

# MATERIALE CERAMICE TIALITICE CU DILATARE TERMICĂ REDUSĂ TIALITE-BASED CERAMIC MATERIALS WITH LOW THERMAL EXPANSION

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*In the present paper it was studied the synthesis of tialite-based ceramic materials with partially stabilized zirconium dioxide.*

*For the synthesis were used: kaolin, TiO<sub>2</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> as raw materials. On the thermal treated samples were determined the real mineralogical composition by using x-ray diffraction (Shimadzu 6000), the firing contraction, the water absorption and the apparent density. The microstructure of ceramics was determined by scanning electron microscopy (SEM / Hitachi 2600N). The dilatometric analysis (Netzsch DIL 402 PC) was carried on the optimal samples, the coefficient of thermal expansion values being in agreement with the literature data.*

*In order to obtain tialite-based ceramic materials in favourable conditions, their compositions must be situated in the quaternary elementary subsystem Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-3Al<sub>2</sub>O<sub>3</sub>-2SiO<sub>2</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>-ZrO<sub>2</sub>.*

*În prezenta lucrare s-a studiat sinteza unor materiale ceramice pe bază de tialit și dioxid de zirconiu parțial stabilizat.*

*Pentru sinteză s-au folosit ca materii prime caolinul, TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>. Pe probele astfel tratate termic, s-a determinat compoziția mineralogică reală prin difracție de raze X (Shimadzu 6000), contracția la ardere, absorbția apei și densitatea aparentă. Microstructura probelor ceramice s-a determinat prin microscopie electronică cu baleiaj (SEM / Hitachi 2600N). Pe probele optime s-a efectuat și analiza dilatometrică (Netzsch DIL 402 PC), coeficientul de dilatare termică al probelor optime fiind în concordanță cu datele din literatura de specialitate.*

*Pentru obținerea materialelor ceramice tialitice în condiții avantajoase, compoziția acestora trebuie să fie situată în subsistemul cuaternar elementar Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-3Al<sub>2</sub>O<sub>3</sub>-2SiO<sub>2</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>-ZrO<sub>2</sub>.*

**Keywords:** tialite, low thermal expansion, SEM

## 1. Introduction

Aluminium titanate distinguish itself by a great number of applications in mechanical engineering due to its low coefficient of thermal expansion, excellent thermal shock resistance, low thermal conductivity and due to the fact that it is not wetted by the most melted metals. Tialite can be used as refractory for metal casting, for pipes withstanding high temperatures and for other important applications such as burner nozzles, thermocouple covers and thermal insulators for thermic engines etc. [1-4]. The application areas of tialite-based products are, still, limited due to their low mechanical resistances and thermodynamic instability of tialite that occurs below 1280°C. Therefore, to improve the thermodynamic stability and breakage behaviour of the tialite-based products, stabilisers such as Fe<sub>2</sub>O<sub>3</sub>, MgO, SiO<sub>2</sub> etc. can be added in the recipes. They enter into the network and reduce the dissociation rate [3]. Tialite was mixed, also, with other phases such as mullite, zirconium dioxide or complex compositions that improve its sintering process [1]. Aluminium titanate is hard to sinter without additives, but it was

observed that they increase the coefficient of thermal expansion, the main property of tialite. Tialite-based ceramic materials with zirconium dioxide stabilised with calcium oxide were synthesised [5], using different synthesis methods: solid-phase reactions or sol-gel method, starting with soluble precursors for aluminium, titan, zirconium and calcium. Breakage behaviour of aluminium titanate-based ceramics with zirconium dioxide and aluminium trioxide was studied in detail and it was shown that these make possible the control of the propagation of the cracks determined by an external mechanical strain. A constant concern can be observed, nowadays, regarding the usage of natural raw materials to obtain accessible products from the cost point of view [6].

The present paper aims the synthesis and sintering of some tialite-based ceramic materials with low thermal expansion.

