

*Dedicated to the memory of
Professor Petru Spacu (1906–1995)*

TIALITE TYPE SOLID SOLUTIONS FORMATION IN THE $\text{MgO}\cdot\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\cdot\text{TiO}_2\text{-Al}_2\text{O}_3\cdot\text{TiO}_2$ PSEUDO TERNARY SYSTEM

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The mechanism of aluminum titanate (tialite) based solid solutions formation in the $\text{MgO}\cdot\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\cdot\text{TiO}_2\text{-Al}_2\text{O}_3\cdot\text{TiO}_2$ pseudo ternary system was studied. The tialite is the main mineralogical component in the system and besides this, two other components are formed (magnesium spinel and iron titanate), which decrease its temperature of formation and improve the thermodynamic stability. Depending on the composition and firing temperature two types of solid solutions are obtained; a ternary $(\text{Fe,Al})_2\text{TiO}_5$ and a quaternary $(\text{Mg,Fe,Al})_2\text{TiO}_5$ solid solution. All samples have a good sintering behaviour during the thermal treatment nevertheless without additives, tialite formation is accompanied by great volume increasing. The sintering of all samples starts at 1300°C. After thermal treatment, the samples have a reduced open porosity and the average pore radius is about 0,1 μm .

INTRODUCTION

Aluminum titanate (tialite) is an interesting compound studied due to its particular properties such as: high refractoriness, an average thermal expansion coefficient near zero (0.2×10^{-6} to 1×10^{-6} K^{-1}) and a good thermal shock resistance (about 500Wm^{-1}).¹⁻³ This compound is thermodynamically unstable⁴⁻⁷ and in order to increase its stability the addition of different oxides are recommended that lead to solid solution formation.

Aluminium titanate formation by solid-state reaction is difficult to realise due to the great chemical stability of aluminium oxide. Also, the sintering tendency of the raw materials mixtures used for obtaining tialite samples is very weak because the formation of tialite takes place with a volume increase.⁸ For these reasons, when obtaining tialite based products, oxides which either stabilise its structure by forming solid solutions, or improve the sintering tendency of the mixture are introduced in the composition, as additives. Such oxides are MgO , Fe_2O_3 , ZrO_2 , SiO_2 and so on.⁹⁻¹⁵ Studies about simultaneous introduction of two oxides in the composition that can influence tialite formation as well as its sintering tendency were undertaken with good results. Although the number of papers in this field is great, the mechanism of stable solid solution formation with good properties was not yet clearly understood.

The purpose of this paper is the study of the tialite formation in correlation with the phase diagram of the $\text{MgO}\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-TiO}_2$ quaternary system, in which the addition of the magnesium oxide and ferric oxide was taken into consideration besides the two oxide components of tialite.

The subsolidus diagram of the quaternary system

Based on the literature data¹⁶, experimental determinations and a computer program, the subsolidus phase diagram of the quaternary $\text{MgO}\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-TiO}_2$ system was drawn and is represented in Fig. 1. Ten binary compounds are present in this system that divide it into 14 elementary quaternary subsystems

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(Table 1). From the point of view of the present research the $\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3\cdot\text{TiO}_2\cdot\text{Al}_2\text{O}_3\cdot\text{TiO}_2$ pseudo ternary system is very interesting, due to the fact that it contains tialite as main mineralogical component, as well as magnesium spinel, as crystallization nuclei (crystal seeds) for tialite.^{3,9,10} Pseudobrookite forms solid solutions with tialite and reduces its dissociation tendency by solid phase incongruence.^{2,13} The place of the five synthesised samples in the pseudo ternary system is presented in Fig. 1b. The content of tialite in the chosen samples varies from 50 to 90 wt%. The amount of magnesium spinel and pseudobrookite ranges from 10 to 50% wt. The analysis of oxide composition shows that magnesium oxide proportion of samples was in the ranges between 1.42 and 7.08% and the iron oxide between 3.33 and 20.01%.

