COMPOZITE ALUMINOASE OBȚINUTE PRIN TEHNICI NECONVENȚIONALE
ALUMINA COMPOSITES OBTAINED BY UNCONVENTIONAL HEAT TREATMENT

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The structural ceramic materials are important because they are usually lightweight, harder than metals, resistant at higher temperatures and also present an impressive series of mechanical properties, including good mechanical strength in extreme conditions. The alumina based materials and composites are of great importance for ballistic protection. The aim of the present paper is focused on behavior of various alumina types after being sintered in different conditions

The materials used in present study are α-Al_2O_3 powder (from 3 different sources) and additions of different rare-earth oxides (La_2O_3, Y_2O_3, Nd_2O_3) [1] in two proportions: 500 ppm and respectively 1000 ppm.

The Al_2O_3 dense ceramics were obtained by various sintering environments, using both traditional sintering ways at temperatures of 1500 ° C (electric furnace) and 1815° C (gas furnace) and a non-conventional technique (cold plasma sintering).

After sintering the samples were analyzed by X-Ray diffraction and scanning electron microscopy (SEM). Ceramic properties like contraction, absorption, porosity, and relative density were also determined.

The final conclusions highlight o series of interpretations and correlations of the sintering parameters with the properties of the sintered materials.

Materialele ceramice structurale sunt importante deoarece sunt de obicei uşoare, mai tari decât metalele, mai rezistente la temperaturi înalte şi, de asemenea, prezintă o serie impresionantă de proprietăți mecanice, incluzând rezistențe mecanice bune în condiții extreme. Materialele şi compozitele pe bază de alumină sunt de mare importanță în domeniul protecției balistice. Scopul prezentei lucrări se axează pe comportamentul diferitelor tipuri de alumină după ce au fost sinterizate in diverse condiții.

Materialele folosite în acest studiu sunt formate din pulberi de α-Al_2O_3 (provenite din 3 surse) şi din adaosuri de oxizi ai pamânturilor rare (La_2O_3, Y_2O_3, Nd_2O_3) [1]) în două proporții: 500 ppm şi respectiv, 1000 ppm.

Ceramicile dense de Al_2O_3 au fost obținute folosind atât tehnici de sinterizare tradițională, la temperaturi de 1500°C (cuptor electric) şi 1815°C (cuptor cu gaz), cât şi printr-o tehnică neconvențională (sinterizare în plasmă rece).

După sinterizare probele au fost analizate prin difracție de raze X şi microscopie electronică de baleiaj (SEM). Proprietăți ceramice precum contracție, absorbție, porozitate şi densitate relativă au fost de asemenea determinate.

Concluziile finale pun în evidență o serie de interpretări şi corelații între parametrii de sinterizare şi proprietățile materialelor sinterizate.

Keywords: *ceramic composites, structural ceramics, cold plasma, alumina ceramics*

1.Introduction

The structural ceramic materials are important because they are usually lightweight, harder than metals, resistant at higher temperatures and also present an impressive series of mechanical properties, including good mechanical strength in extreme conditions. The alumina based materials and composites are of great importance for ballistic protection.[2-5] The aim of the present paper is focused on behavior of various alumina types after being sintered in different conditions.

2. Raw materials characteristics, compositions, experimental procedures

The raw materials used in this research work are α-Al_2O_3 powder (from three different sources) and additions of different rare-earth oxides (La_2O_3, Y_2O_3, Nd_2O_3) in two proportions: 500 ppm and respectively 1000 ppm.

The Al_2O_3 dense ceramics are obtained by different sintering conditions, using the traditional way at temperatures of 1500 ^{O}C (electric furnace) and 1815 ^{O}C (gas furnace). In addition, a non-conventional technique for sintering conditions was used, and this technique is cold plasma, however its treatment temperature is unknown.

The main characteristics of raw materials are presented in table 1.

3. Characterization of the Al_2O_3 – La_2O_3, Y_2O_3, Nd_2O_3 ceramics

The powder mixtures were shaped in cylinders with 1.32 cm diameter and equal cross heights by uniaxial pressing, then were subjected to the thermal treatments at temperatures of 1500 °C, 1815 ° C and finally to a non-conventional technique, named cold plasma.