## 2. Raw materials, working methods and mode

The raw materials used for synthesis were α-Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and kaolin, the oxide composition expressed in oxides for the

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Table 1

No./ Nr.crt.	Theoretical mineralogical composition (%) <i>Compoziția mineralogică teoretică (%)</i>				Oxide composition (%) <i>Compoziția oxidică (%)</i>			
	AT	A <sub>3</sub> S <sub>2</sub>	ZT	ZrO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	ZrO <sub>2</sub>
1	72	18	5	5	53.30	33.60	5.07	8.03
2	54	36	5	5	56.14	25.69	10.14	8.03
3	45	45	5	5	57.55	21.74	12.68	8.03
4	64	16	10	10	47.38	32.05	4.50	16.07
5	48	32	10	10	49.90	25.02	9.01	16.07
6	40	40	10	10	51.16	21.5	11.27	16.07
7	60	15	10	15	44.42	30.29	4.22	21.07
8	45	30	10	15	46.78	23.70	8.45	21.07
9	37.5	37.5	10	15	47.97	20.4	10.56	21.07

synthesised samples being presented in Table 1 (right). The potential mineralogical composition is presented in Table 1 (left). The tialite -  $Al_2O_3 \cdot TiO_2$  – was chosen due to its low coefficient of thermal expansion and because it offers thermal shock resistance to products. The mullite -  $3Al_2O_3 \cdot 2SiO_2$  - has a major importance since it gives high mechanical resistances to products. The presence of  $ZrO_2 \cdot TiO_2$  determines the transformation from monoclinic  $ZrO_2$  to tetragonal  $ZrO_2$ , who have a martensitic reinforcement. All the necessary quantity of silica to form mullite is given by the kaolin. The quantity of alumina necessary to form tialite is obtained from  $Al_2O_3$  given by kaolin and from the supplementary alumina added. The zirconium dioxide was added in order to obtain tetragonal  $ZrO_2$ . A fraction from  $ZrO_2$  will bond in  $ZrO_2 \cdot TiO_2$ , who can dissolve in monoclinic  $ZrO_2$  to form tetragonal  $ZrO_2$ . This can constitute a reinforcement phase for the matrix formed by  $Al_2O_3 \cdot TiO_2$  and  $3Al_2O_3 \cdot 2SiO_2$ .

The synthesised samples were gravimetrically dosed and wet homogenised by using powder:water:balls ratio equal to 1:1:1 for 2 hours. Then they were dehydrated in a stove oven, at 120 C. All the samples were thermally treated in the (1250-1400) °C temperature range, with a two hours plateau at the maximum temperature of thermal treatment. On the so-treated samples were determined the contraction on firing, water absorption and the apparent density. The mineralogical composition of the samples was determined by using X-ray diffraction, using the Shimadzu XRD 6000 diffractometer. The texture of the sintered samples was determined using the Hitachi 2600 N electronic microscope. The thermal expansion curves were determined by using Netzsch DIL 402 PC dilatometer with software that allows the calculus of the coefficient of thermal expansion. The temperature was increased with a rate of 3°C/min.

### 3. Experimental results

#### 3.1. The mineralogical composition of the thermal treated samples

On the thermally treated samples (based on the  $ZrO_2$  content) at 1400°C the real mineralogical composition was detailed and presented on the x-ray patterns below. As we can notice from the diffraction spectra (Figure 1), at 1400°C in sample 1 are formed mullite, tialite, but also t- $ZrO_2$  and  $A_2T_2S$ . Thus,  $ZrO_2 \cdot TiO_2$  was solubilized in m- $ZrO_2$ , transforming itself into tetragonal  $ZrO_2$ . In sample 2, at 1400°C,  $A_2T_2S$  present in sample 1 at 1400°C, disappears. In sample 3, at 1400°C are formed mullite, tialite and small quantities of ZT and t- $ZrO_2$ . In samples 4 and 5, at 1400°C mullite and tialite are very well formed, but we noticed t- $ZrO_2$ , too. In sample 6 (Figure 2), at 1400°C we noticed the appearance of tialite and t- $ZrO_2$ . In sample 7, at 1400°C the same crystalline compounds are formed, but the tialite amount is smaller. In sample 8, at 1400°C  $2Al_2O_3 \cdot 2TiO_2 \cdot SiO_2$  disappears, while in sample 9 we noticed the appearance of small quantities of mullite, tialite,  $ZrO_2 \cdot TiO_2$  and t- $ZrO_2$  (Figure 3).