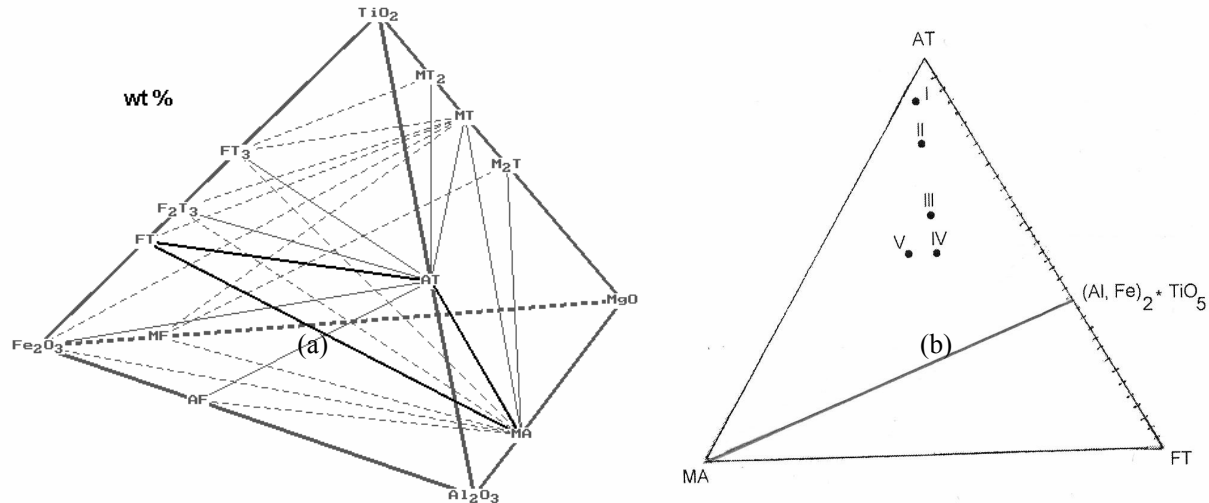


Fig. 1 – Subsolidus phase diagram of the $\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3\cdot\text{TiO}_2$ quaternary system M - MgO; A - Al_2O_3 ; F - Fe_2O_3 ; T- TiO_2
a) Compatibility relations of compounds; b) The place of the synthesized compositions in the $\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3\cdot\text{TiO}_2\cdot\text{Al}_2\text{O}_3\cdot\text{TiO}_2$ pseudo ternary system.

EXPERIMENTAL

The raw materials used for the synthesis were reagent grade aluminum, iron and titanium oxides and magnesium carbonate. The samples were wet-homogenised and the resulted suspension was dried into oven to constant weight. Then, pellets with 20 mm diameter and 5 mm height were obtained by uniaxially pressing at 100 daN/cm^2 . All the samples were thermally treated at temperatures in the range 1250-1350°C with two hours plateau at maximum temperature. On the treated samples the mineralogical composition, by X-ray patterns diffraction (Shimadzu XRD 6000) and the microstructure, by scanning electron microscopy (Scanning Electron Microscope Hitachi S 2600N), were examined. The shrinkage and apparent density were determined as a function of thermal treatment by Archimedes method. Size and pore distribution with mercury porosimeter (Mercury Porosimeter Pascal 240/140) was determined.

Table 1

Quaternary subsystems of the $\text{Al}_2\text{O}_3\cdot\text{TiO}_2\cdot\text{Fe}_2\text{O}_3\cdot\text{MgO}$ quaternary system