After sintering, the samples were subjected to the following analysis:

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- RX diffraction analysis – for its mineralogical composition;
- Determination of ceramic properties – contraction, absorbtion, porosity, and relative density
- Scanning electron microscopy (SEM) for the fracture morphology of sinterized samples

Table 1

Main characteristics of raw materials / *Caracteristicile principale ale materialelor studiate*

Compositional codes / *Coduri compoziționale*				Raw Materials (wt%) / *Materii prime (%greutate)*			
Sample Proba	Alumina types / *Tipuri de alumină*	Rare -earth oxides *Tip de adaos*	Doping *Dopant* (ppm)	Al_2O_3	La_2O_3	Y_2O_3	Nd_2O_3
A1La5	A1 (Al_2O_3– from sulphate / *din sulfat*)	La_2O_3	500	99.9995	0.0005	-	-
A1La10			1000	99.999	0.001	-	-
A2La5	A2 (Al_2O_3–very fine powder / *pulbere foarte fină,* 325 mesh)	La_2O_3	500	99.9995	0.0005	-	-
A2La10			1000	99.999	0.001	-	-
A2Y5		Y_2O_3	500	99.9995	-	0.0005	-
A2Y10			1000	99.999	-	0.001	-
A2Nd5		Nd_2O_3	500	99.9995	-	-	0.0005
A2Nd10			1000	99.999	-	-	0.001
A3La5	A3 (Al_2O_3 ACS)	La_2O_3	500	99.9995	0.0005	-	-
A3La10			1000	99.999	0.001	-	-
A3Y5		Y_2O_3	500	99.9995	-	0.0005	-
A3Y10			1000	99.999	-	0.001	-
A3Nd5		Nd_2O_3	500	99.9995	-	-	0.0005
A3Nd10			1000	99.999	-	-	0.001

The ceramic samples were obtained according to the processing flow chart presented in Figure 1.