#### 3.2. Thermal treatment behaviour

The behaviour on firing was determined by measurements of water absorption, porosity, apparent density and firing contraction (Table 2). For samples 1-3 containing 5%  $ZrO_2$  we noticed a decrease of water absorption for the entire domain of temperature. At 1400°C the value of water absorption is in very tight limits around 13-14%, corresponding to refractory materials. For samples 4-6 containing 10%  $ZrO_2$ , the water absorption values are within the limits of 12-13% at 1400°C. For samples 7-9 containing 15%  $ZrO_2$  we noticed a continuous decrease of the water absorption throughout the temperature range, and the water absorption values are within the limits of 11-12%. In terms of water absorption all samples are suitable because they have values below 15%, which is an allowable limit for refractories.

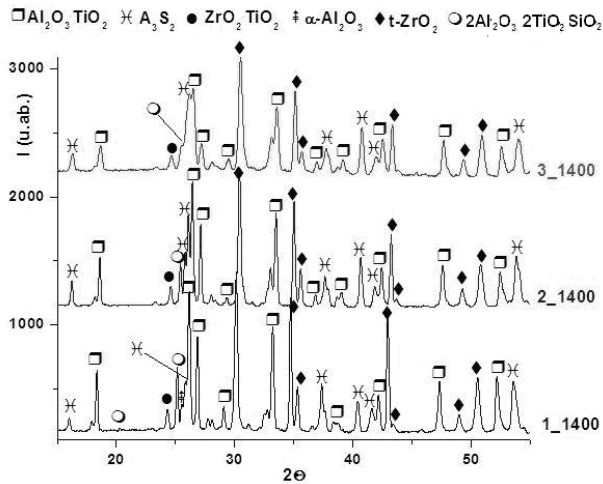


Fig 1 - X-ray spectra of samples 1-3 thermally treated at 1400°C / Spectrul RX pe probele 1-3 tratate termic la 1400 °C.

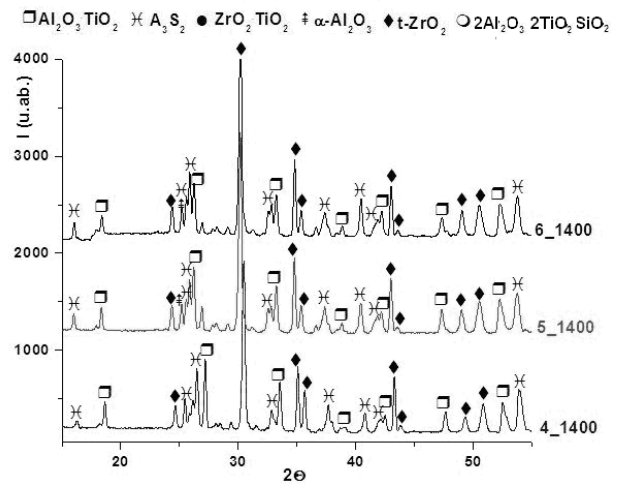


Fig 2 - X-ray spectra of samples 4-6 thermally treated at 1400°C / Spectrul RX pe probele 4-6 tratate termic la 1400 °C.

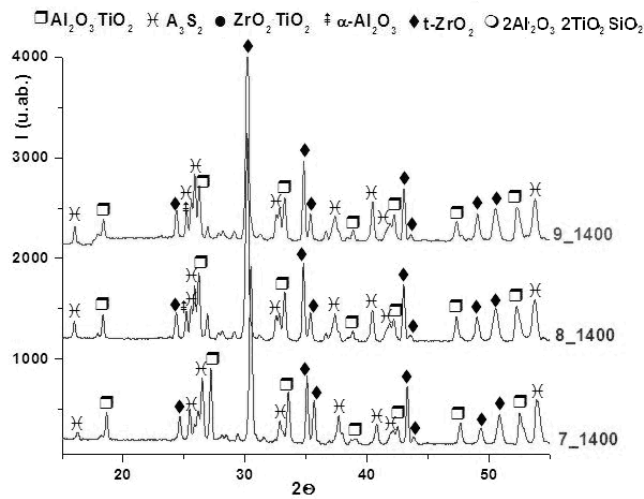


Fig 3 - X-ray spectra of samples 7-9 thermally treated at 1400°C / Spectrul RX pe probele 7-9 tratate termic la 1400 °C.