No.	Quaternary subsystems	Relative volume of the elementary quaternary subsystems	
		% weight	% molar
1	$\text{Al}_2\text{O}_3\cdot\text{AT}\cdot\text{AF}\cdot\text{MA}$	7.59	12.50
2	$\text{Fe}_2\text{O}_3\cdot\text{AT}\cdot\text{AF}\cdot\text{MA}$	4.85	12.50
3	$\text{Fe}_2\text{O}_3\cdot\text{AT}\cdot\text{MA}\cdot\text{FT}$	5.29	12.50
4	$\text{AT}\cdot\text{MA}\cdot\text{F}_2\text{T}_3\cdot\text{FT}$	1.51	2.50
5	$\text{Fe}_2\text{O}_3\cdot\text{MA}\cdot\text{MT}\cdot\text{FT}$	8.01	12.50
6	$\text{MA}\cdot\text{MT}\cdot\text{F}_2\text{T}_3\cdot\text{FT}$	2.28	2.50
7	$\text{AT}\cdot\text{MA}\cdot\text{FT}_3\cdot\text{F}_2\text{T}_3$	2.72	3.75
8	$\text{Fe}_2\text{O}_3\cdot\text{MA}\cdot\text{MF}\cdot\text{MT}$	9.60	12.50
9	$\text{MA}\cdot\text{MT}\cdot\text{FT}_3\cdot\text{F}_2\text{T}_3$	4.12	3.75
10	$\text{AT}\cdot\text{MA}\cdot\text{MT}\cdot\text{FT}_3$	8.44	6.25
11	$\text{MA}\cdot\text{MF}\cdot\text{M}_2\text{T}\cdot\text{MT}$	9.55	4.16
12	$\text{AT}\cdot\text{MT}\cdot\text{MT}_2\cdot\text{FT}_3$	3.00	2.08
13	$\text{MgO}\cdot\text{MA}\cdot\text{MF}\cdot\text{M}_2\text{T}$	28.48	8.33
14	$\text{TiO}_2\cdot\text{AT}\cdot\text{MT}_2\cdot\text{FT}_3$	4.51	4.16
Total volume		100.0	100.0

Note: M- MgO; A - Al_2O_3 ; F- Fe_2O_3 ; T- TiO_2

RESULTS

Mineralogical composition of the synthesised samples

The mineralogical composition of samples thermally treated in the 1250-1350°C temperature range was determined. X-ray diffraction lines of the sample 1, which in equilibrium conditions should contain the smallest magnesium spinel and pseudobrookite amounts (5 wt%), are presented in the Fig. 2 as a function of firing temperature. At the temperature of 1250°C, only two phases were identified, a ternary solid solution resulted by dissolution of Fe_2TiO_5 in the tialite lattice and α -alumina. When the temperature of the thermal treatment was increased to 1300°C and 1350°C, it was found that the solid solution becomes quaternary and the characteristics lines of α -alumina decrease. The sample 2 (Fig. 3) with a double quantity of the two components mentioned above (10 wt%), shows at 1250°C also a ternary solid solution but the presence of the rutile and α -alumina was also noticed; a similar situation is also observed at 1300°C. By the increasing of temperature to 1350°C the diffraction lines specific for rutile disappear and the $(\text{Mg,Fe,Al})_2\text{TiO}_5$ quaternary solid solution is formed.

Fig. 2 – Phase evolution of sample 1 versus firing temperature.

