CERAMICI TIALITICE CU VOCAȚIE TERMO-MECANICĂ
TIALITE CERAMICS WITH THERMO-MECHANICAL VOCATION

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This work is dedicated to studying the synthesis of some ceramic materials, based on aluminum titanate and magnesium oxide addition so that the composition could be found in the binary pseudosystem Al_2TiO_5-$MgTi_2O_5$.

The chemically pure raw materials used for synthesis were TiO_2, Al_2O_3 and $MgCO_3$ and the synthesis took place by the solid state reaction method. The powders were heat treated at temperatures between 1200°C-1400°C. The real mineralogical composition of the samples was determined by X-ray diffraction, being observed that, at 1400°C a solid state solution of aluminum titanate structure was formed. The microstructural analysis of the synthetized samples showed that, after the heat treatment process, different shape and size crystals were formed, with dimensions ranging between 4 and 8 μm. The formation of bridges between particles was observed due to the sintering of the samples and the presence of both closed and open pores. Measurement of thermal expansion coefficients showed that they increase with increasing $MgTi_2O_5$ content.

În prezenta lucrare s-a studiat sinteza unor materiale ceramice pe bază de titanat de aluminiu şi adaos de oxid de magneziu astfel incât compoziția să se situeze în pseudosistemul binar Al_2TiO_5-$MgTi_2O_5$.

Pentru sinteză s-au folosit ca materii primeTiO_2, Al_2O_3 și $MgCO_3$ de puritate chimică, iar sinteza probelor s-a realizat prin metoda reacțiilor în fază solidă. Probele au fost tratate termic la temperaturi cuprinse intre 1200 și 1400°C.Compoziția mineralogică reală a probelor s-a determinat prin difracție de raze X, constatându-se că, la temeratura de 1400°C, s-a format o soluție solidă cu structura titanatului de aluminiu. Analiza microstructurală a probelor sintetizate a arătat că, în urma procesului de tratament termic se formează cristale de diferite forme și cu dimensiuni cuprinse între 4 și 8 μm. S-a observat formarea punților de legătură între particule ca urmare a sinterizării probelor și prezența porilor atât închiși cât și deschiși. Măsurarea coeficienților de dilatare termică a arătat că aceștia cresc odată cu mărirea conținutului de $MgTi_2O_5$.

Keywords: *aluminum titanate, AT-MT_2 solid solution, SEM, XRD*

1. Introduction

Aluminum titanate (tialite) is a material that interests the researchers in this field, due to the very low coefficient of thermal expansion, high thermal shock resistance, low thermal conductivity, high melting temperature, but also due to the fact that it is a compound with low reactivity and does not react with many molten metals or alloys [1, 2].

Aluminum titanate is recommended for many applications where high wear resistance, thermal insulation and thermal shock resistance are required, for example, thermal and corrosion-resistant coatings, catalytic converter spacer rings and insulating components in car engines, such as gaskets, piston head, soot particle filter and cylinder in diesel engines [3], but also in foundry crucibles, nozzles, thermocouple components, molds for the glass industry, rollers and bearings [2].

Recent studies show that the melting temperature of aluminum titanate is 1840°C, and the temperature below which the compound becomes incongruent is 1280°C [4,5]. Since tialite is an unstable material below 1280°C, its stabilization was attempted below this temperature, by adding stabilizers, such as: MgO, SiO_2, Fe_2O_3.

Aluminum titanate (AT) is a compound with a very low coefficient of thermal expansion with values between $0.2\text{-}1\cdot10^{-6}K^{-1}$ [6] due to the anisotropy of single crystals, therefore the thermal shock resistance is high and the breaking strength is small. The resistance to thermal shock is directly correlated with the temperature, thus, at low temperatures, due to anisotropy, at the grain's boundary appear microcracks that decrease the mechanical resistances of the products, and at high temperatures some of these microcracks disappear increasing the mechanical resistances.

An adequate amount of MgO addition has been shown to be effective not only in restricting the thermal decomposition of tialitic ceramics, but also in improving mechanical strength. The addition of MgO can lead to the formation of a solid solution type Al_2TiO_5-$MgTi_2O_5$ showing that, a substantial amount of MgO (10-25% mol) is needed to significantly increase the life of ceramic components [7-9]. Thus, $MgTi_2O_5$ was thought of as a "pseudobrookit phase stabilizer" for Al_2TiO_5 with a role in creating Al_2TiO_5-$MgTi_2O_5$ solid solutions [10-12].

