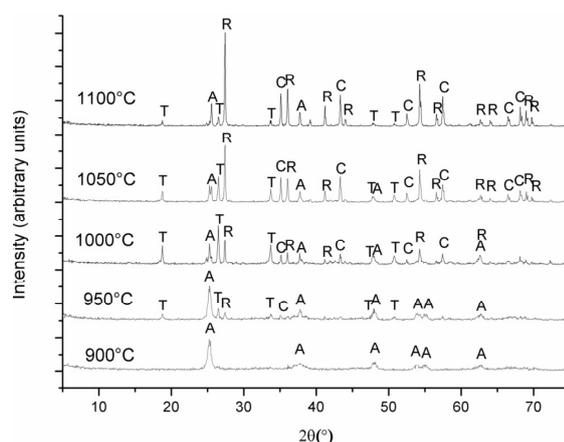


Fig. 5. X-ray diffractograms of samples calcined at temperatures of 900, 950, 1000, 1050, and 1100 °C with a 30-min dwell time, revealing the presence of phases A: Anatase; R: Rutile; C: Corundum; and T: Tialite.

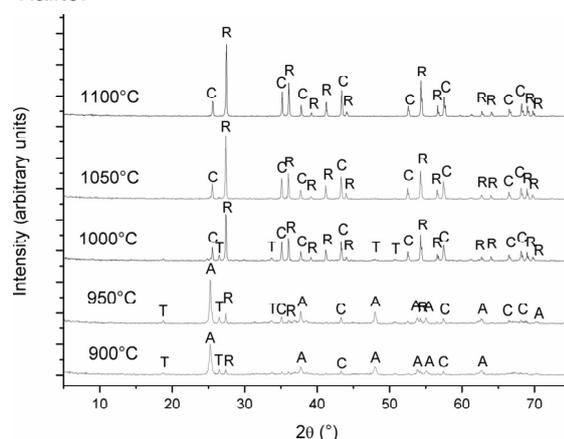


Fig. 6. X-ray diffractograms of samples calcined at temperatures of 900, 950, 1000, 1050, and 1100 °C with dwell time of 6 hours, revealing the presence of phases A: Anatase; R: Rutile; C: Corundum; and T: Tialite.

Based on the TGA results, the gel was calcined at a temperature of 600 °C for 6 h to ensure the complete elimination of the by-products of the sol-gel process, leaving only the oxides of interest. After calcination, a white ceramic powder in the form of fragile aggregates remained. X-ray diffraction analysis showed that the oxides formed in the coprecipitation process were amorphous oxides (Fig. 4).

Calcinations with a 30-min dwell time showed that at 900 °C the sample exhibited only the formation of anatase as a crystalline phase. At 950 °C, we observed, in addition to anatase, the formation of tialite, rutile and traces of corundum. The maximum formation of tialite took place at 1000 °C. At

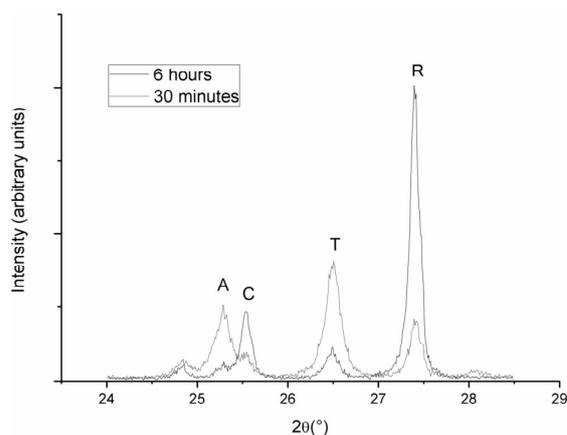


Fig. 7. Comparison of X-ray diffractograms of samples calcined at 1000 °C with dwell time of 6 hours, revealing the presence of phases A: Anatase; R: Rutile; C: Corundum; and T: Tialite.

this temperature it coexisted with the anatase, rutile, and corundum phases. Above 1000 °C, the anatase and tialite metastable phases tended to decompose in rutile and corundum (Fig. 5).