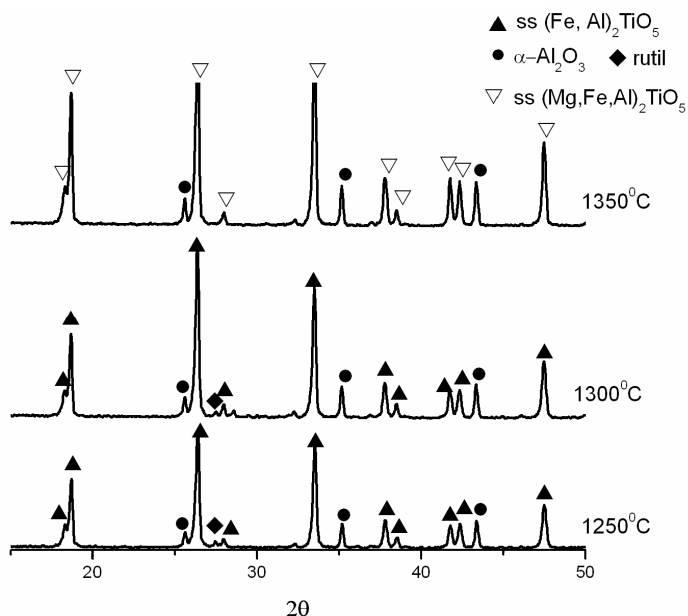
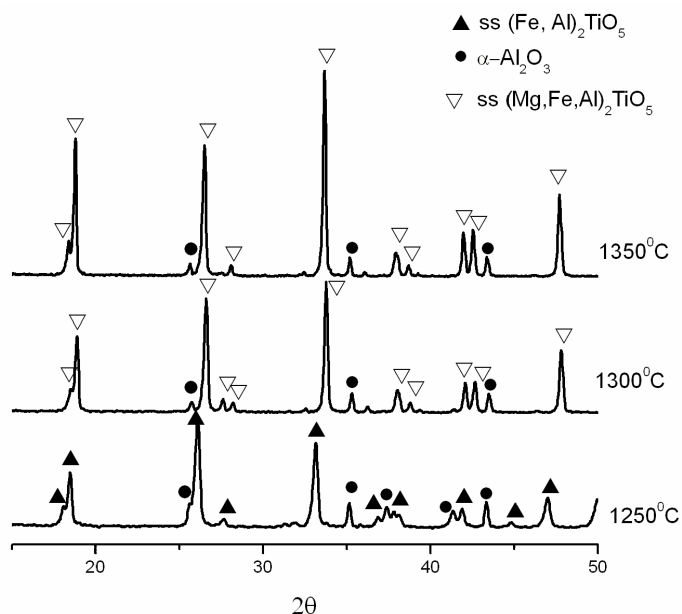


Fig. 3 – Phase evolution of sample 2 versus firing temperature.

For the sample 3 (Fig. 4) the formation of a quaternary solid solution starting even from 1250°C can be noticed, but beside of this compound the specific peaks of magnesium spinel and the diffraction lines for the two raw materials, rutile and α -alumina, are also found. By temperature increasing to 1300°C and respectively 1350°C, practically the same intermediate phases are noticed, but their proportion decreases. This fact shows on the one hand that the limit of magnesium spinel solubility for the solid solution formation was exceeded, and on the other hand that the solid state reaction between the components is not fully realized. For the sample 4 (Fig. 5) the X-ray diffraction patterns at the temperature of 1250°C and 1300°C show the presence of the $(\text{Fe,Al})_2\text{TiO}_5$ ternary solid solution formed by pseudobrookite (Fe_2TiO_5) dissolution in tialite lattice and the peaks for magnesium spinel, rutile and α -alumina. At the temperature of 1350°C the rutile lines were not observed because this compound reacted with the ternary solid solution leading to the formation of the $(\text{Mg,Fe,Al})_2\text{TiO}_5$ quaternary solid solution. For the sample 5 (Fig. 6), in the studied temperature range, the presence of three phases, that are a ternary solid solution, magnesium spinel and α -alumina (like in the case of the sample 4) can be noticed.