Table 2

Establish of the sintering characteristics / Determinarea caracteristicilor de sinterizare

No. Nr.	Temperature Temperatura (°C)	Water Absorption Absorbția apei, A(%)	Apparent density Densitatea aparentă, ρ <sub>ap</sub> (g/cm <sup>3</sup> )	Apparent porosity Porozitate aparentă, P <sub>a</sub> (%)	Contraction Con tracție, C (%)
1	1250°C	19.92	2.18	43.42	5.42
2		18.00	2.21	39.79	5.00
3		17.57	2.20	38.65	5.19
4		18.60	2.30	42.78	6.33
5		16.33	2.36	38.53	5.38
6		16.20	2.34	37.90	5.42
7		16.98	2.41	40.92	5.23
8		16.04	2.42	38.81	5.76
9		15.87	2.50	39.67	4.95
1	1300°C	17.91	1.88	33.67	5.85
2		17.10	1.85	31.63	6.00
3		16.32	1.87	30.51	5.85
4		16.07	2.02	32.46	7.95
5		15.10	1.99	30.04	8.14
6		14.85	1.92	28.51	6.61
7		15.20	1.98	30.09	8.24

Table 2 continued

No. Nr.	Temperature Temperatura (°C)	Water Absorption Absorbția apei, A(%)	Apparent density Densitatea aparentă, $\rho_{ap}$ (g/cm <sup>3</sup> )	Apparent porosity Porozitate aparentă, $P_a$ (%)	Contraction Contractie, C (%)
8	1300 °C	16.04	2.42	38.81	5.76
9		15.87	2.50	39.67	4.95
1	1300°C	17.91	1.88	33.67	5.85
2		17.10	1.85	31.63	6.00
3		16.32	1.87	30.51	5.85
4		16.07	2.02	32.46	7.95
5		15.10	1.99	30.04	8.14
6		14.85	1.92	28.51	6.61
7		15.20	1.98	30.09	8.24
8		14.56	2.11	30.72	7.14
9		14.41	2.10	30.26	7.66
1	1350°C	15.03	2.41	36.22	8.14
2		15.90	2.42	38.47	6.90
3		15.05	2.30	34.61	6.52
4		13.62	2.59	35.27	9.00
5		14.04	2.48	34.80	6.95
6		13.84	2.45	33.90	6.61
7		12.04	2.32	27.93	9.14
8		12.99	2.59	33.64	7.47
9		12.78	2.57	32.84	7.80
1	1400°C	13.54	3.36	45.49	8.14
2		14.18	2.02	28.64	6.33
3		13.42	2.04	27.37	7.33
4		11.82	2.30	27.18	9.52
5		12.61	2.12	26.73	6.47
6		11.90	2.13	25.34	7.52
7		11.05	2.27	25.08	10.28
8		11.76	2.15	25.28	8.90
9		11.34	2.09	23.70	7.57

For the same sets of samples the firing shrinkage was determined. For samples 1-3 containing 5% ZrO<sub>2</sub> there was an increase of firing contraction throughout temperature range. sample 1 having a pronounced contraction variation compared with 2 and 3. For the set of samples 4-6 containing 10% ZrO<sub>2</sub> we observed a constant increase for sample 4, while samples 5 and 6 present variations of the contraction depending on the temperature; a greater reduction was seen at around 1400°C for sample 5. The firing contraction is permanently correlated with the water absorption – the contraction increases as the water absorption decreases.

The density is the result of the reactions that occur in the solid phase comprising the water removal from kaolin. polymorphic transformations of zirconium dioxide. forming reactions of the compounds and, in the end, sintering. For samples

1-3, containing 5% ZrO<sub>2</sub>, the change in density is not very large, but for the temperature of 1400°C there was a significant increase in density. For samples 4-6, containing 10% ZrO<sub>2</sub>, the density change is very obvious. Around 1350°C we observed a more pronounced increase of the density. For samples 7, 8 and 9, containing 10% ZrO<sub>2</sub>, we determined the change of the apparent density with the temperature of thermal treatment. Below 1300°C, the density of the material is determined only by the tendency of agglomeration.