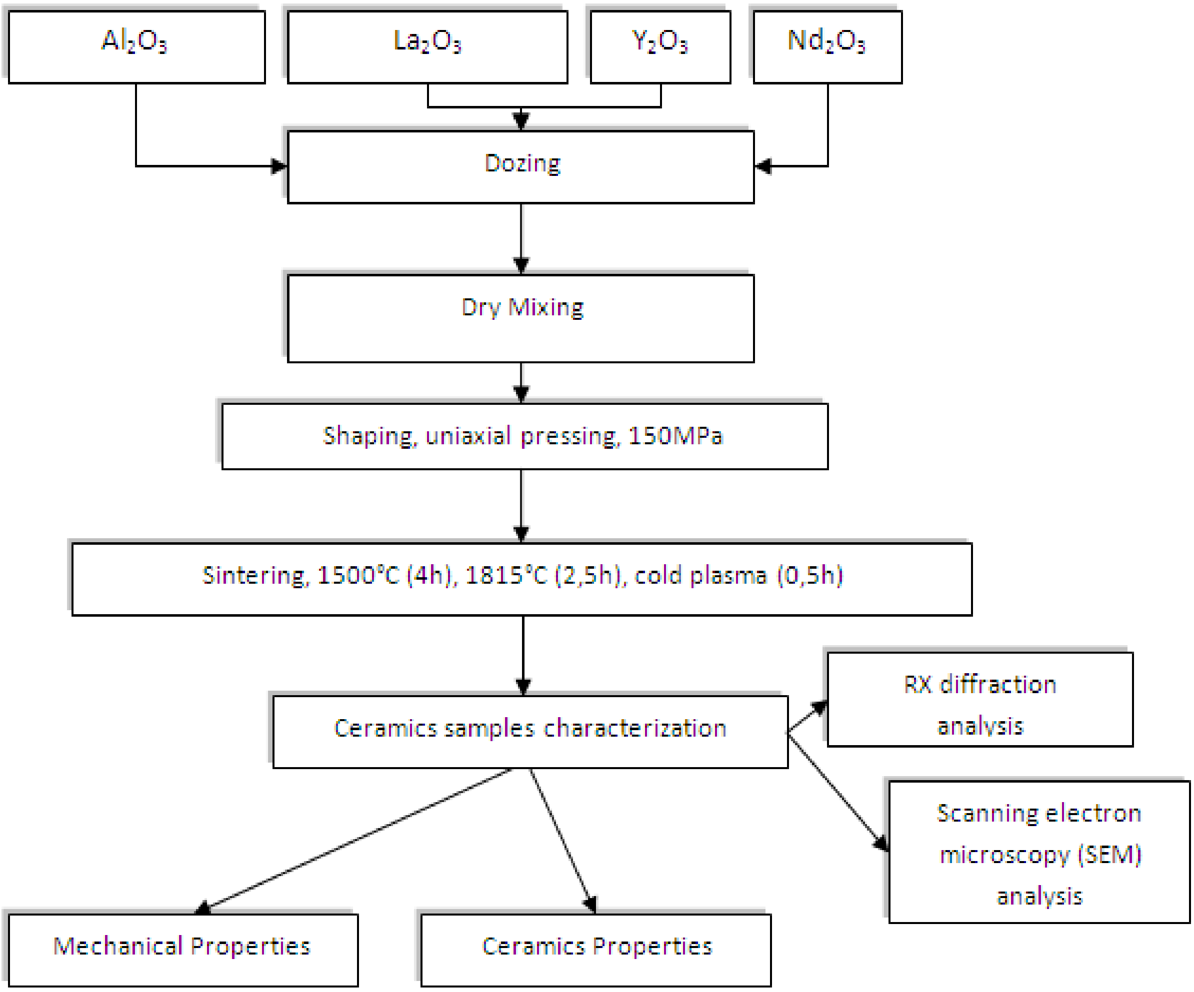

Fig. 1- Processing flow chart / *Fluxul tehnologic*.

3.1 Ceramic characterization of the sintered composites

For the compositions that were sintered at temperatures of 1500 °C, 1815 °C and those that were subjected to the cold plasma treatment, there were determined the ceramic characteristics which are presented in the following tables.

4. Results and Discussions

The results of the experiments performed related to the sintering behaviour of alumina have revealed several interesting aspects.

Table 2

Sintering at: / Sinterizare la: 1500 °C

Mixture Amestec	A3Y5	A3Nd10	A2La5	A2La10	A2Y5	A2Y10	A2Nd5	A2Nd10	A3Y10	A3La5	A3La10	A3Nd5	A1La5
ρ_{ap} (g/cm^3)	3.553	3.571	2.641	2.596	2.621	2.620	2.580	2.5□4	3.5□5	3.461	3.481	3.431	2.558
A (%)	2.378	1.802	10.424	11.372	10.766	10.823	11.523	11.094	2.870	3.00	2.624	3.476	11.837
P (%)	9.99	7.570	35.49	38.472	36.509	36.723	38.801	37.373	12.049	12.362	10.831	14.267	39.662

Table 3

Sintering at / Sinterizare la : 1815 °C

Mixture	A3Y5	A3Nd10	A2La5	A2La10	A2Y5	A2Y10	A2Nd5	A2Nd10	A3Y10	A3La5	A3La10	A3Nd5	A1La5
ρ_{ap} (g/cm^3)	2.744	3.448	3.346	2.621	3.247	3.459	3.397	3.069	2.364	2.582	3.600	2.705	3.536
A (%)	7.571	1.982	2.894	9.191	2.170	0.644	1.057	3.540	11.868	6.654	0.10	8.230	0.057
P (%)	26.241	8.050	11.513	30.636	8.314	2.590	4.190	13.007	36.761	23.472	0.417	28.008	0.234

Table 4

Sintering using cold plasma non-conventional technique / Sinterizare în plasmă rece

Mixture	A3Y5	A3Nd10	A2La5	A2La10	A2Y5	A2Y10	A2Nd5	A2Nd10	A3Y10	A3La5	A3La10	A3Nd5	A1La5
ρ_{ap} (g/cm^3)	2.630	2.279	2.355	2.462	2.595	2.588	1.929	2.193	2.049	2.284	2.075	2.104	1.600
A (%)	9.848	13.787	12.679	11.477	13.369	10.314	18.487	14.797	16.289	4.281	15.886	15.576	24.075
P (%)	33.17	42.079	39.487	36.864	40.897	34.373	50.520	43.976	46.037	11.794	45.248	44.834	58.576

The ceramic properties are dependent of treatment temperature and of the doping amount added in each mixture. The usage of the highest possible thermal treatment as well as a low percentage of doping leads to the achievement of the best alumina ceramic properties.