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Tabel 1

Compoziția oxidică și mineralogică teoretică a probelor studiate
The oxide and the theoretical mineralogical compositions of the studied samples

Compoziție oxidică *Oxide composition (%)*	Al_2O_3	TiO_2	MgO
1	50.44	44.54	5.02
2	47.64	44.83	7.53
3	44.83	45.13	10.04
Compoziție mineralogică teoretică *Theoretical mineralogical composition (%)*	AT	MT_2	
1	90	10	
2	85	15	
3	80	20	

The present paper aims to study and process some tialitic materials included in the binary system AT-MT_2 and the complex characterization of the obtained ceramics.

2. Raw materials, procedure and working methods

The starting materials used for the synthesis were chemically pure α-Al_2O_3, TiO_2, $MgCO_3$. The oxide composition, expressed in oxides, as well as the theoretical mineralogical composition for the three types of synthesized samples is given in Table 1.

It can be seen that 3 compositions were chosen on the AT-MT_2 compatibility line so that the proportion of AT varies between 80 and 90% and that of MT_2 between 10 and 20%.

The synthesized samples were gravimetrically dosed and wet homogenized. They were then dehydrated in an oven at 1200°C. Uniaxially cylindrical samples were pressed at a pressure of 100 MPa. All the samples were heat treated in the temperature range 1200°C -1400°C, with two hours bearing/maintaining at the maximum heat treatment temperature. The mineralogical composition of the samples was determined by X-ray diffraction, using the Shimadzu XRD 6000 diffractometer. The microstructure of the sintered samples was determined with the SEM Quanta FEG scanning electron microscope. The mechanical resistance at compression was determined by a Walter type machine and also the dilatometric behaviour by the DIL 402 Netzsch dilatometer.

3. Experimental results/ results and discussion

3.1. Mineralogical composition of heat-treated samples

The heat treatments were first performed in the range of 1200-1400°C, finding that at 1200°C alumina and rutile are present as the majority mineralogical phases, so we went with the DRX analysis on the heat-treated samples at 1300°C. From these diffractograms it can be seen that the major mineralogical phase is this time the solid solution (AT-MT_2) and the secondary mineralogical phases rutile and alumina decrease in proportion.

