

## REACTION MECHANISMS OF TIALITE FORMATION IN THE PRESENCE OF MINERALIZERS

M. Preda, A. Ianculescu, M. Crisan<sup>a</sup>, A. Jitianu<sup>a</sup>, D. Crisan<sup>a</sup>, M. Zaharescu<sup>a</sup>

University "Politehnica", 1 Polizu Str., Bucharest, Romania

<sup>a</sup>Romanian Academy, Institute of Physical Chemistry "I.G.Murgulescu". 202 Splaiul Independentei, 77208, Bucharest, Romania

The tialite based ceramics are intensively studied due to their special properties as the very low thermal expansion coefficient, high refractivity, high chemical stability and so on. However the tialite presents some disadvantages as thermodynamic instability at temperatures lower than 1200°C and reduced sintering tendency. There are two ways that can eliminate these deficiencies: the texture improvement by using unconventional methods of preparation and addition of mineralizers. In the present work studies concerning the synthesis and sintering of some tialite based ceramics in the presence of MgO, SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> respectively were realized. The samples were selected in a composition range corresponding to the magnesium spinel, mullite and ferrite formation. The mixtures of raw materials were obtained both by conventional ceramic route and by sol-gel procedure. The reaction mechanisms, which occur during the tialite formation, were established based on the DTA/TGA analysis. It was established that when starting with commercial oxides the mineralizers bonded in different compounds, represent crystallization centers for tialite, and determine its formation at about 1200°C. By XRD it was observed that the tialite ratio increases with temperature increasing. When sol-gel method was used the amount of tialite formed was higher (80% at 1200°C), presenting also the great advantage of a very fine texture which is preserved even after sintering. By apparent density measurements it was established that some mineralizers improve also the sintering tendency of the samples as well.

**Keywords:** Tialite, Ceramics mineralizers

### 1. Introduction

Tialite (Al<sub>2</sub>TiO<sub>5</sub>) is a very interesting compound due to some special properties as: high refractivity, low thermal conductivity and low thermal expansion coefficient, that confers to the tialite containing products high resistance to the thermal shock. The synthesis of this compound was very much studied, using several procedures, which start either with commercial oxides or are using powders obtained by chemical methods. Due to the fact that tialite is thermodynamically instable its synthesis was studied in the presence of mineralizers, that may enhance its formation, lead to its thermodynamic stabilization or improve the sintering ability. Some of the stabilizers mostly used are: MgO, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> at al. Prasadarao et al [1] studied the tialite formation without and with mineralizers using the sol-gel method (Table 1). The mentioned authors have used a diphasic mixture starting with boehmite and anatase and a gel mixture of the two oxides. In the first case the alumina crystallization and the tialite formation at 1350°C with an endothermic effect was noticed. In the case of the gel mixture the both effects were noticed, but the tialite formation takes place at 1250°C. The same authors have also studied stoichiometric mixtures corresponding to the tialite composition with magnesium and iron oxide addition. In both cases the tialite formation is marked by two endothermic effects, but at different temperatures, mainly at 1350 and 1250°C, respectively. Okamura and colab. [2] have obtained tialite at 1375°C starting with alumina oxide and titanium oxide gel. Buscaglia and colab. [3] have studied the phase formation mechanism of the tialite in the presence of magnesium oxide. At low temperatures (1100-1200°C) magnesium spinel is formed, that react with the tialite at

higher temperature forming a solid solution with tialite structure. Damaestri and Giachello [4] have studied the influence of iron oxide on the tialite stability showing that it is connected to the  $\text{Fe}_2\text{O}_3\cdot\text{TiO}_2$  formation that dissolves in tialite leading to its thermodynamic stabilization. Zaharescu and colab. [5] have studied the tialite formation starting either with mixtures individual reactive powders obtained by sol-gel method or by binary powders obtained by simultaneous gelation of the two cations. In the first case the tialite formation takes place at  $1208^\circ\text{C}$ , by an exothermal effect, contrary to the results mentioned above. When binary powders obtained by simultaneous gelation were used, different results were obtained depending on the preparation procedures. The tialite formation was accompanied by an endothermic effect at  $1350$  or  $1305^\circ\text{C}$ .

Table 1. Results obtained by different researchers concerning the thermal effects recorded at tialite formation.