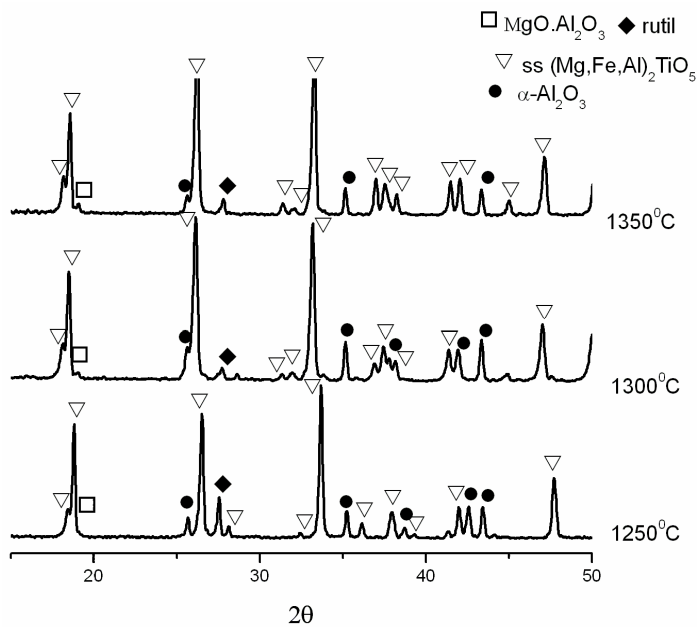


Fig. 4 – Phase evolution of sample 3 versus firing temperature.

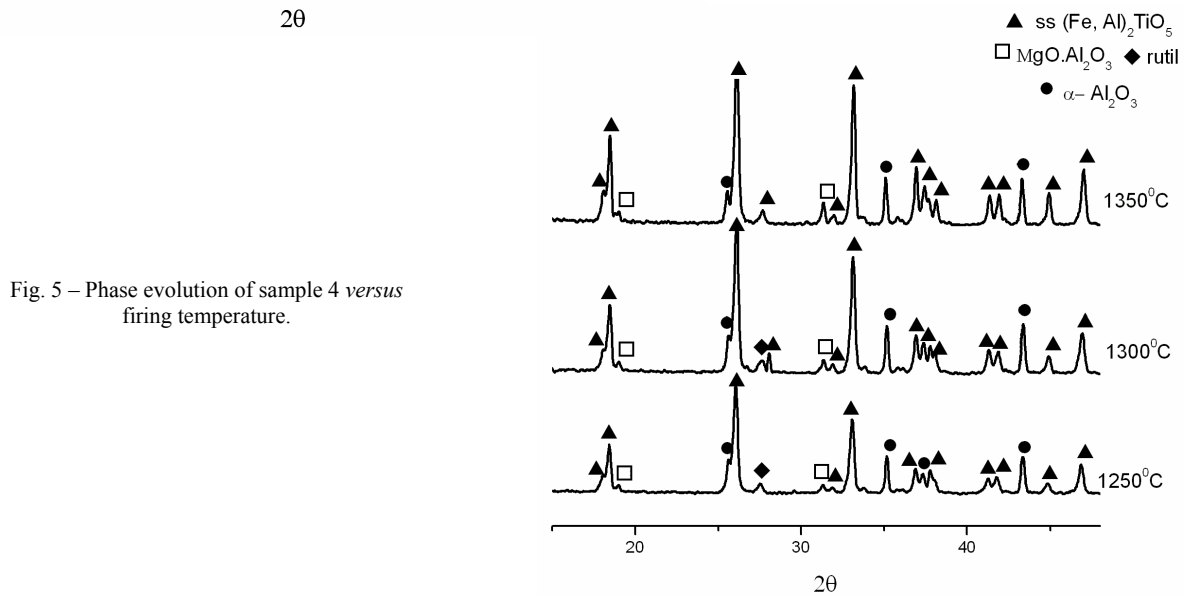
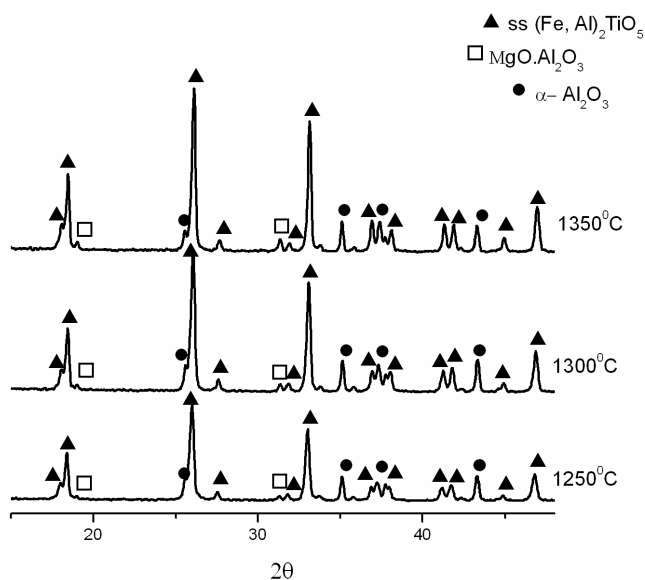


Fig. 5 – Phase evolution of sample 4 versus firing temperature.