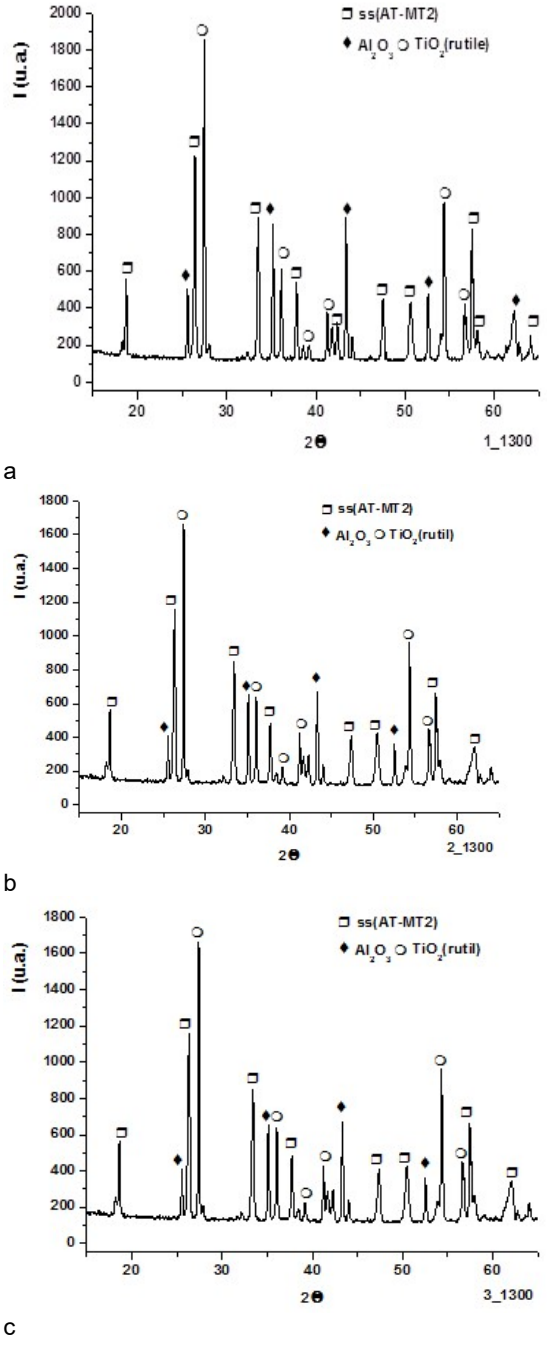


Fig. 1 a-c - X-ray spectra of 1-3 samples heat treated at 1300°C / *Spectrele de difracție de raze X ale probelor 1-3 tratate termic la 1300°C.*

However, it is desired to stabilize the tialitic solid solution, so the heat treatment was increased by 100°C, in the heat-treated samples at 1400°C, finding the formation of the entire desired mineralogical phase ss(AT-MT_2). Figure 1a-c shows the X-ray diffraction spectra of the heat-treated samples at 1300°C and Figure 2a-c shows the X-ray diffraction spectra of the same samples, but heat-treated at 1400°C.

3.2. Samples Microstructures

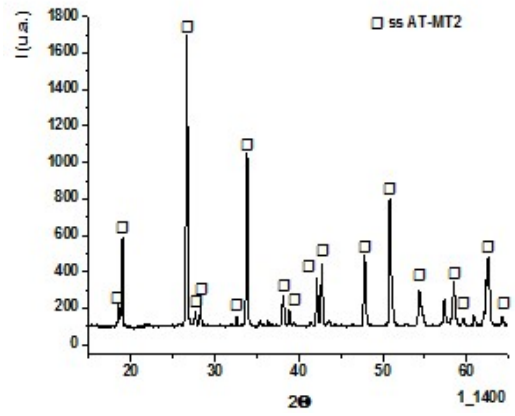
The texture of the samples was examined by SEM, the samples being metallized for 60 sec with an Au film in order to perform electron-microscopic analyses. Analysing sample 1 at 1400°C (Fig. 3a), a dense ceramic is observed, with uneven grain distribution, with random grain orientation, combined porosity (closed and open). Also, it can be seen in Figure 3b an average grain size of 4.63 μm, well-defined granular limits, but also fine capillary pores with an average size of 2.85 μm. By examining sample 2 with a proportion of 15% MT_2 it was observed to obtain a polycrystalline ceramic in the shape of polyhedral grains, with an average grain size of 7.3 μm (see figure 4a) as well as the presence of perfect and imperfect triple junctions, but and fine capillary pores with an average size of 1.35μm (see Figure 4b). Analysing by SEM the sample 3, heat-treated at 1400°C, it can be seen an interconnected porosity, a polyhedral grain shape specific to the tialitic solid solution, as well as an average grain size of 4.07μm (Fig. 5a).

3.3. Dilatometric behavior

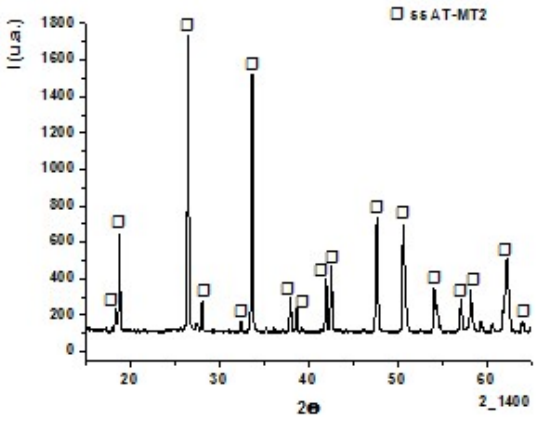
Regarding the coefficient of thermal expansion, it can be said that it varied between $1{,}86 \cdot 10^{-6}$ (for sample 1) and $3{,}86 \cdot 10^{-6}$ 1/K (for sample 3), the best registered coefficient of thermal expansion having very good values, comparable to those in the literature. As the MT_2 content increases, the coefficient of thermal expansion also increases. However, the values of the expansion coefficients are very low, which shows that the products obtained based on these compositions can have very good resistance to thermal shock (Figure 6).