No.	Composition	Method of preparation	Temperature range ( $^\circ\text{C}$ )	Characteristic effects and assignement ( $^\circ\text{C}$ )	Ref
1.	$\text{Al}_2\text{O}_3\cdot\text{TiO}_2$	a) diphasic from boehmite and anatase	810–1410	1090 (exo) – $\alpha$ -A crystallisation	[1]
				1350 (endo) – AT formation	
	$\text{Al}_2\text{O}_3\cdot\text{TiO}_2 + \text{MgO}$	b) sol-gel mixtures	690–1330	1010 (exo) – $\alpha$ -A crystallisation	
				1250 (endo) – AT formation	
	$\text{Al}_2\text{O}_3\cdot\text{TiO}_2 + \text{Fe}_2\text{O}_3$		810-1410	980 (exo) – $\alpha$ -A crystallisation	
				1350 (endo) – AT formation	
2.	$\text{Al}_2\text{O}_3\cdot\text{TiO}_2$	Sol-gel	100-1500	90-250 (endo) – $\text{H}_2\text{O}$ removal	[2]
				450 (exo) - burning out organics	
				1375 (endo) – AT formation	
3.	$\text{Al}_2\text{O}_3\cdot\text{TiO}_2$	Sol-gel	800-1300	800-900 (exo) – $\alpha$ -A crystallisation	[3]
				650-750 (exo) – anatase crystallisation	
				750-900 (exo) – rutile crystallisation	
				1350 (endo) – AT formation	
4.	$\text{Al}_2\text{O}_3\cdot\text{TiO}_2$	Mixtures of monocomponent sol-gel oxides	500-1400	960 (exo) – $\alpha$ -A crystallisation	[5]
				1208 (exo) – AT formation	
		Sol-gel simultaneous gelation	a	775 (exo) – rutile crystallisation	
				960 (exo) – $\alpha$ -A crystallisation	
				1350 (endo) – AT formation	
			b	740 (exo) – rutile crystallisation	
				970 (exo) – $\alpha$ -A crystallisation	
				1350 (endo) – AT formation	

On may notice that although the reaction of tialite formation was studied very much the results are not concordant, in some cases being contradictory.

In the present work the reaction of tialite formation with addition of two mineralizers, which act simultaneously, in correlation with the phase equilibria relations, was studied.

## 2. Experimental

Four types of samples were synthesized using as mineralizers  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$ . The composition of the studied samples were selected in such way to belong to the  $\text{Al}_2\text{O}_3\text{-TiO}_2$  -  $\text{MgO}\cdot\text{Al}_2\text{O}_3$  -  $\text{MgO}\cdot\text{TiO}_2$  ternary subsystem or to the  $\text{Al}_2\text{O}_3\text{-TiO}_2$ -  $\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$  -  $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3\cdot\text{TiO}_2$  -  $\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$  -  $\text{MgO}\cdot\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3\cdot\text{TiO}_2$  -  $\text{MgO}\cdot\text{Al}_2\text{O}_3$  -  $\text{Fe}_2\text{O}_3\cdot\text{TiO}_2$  pseudo- ternary systems. The corresponding ratio of each compound is presented in the Table 2.

Table 2. Theoretical mineralogical compositions of the synthesized masses.

No. sample	Mineralogical composition, %					
	AT	AF	$\text{A}_3\text{S}_2$	MA	MT	FT
1*	72	10	18	-	-	-
2	80	-	-	10	10	-
3*	80	10	-	10	-	-
4	80	-	-	10	-	10

- 1a - synthesized from oxides; sand was used as  $\text{SiO}_2$  source
- 1b - synthesized from oxides and kaolin
- 1c - synthesized from oxide mixtures obtained by sol-gel method
- 3a - synthesized from commercial raw materials
- 3b - synthesized from oxide mixtures obtained by sol-gel method

The raw materials used and the preparation procedures were different. For the sample (1) the  $\text{SiO}_2$  source was either sand (1a), or kaolin which brings also part of alumina (1b). Sample (1c) was prepared from oxide mixtures obtained by sol-gel method. The samples 2 and 4 were obtained from reagent grade oxides and sample 3 was prepared both from reagent grade chemicals and sol-gel method. The samples were submitted to thermal analysis in order to establish the solid state reactions which occur by heating. The phase composition obtained after thermal treatment was determined by X-ray diffraction.