### 3.3. Thermal expansion

Thermal expansion is one of the properties that determines in the highest measure the behaviour of a material to thermal applications and can estimate the thermal shock stability. Most pseudobrookite structures are characterized by unusually high expansion coefficients (CTE) along

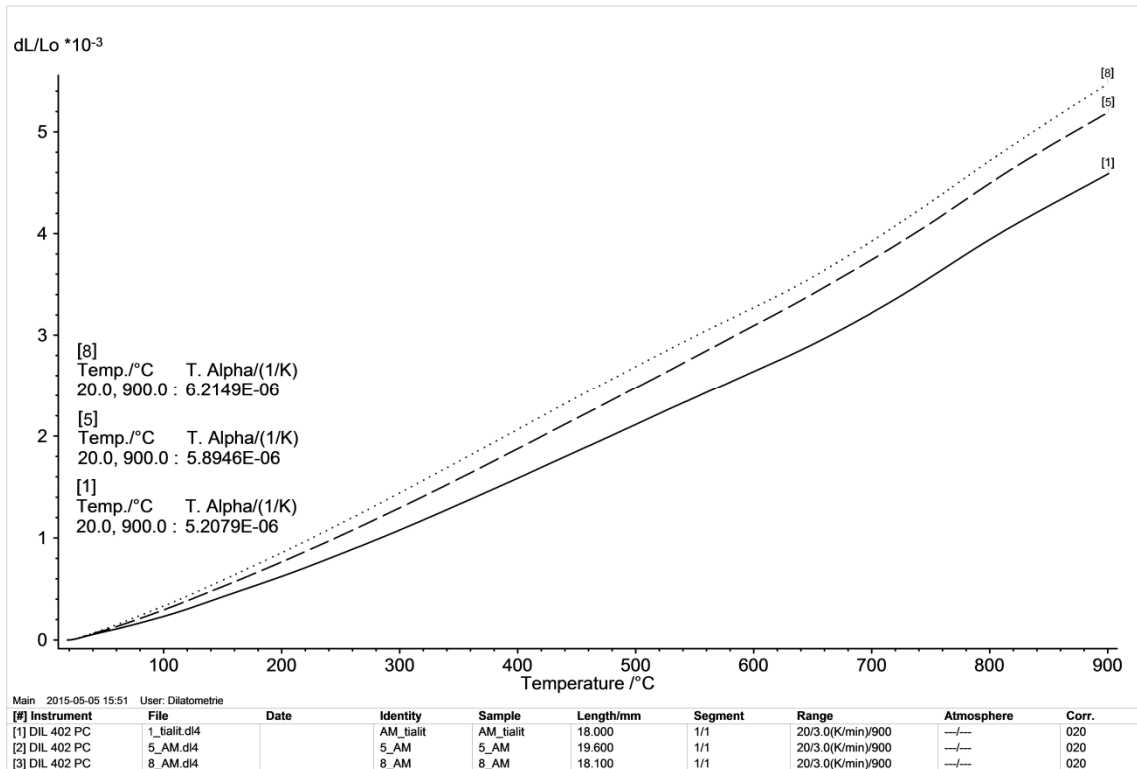


Fig 4 - The thermal expansion of samples 1, 5 and 8 / Dilatarea termică a probelor 1, 5 și 8.

the principal crystallographic directions [6]. Based on the crystallographic expansion the bulk thermal expansion value is estimated to be  $9.4 \times 10^{-6} \text{K}^{-1}$ . However, the experimentally observed bulk thermal expansion is around  $1 \times 10^{-6} \text{K}^{-1}$ , which can be attributed to the stresses at grain boundaries due to anisotropic expansion [7]. Mullite is a strong material with moderate thermal expansion behaviour ( $\alpha_{25}^{1500} = 6.9 \times 10^{-6} \text{K}^{-1}$ ) so it affects the CTE of tialite. The values of the coefficient of thermal expansion for samples 1, 5 and 8 (see Table 1) are low, ranging between  $\alpha_{20}^{900} = 5.21 \cdot 10^{-6} \text{K}^{-1}$  and  $\alpha_{20}^{900} = 6.21 \cdot 10^{-6} \text{K}^{-1}$  (Figure 4), increasing with the content of mullite and  $\text{ZrO}_2$ .