3.4. Mechanical behavior

From a mechanical point of view, the optimal samples, heat-treated at 1400°C were subjected to the compressive strength test on a Walter type machine, the results of the mechanical tests being shown in Table 2. The presented table reveals the data obtained for the Young modulus, which varies between 1.81 and 2.02 GPa, as well as the compressive strength data, the highest being the ample with the highest proportions of tialite.



a



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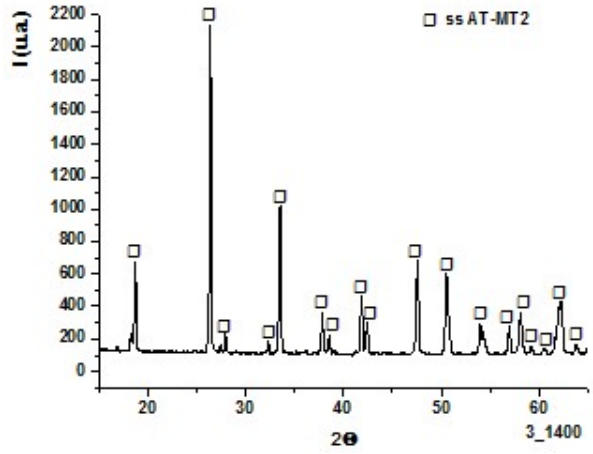

c

Fig. 2 a-c - X-ray spectra of 1-3 samples heat treated at 1400°C
Spectrele de difracție de raze X ale probelor 1-3 tratate termic la 1400°C.

Compression strength data range from 105 to 128 MPa, values in accordance to those in the literature [13] for such products.

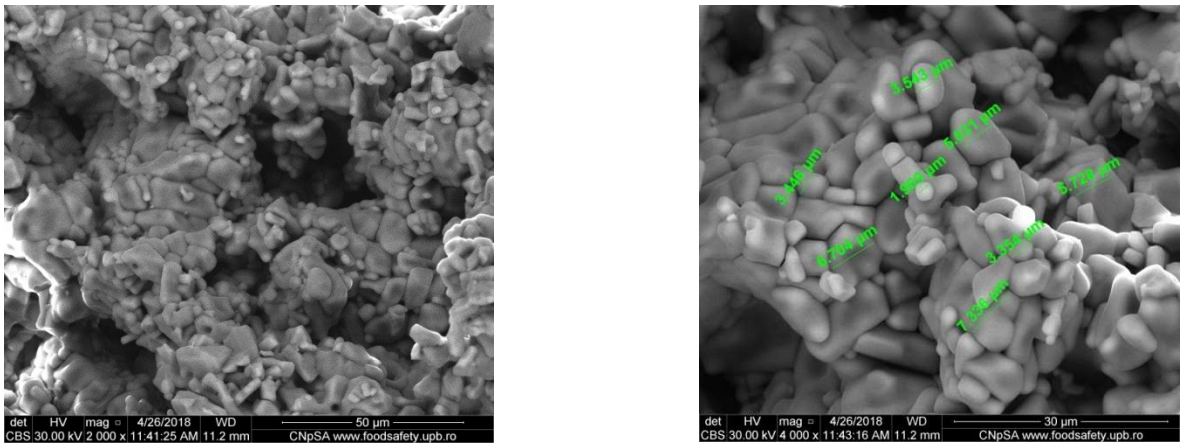

Fig. 3 a-b SEM images of sample 1 - 1400°C / *Imagini SEM ale probei 1 - 1400℃* .