The samples 4 and 5 are placed in the stability range of the $(\text{Al,Fe})_2\text{TiO}_5$ solid solution, in which the magnesium spinel is not soluble. It results that, the first compound, Fe_2TiO_5 , formed at thermal treatment below

1250^oC, totally dissolves into the Al₂TiO₅ lattice and determines a ternary solid solution formation. The obtained results show that using of iron oxide in composition improves the thermodynamic stability of tialite. The second phase resulted from the solid state chemical reaction was magnesium spinel which was totally sublimised in the case of the samples 1 and 2, even at 1250^oC leading to (Mg,Al,Fe)₂TiO₅ quaternary solid solution formation. In the case of sample 3, although the quaternary solid solution was formed, magnesium spinel can be found between mineralogical components at all thermal treatment temperatures and this shows that it was introduced into composition in a greater proportion than its solubility limit. The last two samples are constituted of (Al,Fe)₂TiO₅ ternary solid solution and no a quaternary one, as was found in previous cases.

Fig. 6 – Phase evolution of sample 5 versus firing temperature.



Ceramic properties

The ceramic properties of the synthesised samples were determined by the measuring of shrinkage, apparent density and water absorption as a function of firing temperature. The results are presented for three selected samples (1, 3 and 5). For the sample 1, the variation of these properties were presented in Fig. 7 and present a normal evolution, namely the apparent density and shrinkage increases, while the water absorption decreases. A similar variation can be noticed for samples 3 and 5 (Figs. 8 and 9).

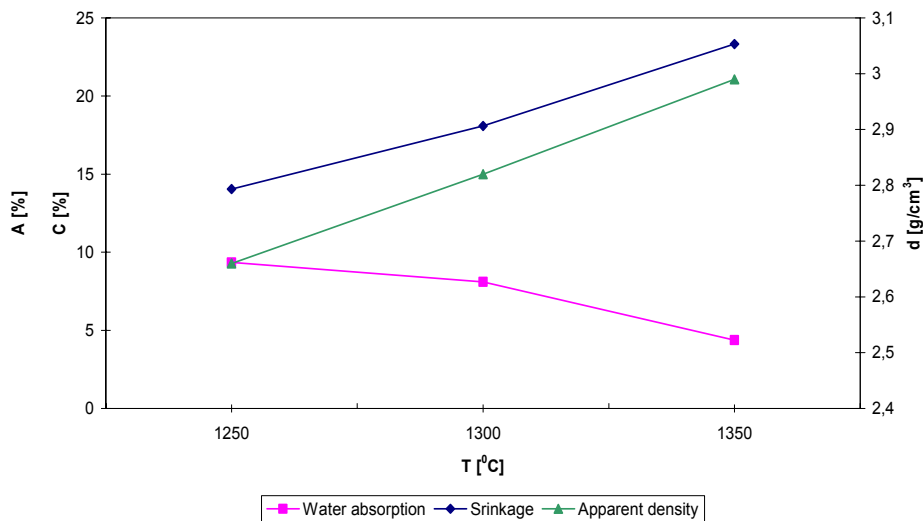


Fig. 7 – Water absorption, shrinkage and apparent density versus firing temperature for sample 1.