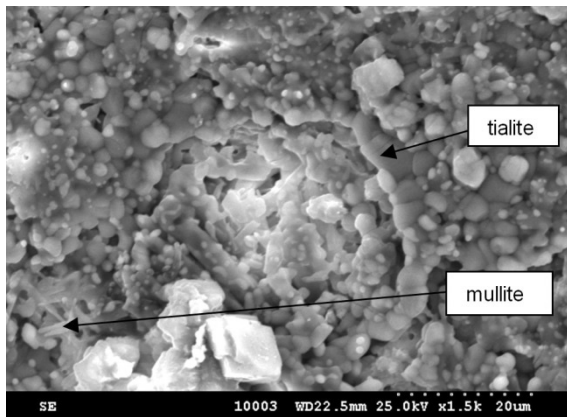


Fig. 5 - The SEM image on sample 1 (x1500) / Imaginea SEM pe proba 1 (x1500).

### 3.4. The microstructure of samples

The microstructure was determined on samples 1, 5 and 8, fired at  $1400^\circ\text{C}$ , with scanning electron microscopy analysis. In Figure 5 a homogenous texture made from tabular form grains of tialite was observed; there are also prismatic form grains that represent mullite. It can be noticed the presence of tialite grains with sizes between 1 and  $5 \mu\text{m}$ . In Figure 6 is observed the presence of tabular grains corresponding to  $\text{ZrO}_2 \cdot \text{TiO}_2$ . The presence of grains with sizes between  $10\text{-}20 \mu\text{m}$  confirms what has been obtained by X-ray diffraction. In Figure 7 the presence of mullite grains can be observed. Mullite

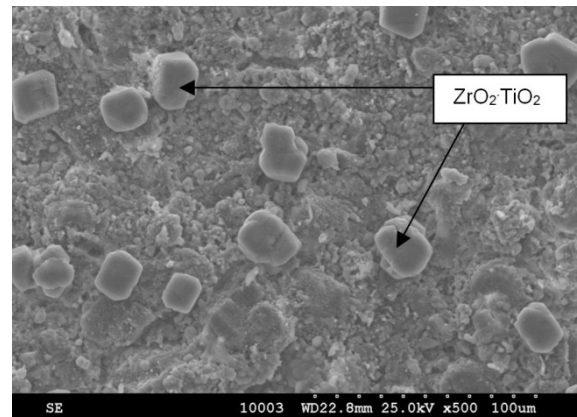


Fig. 6 - The SEM image on sample 5 (x1500) / Imaginea SEM pe proba 5 (x1500).

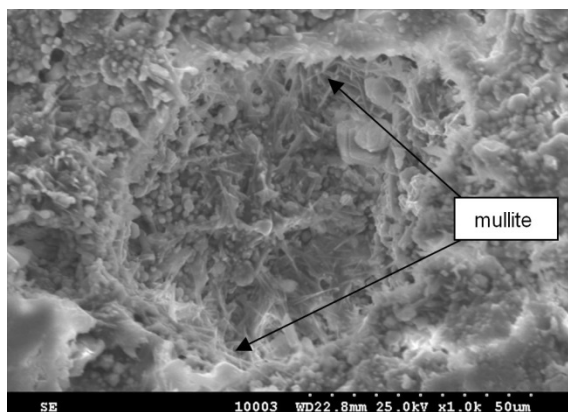


Fig. 7 - The SEM image on sample 5 (x1000) / *Imaginea SEM pe proba 5 (x1000)*.

grows as needle-like shape, especially in the pores. We noticed the presence of tialite, but the grains are of smaller sizes. In Figure 8 we can observe the presence of tialite with fine texture. The granules are well defined, with sizes of 10 $\mu$ m. These microstructures confirm a good degree of sintering for the tialite-based studied ceramics.