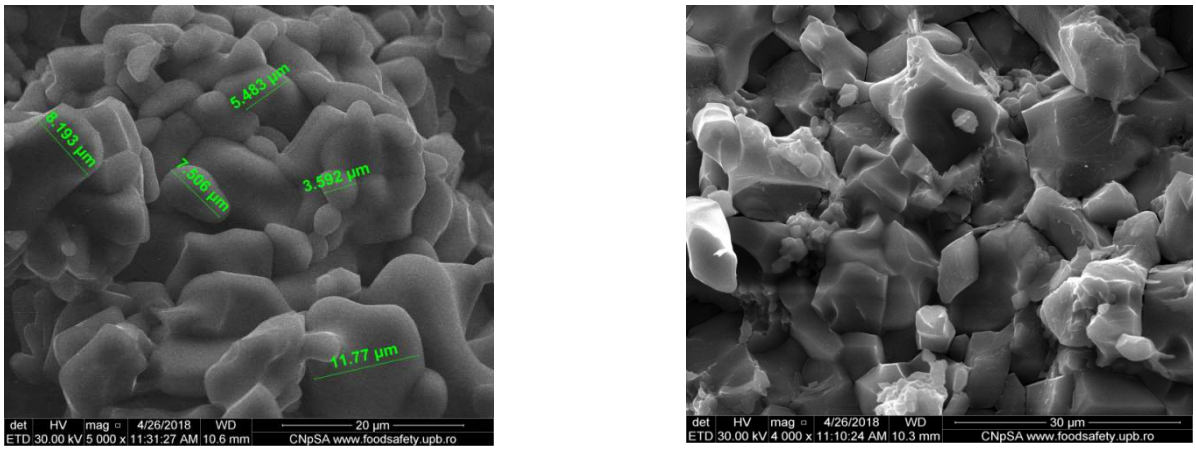

Fig. 4 a-b SEM images of sample 2 - 1400°C */ Imagini SEM ale probei 2 - 1400℃.*

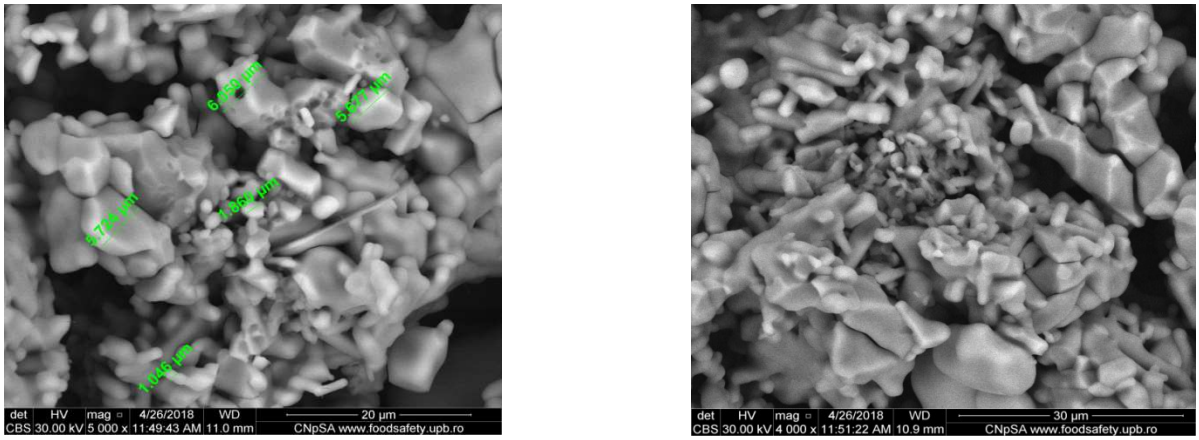

Fig. 5 a-b SEM images of sample 3 - 1400°C / *Imagini SEM ale probei 3a - 1400℃* .

Table 2

Proprietăți mecanice */ Mechanical properties*

Nr.crt.	Φ(mm)	h(mm)	E(GPa)	R_C(MPa)
1-1400°C	12.45	12.56	1.81	128.18
2-1400°C	12.42	12.57	2.02	114.81
3-1400°C	12.44	12.48	1.93	104.92