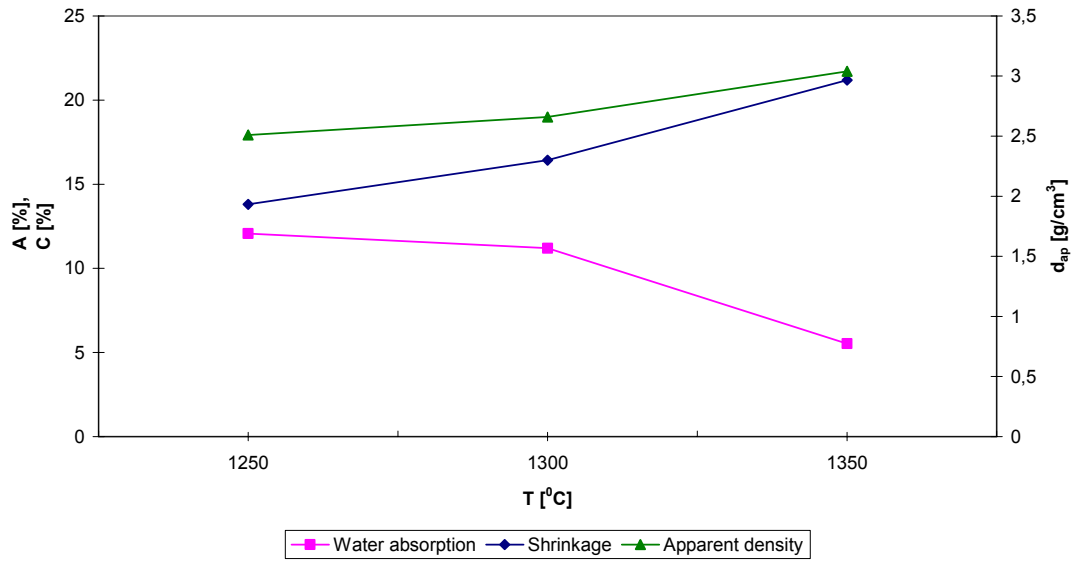


Fig. 8 – Water absorption, shrinkage and apparent density *versus* firing temperature for sample 3.

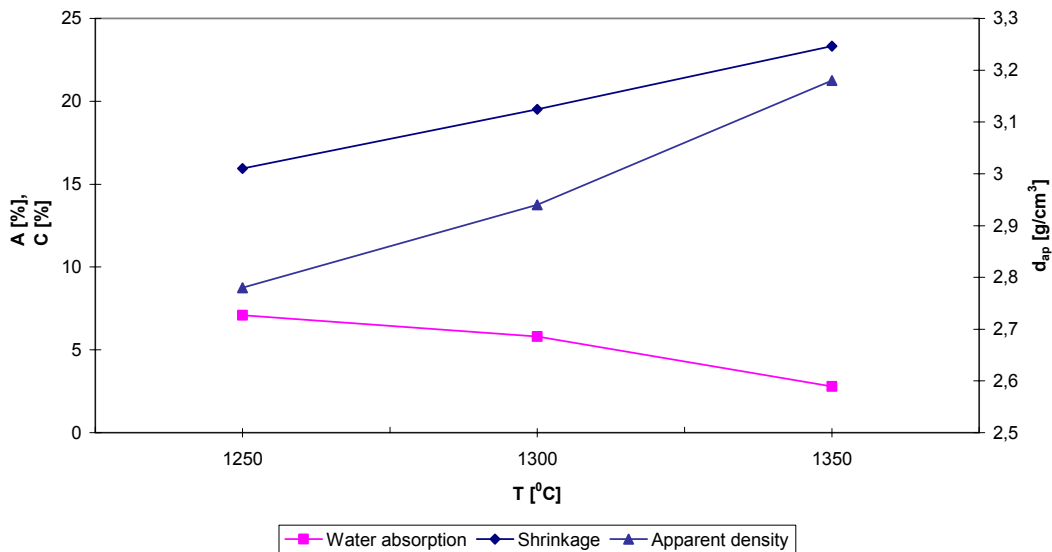


Fig. 9 – Water absorption, shrinkage and apparent density *versus* firing temperature for sample 5.

The measured shrinkages are remarked by high values nevertheless that the tialite formation, by solid phase reactions, is accompanied by a volume increase. This fact could be explained by ternary or quaternary solid solution formation. For all three samples a discontinuity at 1300°C was observed. Due to the fact that, the samples have different mineralogical compositions, it results that at this temperature, the common sintering process begins for all the synthesised samples.