## 3. Results

### 3.1. Study of the solid state reactions by thermal analysis

The results obtained by thermal analysis are presented in Table 3. For the sample (1a) only an endothermic effect at  $1205^\circ\text{C}$  is noticed, which may be assigned to the tialite formation. For the same composition, when kaolin was used as  $\text{SiO}_2$  and partially  $\text{Al}_2\text{O}_3$  source, two thermal effects were noticed. The first effect occurs at  $540^\circ\text{C}$  and is followed by mass loss. It may be assigned to water evolution from the kaolin according to the reaction presented in Table 3. The second effect, at  $1000^\circ\text{C}$ , is assigned to the formation of mullite from meta-kaolinite. In the case when the same composition was obtained from oxide mixture obtained by sol-gel method, two exothermal effects are noticed, at  $850^\circ\text{C}$ , assigned to the rutile crystallization and at  $1310^\circ\text{C}$ , assigned to the tialite formation. For the sample (2) an endothermic effect at  $400^\circ\text{C}$  and an exothermal effect at  $990^\circ\text{C}$  are observed. The first effect is assigned to the  $\text{CO}_2$  elimination from  $\text{MgCO}_3$ , and the second is assigned to the magnesium spinel formation. In this case no special effect assigned to the tialite formation was noticed. In the case of the sample (3a), the first effect at  $400^\circ\text{C}$ , is characteristic to the  $\text{MgCO}_3$  decarbonation and the second one, which occurs at  $1240^\circ\text{C}$ , to the tialite formation. In the case of sample (3b) only one thermal effect is noticed at  $1185^\circ\text{C}$  corresponding to the tialite formation. For the sample (4), only the effect assigned to the  $\text{MgCO}_3$  decomposition was noticed.

Table 3. Thermal effects obtained by DTA/TG analysis.

Composition	Temperature °C	Type of effect	Reactions
1a	1205	endothermic	tialite formation
1b	540 1000	endothermic exothermal	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \Rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{H}_2\text{O}$ $3(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \Rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 4\text{SiO}_2$
1c	850 1310	exothermic exothermic	rutile crystallization tialite crystallization
2	400 990	endothermic exothermic	$\text{MgCO}_3 - \text{CO}_2 \Rightarrow \text{MgO}$ $\text{MgO} + \text{Al}_2\text{O}_3 \Rightarrow \text{MgO} \cdot \text{Al}_2\text{O}_3$
3a	400 1240	endothermic endothermic	$\text{MgCO}_3 - \text{CO}_2 \Rightarrow \text{MgO}$ tialite formation
3b	1185	endothermic	tialite formation
4	400	endothermic	$\text{MgCO}_3 - \text{CO}_2 \Rightarrow \text{MgO}$

### 3.2. Studies of the mineralogical composition

The mineralogical composition of the samples thermally treated in dynamic and isothermal conditions was studied by X-ray diffraction. The results obtained in dynamic conditions are presented in Table 4. From this table results that the main mineralogical component in all cases is tialite. Besides tialite diffraction lines, some diffraction peaks corresponding to the raw materials rutile and  $\alpha$ -alumina were noticed. The rutile is not present in the samples prepared by sol-gel method, in which alumina is almost detectable. As concern the equilibrium components  $\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  and  $\text{MgO} \cdot \text{TiO}_2$  they were not detected by X-ray diffraction and  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  was present only in the samples 2 and 3a.

Table 4. Mineralogical composition of the samples thermally treated at 1400°C in nonisothermal conditions.

Composition	$\text{Al}_2\text{TiO}_5$	Rutile	$\alpha\text{-Al}_2\text{O}_3$	$\text{MgO} \cdot \text{Al}_2\text{O}_3$
1a	+++	++	++	-
1b	+++	++	++	-
1c	+++	-	traces	-
2	+++	+	++	+
3a	+++	+	++	traces
3b	+++	-	traces	-
4	+++	+	++	-

In order to clear up the evolution of chemical reactions versus temperature and time, the mineralogical composition of the samples thermally treated in isothermal conditions with a 2 hours plateau at highest temperature was studied. A more detailed analysis was realized for the samples prepared by sol-gel method, the results being presented in Table 5.

Table 5. Mineralogical composition of the samples obtained by sol-gel method submitted to thermal treated for 2 ours at several temperatures.

Composition	Temperature, [°C]	Mineralogical components
1c	450	amorphous powder
	900	rutile, mullite
	1400	tialite, traces of $\alpha$ -alumina
3b	450	amorphous powder
	900	rutile, $\alpha$ -alumina, aluminum iron oxide
	1400	tialite, traces of $\alpha$ -alumina

It was noticed that at after annealing at 450<sup>0</sup>C, both (1c) and (3b) powders were amorphous. At 900<sup>0</sup>C for the sample (1c) the mullite formation was already observed, which is an equilibrium component and that of crystallized rutile. At 1400<sup>0</sup>C the tialite diffraction lines, which is an equilibrium component and traces of un-reacted  $\alpha$ -alumina were noticed. For the sample (3b) the formation of aluminum iron oxide is observed, which is an equilibrium component, that vanishes at 1400<sup>0</sup>C. The mineralogical composition for all other samples is presented in Table 6.