Calcinations with a long firing dwell (6 h) showed a lower tendency to tialite formation (Fig. 6). The conditions at which the highest conversion into tialite occurs, are with calcination at 1000 °C with a 30-min dwell time. A longer dwell clearly resulted in a greater formation of rutile and corundum phases, starting at 900 °C. At 1050 °C, these phases already corresponded to practically 100% of the phases present with only traces of tialite remaining. In contrast to calcination with a short dwell time,

the tialite phase was no longer present in calcination at 1050 °C.

To better compare the relative intensities of tialite, corundum, rutile, and anatase peaks, a better detailed scan diffraction was performed and the diffractograms were superimposed. X-ray diffraction analyses of the samples calcined at 1000 °C clearly showed the strong influence of the length of time the powders remained at the dwell temperature. The longer the sample was exposed to high temperatures, the higher the conversion of tialite into corundum and rutile (Fig. 7).

Varying the cooling rate for calcination at 950 °C (Fig. 8a), we obtained the formation of anatase in both samples in addition to the incipient formation of the tialite, rutile, and corundum phases only for the furnace-cooled sample. No significant differences were observed in the proportions of calcination phases at 1000 °C (Fig. 8b). Based on these data and on the calcination results with different dwell times, it is suggested that for powders obtained by co-precipitation of their salts, the conversion and reverse conversion of tialite at temperatures below its thermodynamic stability temperature (~ 1280 °C) and above 900 °C depend more on the dwell time at high temperatures than on the cooling rate.

4. CONCLUSIONS

From powders obtained by co-precipitation of inorganic salts it is possible to obtain tialite at temperatures below the formation temperature thermodynamically predicted by the system phase diagram.

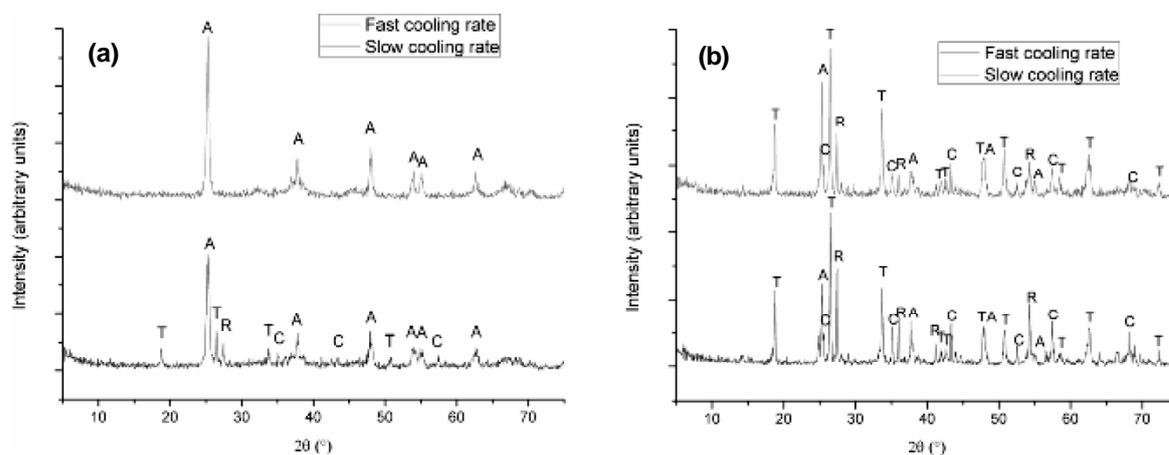


Fig. 8. Comparison of X-ray diffractograms for furnace-cooled (slow) and air-cooled (fast) samples that were calcined at (a) 950 °C and (b) 1000 °C, revealing the presence of phases A: Anatase; R: Rutile; C: Corundum; and T: Tialite.

Firing dwell time is a determining factor in the residual proportion of the tialite phase formed under metastable conditions (below 1280 °C). With a dwell time of 6 h, the amount of tialite phase sinterized is lower than when fired with a dwell time of 30 min.

The cooling rates studied did not significantly influence the proportion of tialite formed.

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