Pore distribution

The above presented data show that the samples have a low porosity, which makes them suitable to be used as refractory materials. The pore size distribution was determined for sample 5, which has the lowest porosity according to the previous water absorption determinations (Fig. 10). It was found that the pore size distribution is situated in a narrow range around 0.1 μm. The volume of the pores with sizes above 1 μm is insignificant and the total area of the pores is 0.88 m²/g.

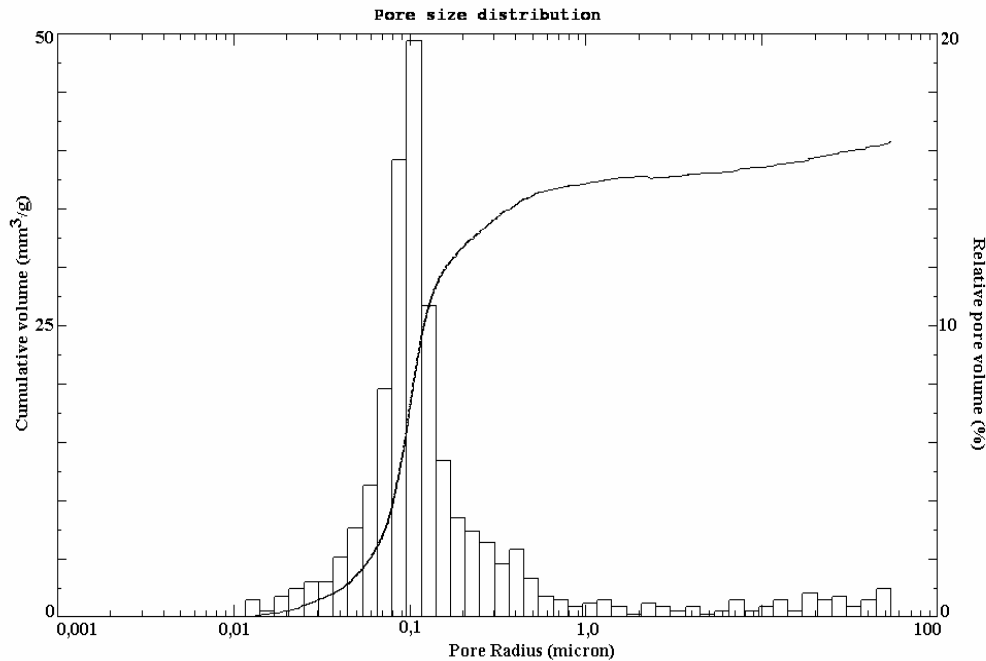


Fig. 10 – Pore size distribution for sample 5, thermally treated at 1350°C.

CONCLUSIONS

A study referring to the tialite synthesis was undertaken in correlation with phase diagram. The samples composition was chosen in the $\text{MgO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-TiO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2$ pseudo ternary system in which the addition of the magnesium oxide and iron oxide was taken into consideration besides the two oxide components of tialite. Mineralogical composition determined by X-ray diffraction patterns showed that a ternary solid solution $(\text{Fe,Al})_2\text{TiO}_5$ was formed in all cases at temperature of 1250°C. For the samples with a content of 10-20 wt% of magnesium and iron oxide, magnesium spinel and pseudobrookite were identified, that solubilised in tialite and a $(\text{Mg,Fe,Al})_2\text{TiO}_5$ quaternary solid solution is formed. For the samples with 50 wt% total amount of the two mentioned components, it was found that only the ternary solid solution was noticed and magnesium spinel is formed. All the samples no matter of the composition or thermal treatment contain α -alumina as a non-equilibrium compound, due to its amphoteric character low reactivity. The sintering of all samples starts at 1300°C. After thermal treatment, the samples have a reduced open porosity and the average pore radius is about 0.1 μm .

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