Table 6. Mineralogical composition of the samples thermally treated at 1400<sup>0</sup>C, 2 hours in isothermal conditions.

Composition	Al <sub>2</sub> TiO <sub>5</sub>	rutile	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	3Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub>	MgO.Al <sub>2</sub> O <sub>3</sub>
1a	+++	-	+	+	-
1b	+++	-	+	traces	-
1c	+++	-	traces	+	-
2	+++	+	+	-	+
3a	+++	-	++	-	-
3b	+++	-	+	-	+
4	+++	-	++	-	traces

On may notice that, as compared to the results obtained on samples obtained by dynamic thermal treatment, in the latter case the reactions proceed to the raw materials consumption. In the same time in the samples (1a) and (1b) the diffraction lines corresponding to the mullite that is an equilibrium component are noticed.

#### 4. Discussion

In the paper the solid state reactions at tialite formation in the presence of mineralizers in correlation with the phase equilibria were studied.

The studies realized by thermal analysis have shown the complexity of the reactions, depending on the sub-system to which the compositions belong and the type of raw materials used. The tialite formation takes place in most cases with and endothermic effect (exception samples 1c), confirming the literature data. However, the temperature of tialite formation occurs in a large domain of temperature ranging between 1185 and 1350<sup>0</sup>C. That means that the addition of mineralizers decreases the temperature of tialite formation. In the presence of mineralizers the equilibrium components are formed in first stage (aluminates, ferrites, titanates), which represents crystallization centers for tialite crystallization. The lowest temperature was obtained when sol-gel method was used in order to prepare the reaction mixtures and the mineralizers used were Fe<sub>2</sub>O<sub>3</sub> and MgO, respectively.

The studies have shown that in all cases the tialite formation, which is the main component in all selected samples, was enhanced. The reactions proceed slowly to the equilibrium, showing some unreacted raw materials even at 1400<sup>0</sup>C. Some of the equilibrium components that should be formed were not determined by X-ray diffraction, due to their solubilisation, in the tialite structure fact that confirms the previous literature data. The magnesium spinel was identified only in some samples, in which it co-existed with aluminum iron oxide and especially in dynamic conditions. That means that aluminum iron oxide is the first to be dissolved in tialite structure.

The incorporation of the binary compounds mentioned in the tialite network leads to the thermodynamic stabilization of this compound at low temperatures

#### 5. Conclusions

In the present paper the simultaneous influence of some groups of two mineralizers on the tialite formation by solid state reaction was studied. It was noticed that in all studied cases the mineralizers addition was favorable, leading to the decrease of the formation temperature as compared

with the literature data. The X-ray diffraction study has shown that for the samples thermally treated in dynamic conditions the main component was tialite, but some un-reacted raw materials still exists even at 1400<sup>0</sup>C. For the samples thermally treated in isothermal conditions, at 1400<sup>0</sup>C, among the raw materials only traces of  $\alpha$ -alumina still exist. Among the phase equilibrium components which should formed at high temperature only mullite and magnesium spinel was noticed. The other compounds were dissolved in the tialite structure, determining both its formation in a very high amount at low temperature and their thermodynamic stabilization.

### References

- [1] A.V. Prasadaraao, U. Selvaraj, S. Komarneni, A. S. Bhalla, R. Roy, J. Am. Ceram. Soc., **75**, 1529 (1992).
- [2] H. Okamura, E. A. Baringer, H. K. Bowen, J. Mater. Sci., **24**, 1867 (1989).
- [3] V. Buscaglia, P. Nanni, G. Battilana, G. Aliprandi, C. Carry, J. Eur. Ceram.Soc., **13**, 411 (1994).
- [4] P. P. Damaestri, A. Giachello, Proc. 4<sup>th</sup> Int. Symp. Ceram. Mater. Compon. Engines, Goteborg, June 10-12, p.1170, 1991.
- [5] M. Zaharescu, M. Crisan, D. Crisan, N. Dragan, A. Jitianu, M. Preda , J. Eur. Ceram. Soc., **18**, 1257 (1998).