#### 4. Conclusions

Nine samples placed in the quaternary system  $\text{Al}_2\text{O}_3\cdot\text{TiO}_2\cdot 3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot\text{ZrO}_2\cdot\text{TiO}_2\cdot\text{ZrO}_2$  were sintered. Thus, tialite gives good resistance to thermal shock, behaving very well as refractory material, too. Mullite is a refractory compound and it may also give good sintering tendency for tialite compositions. The  $\text{ZrO}_2$  percentage ranged between 5%-15%, forming t- $\text{ZrO}_2$  during sintering process. Sintered samples were heat-treated at temperatures between 1250 $^\circ\text{C}$ -1400 $^\circ\text{C}$  and the firing behaviour of the material was determined. We found that when the temperature increases the water absorption decreases and the apparent density increases, this being an appropriate behaviour on sintering for tialite-based ceramic materials. The water absorption for all the samples at 1400 $^\circ\text{C}$  is situated below 15%, which is a suitable value for the studied ceramic materials. Firing shrinkage of the samples was below 12%, which ensures good volume constancy. If the shrinkage is so small then we are confident that the products will not suffer deformations on firing. The samples have low coefficients of thermal

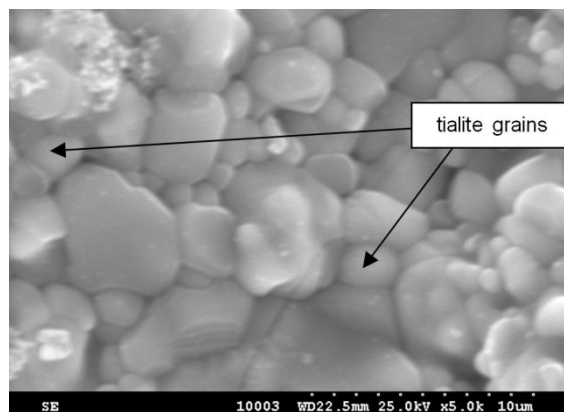


Fig. 8 - The SEM image on sample 8 (x5000) / *Imaginea SEM pe proba 8 (x5000)*.

expansion even within wide temperature ranges (20-900  $^\circ\text{C}$ ). Using X-ray diffraction we determined the mineralogical composition of the thermally treated samples. We noticed that, for all the studied samples, mullite and tialite are present alongside to t- $\text{ZrO}_2$ . These measurements confirmed that we obtained tialite-based materials with low thermal expansion, with potential thermo-mechanical vocation.

#### REFERENCES

1. N. Lequeux, L. Bonhomme-Courry, S. Mussote and P. Boch, Reaction Sintering of  $\text{ZrO}_2\text{-Al}_2\text{TiO}_5$  Composites, Third EURO-CERAMICS. 1993, **1**, 1011.
2. V.N. Antsiferov, S.E. Porozova and E.V. Matygullina. Influence of Mecanochemical Activation of a Charge on Properties of Mullite-Tialite Materials, Science of Sintering. 2004, **36**, 21.
3. M. Preda, A. Melinescu, M. Crişan, S. Preda and M. Zaharescu, Tialite type solid solution 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, Rev. Roum. Chim., 2006, **51**(6), 509.
4. H.Qi, Y. Fan and W. Xing, Effect of  $\text{TiO}_2$  doping on the characteristics of macroporous  $\text{Al}_2\text{O}_3/\text{TiO}_2$  membrane supports, J. Eur. Cer. Soc., 2010, **30**, 1317.
5. U.O. Akkaya and F.Z. Tepehan, Influence of  $\text{Al}_2\text{O}_3\cdot\text{TiO}_2$  ratio on the structural and optical properties of  $\text{TiO}_2\text{-Al}_2\text{O}_3$  nanocomposite films produced by sol gel method. Composites: Part B 2014, **58**, 147.
6. P.Oikonomou, Ch. Dedeloudis, C.J. Stourmaras and Ch. Ftikos, Stabilized tialite-mullite composites with low thermal expansion and high strength for catalytic converters, J. Eur. Cer. Soc., 2007, **27**, 3475.
7. R. Papitha, M. B. Suresh, D. Das and R. Johnson, Effect of micro-cracking on the thermal conductivity and thermal expansion of tialite ( $\text{Al}_2\text{TiO}_5$ ) ceramics, Processing and Application of Ceramics, 2013, **7**(3), 143.

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