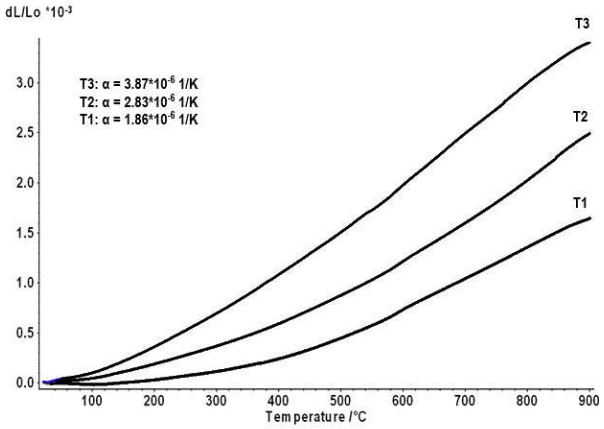

Fig 6 - Dilatometric curves of heat treated samples; T1 curve – sample1, T2 curve – sample 2, T3 curve – sample 3 / *Curbele dilatometrice ale probelor tratate termic la 1400^{0}C; curba T1 – proba 1; curba T2 – proba 2; curba T3 – proba 3.*

4. Conclusions

Three samples were examined, containing variable amounts of tialite, obtained from chemically pure raw materials (alumina, magnesium carbonate and titanium dioxide), heat treated at temperatures between 1200 and 1400°C. Tialitic ceramic materials with MgO additives, so that solid solution ss(AT-MT_2) type to be formed, presents superior properties to tialitic ceramics without sintering additives. By MgO addition, both the thermodynamic stability and the mechanical resistance are improved. All these acquired properties expand the range of uses of the studied materials, finding applicability in several fields and industries.

REFERENCES

1. Thomas, H. A. J., Stevens, R., Aluminium titanate – a literature review – part 1: microcracking phenomena, Br. Ceram. Trans. J., 1989.
2. Thomas, H. A. J., Stevens, R., Aluminium titanate – a literature review – part 2: engineering properties and thermal stability, Br. Ceram. Trans. J.,1989, **88**,184.
3. I.J.Kim, Thermal stability of Al_2TiO_5 Ceramics for new diesel particulate filter applications - a literature review, Journal of Ceramic Processing Research. 2009, **15** (5),1.
4. Zambazov, S., Lepkova, D., Synthesis and properties of Al_2TiO_5, Third Euro-Ceramics, Madrid, 1993, **3**, 1013.
5. I.J.Kim, L.G.Gauckler, Formation, decomposition and thermal stability of Al_2TiO_5 ceramics, J. Ceram Sci Tech, 2012, **3**, 49.
6. V.Buscaglia, F.Caracciolo, M. Leoni, P. Nanni, M. Viviani, J. Lemaitre, Synthesis, sintering and expansion of $Al_{0,8}Mg_{0,6}Ti_{1,6}O_5$: a low-thermal-expansion material resistant to thermal decomposition, Journal of Materials Science, 1997, **32**, 6525.
7. M.Preda, A.Melinescu, M. Crisan, S. Preda, M. Zaharescu, Tialite type solid solution formation in the $MgO{\cdot}Al_2O_3$-$Fe_2O_3{\cdot}TiO_2$-$Al_2O_3{\cdot}TiO_2$ pseudo-ternary system, Revue Roumaine de Chimie, 2006, **51** (6), 509.
8. R.S.S. Maki, Y. Suzuki, Mechanical strength and electrical conductivity of reactively-sintered pseudobrookite-type Al_2TiO_5-$MgTi_2O_5$ solid solutions, Journal of the Ceramic Society of Japan, 2016, **124**, 1.
9. S. Lashkarin, T. Ebdadzadeh, Microwave sintering of $Al_{2(1-x)}Mg_xTi_{(1+X)}O_5$ ceramics obtained from mixture of nano-sized oxide powrders, Ceramics International, 2014, **40**, 12669.
10. Y Suzuki, M.Morimoto, Uniformly porous $MgTi_2O_5$ with narrow pore-size distribution: in situ processing, microstructure and thermal expansion behavior, 2010, **118** (12), 1212.
11. CGSilva, F.M.Carvalho, T Ferreira, L A Genova, Formation of Aluminum Titanate with Small Additions of MgO and SiO_2, Materials Research. 2016, **19** (2), 384.
12. K.Kornaus, R.Lach, M.SZumera, K.Swierczek, Synthesis of aluminium titanate by means of isostructural heterogeneous nucleation, Journal of the European Ceramic Society, 2019, **39**, 2535.
13. R Maki, Y. Suzuki, Microstructure and mechanical properties of MgO-doped Al_2TiO_5 prepared by reactive sintering, Journal of the Ceramic Society of Japan, 2013, 121 (7), 568.

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