3.2 Determination of porosity and density

Method description: The samples are weighted in air (m_0) on the analytical balance, and then are kept in vacuum for two hours. They are emerged in xylene and the vacuum pump is then turned off. After 30 minutes, then the saturated samples are weighted in normal pressure conditions.

- Relative density:

$$\rho_a = \frac{m_p}{V_a}(g/cm^3)$$

Where mp is the sample mass, V_a is the sample volume

- Adsorption

$$A = \frac{m_s - m_p}{m_p} \cdot 100(\%)$$

Where ms is the saturated sample mass;

- Porosity

$$P_d = A \cdot \rho_a(\%)$$

The main factors that have been considered in our investigations were: sintering temperature, different sintering aids from the family of rare earth oxide family, the nature of alumina's precursor and the way of applying of the sintering heat treatment (firing, cold-plasma, and microwave). As expected, all these factors were more or less involved in the sintering process of different type of aluminas. Further, it will be presented some of the findings of our experiments.

The values of the ceramic properties (porosity, adsorption and density) are directly influenced by the sintering temperature and the way of applying the heat transfer. So, in Fig. 2 it can be noticed that the best behaviour during sintering at 1500 ^{o}C has been shown by the A3 alumina, irrespective of the nature of the sintering aid (La, Y or Nd) and of their concentration. In opposite position is the A1 alumina with the highest values of adsorption and porosity.

The sintering performed at 1815 ^{o}C for similar compositions has emphasized a more complicated behaviour even when using the same sintering aid. Thus, in Fig. 3 one can observe that adsorption and related porosity achieve minimum values in the case of all tree type of aluminas but for different sintering aids. For instance, we can nominate for low and very low adsorption and porosity, the following compositions: A3La10, A2Y10, A2Nd5, and A1La5. This random behaviour suggests that the mechanism of sinte-

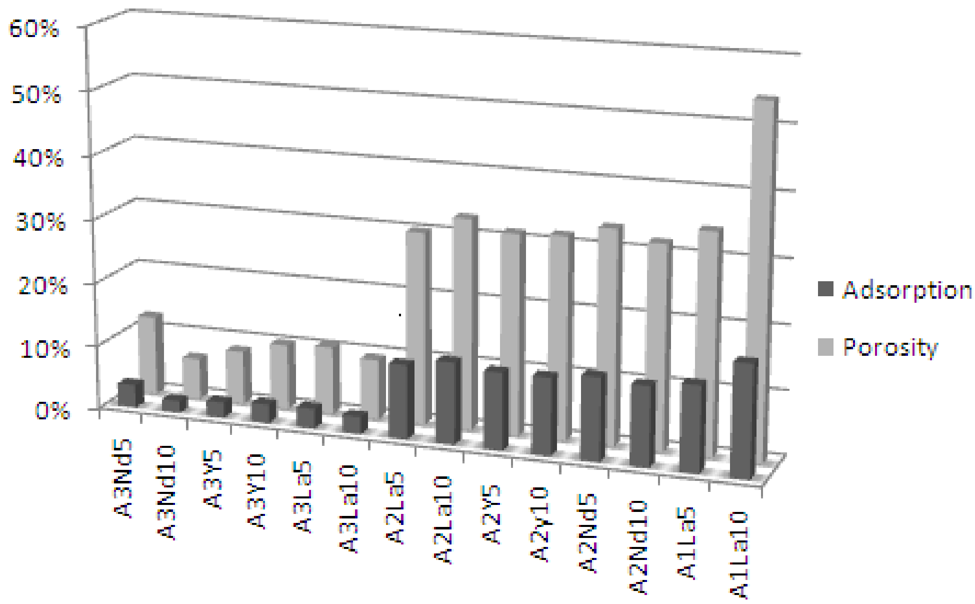

Fig. 2 – Variation of adsorption and porosity with composition for T=1500 ˚C / *Variaţia absorbţiei şi a porozităţii la T=1500 °C.*

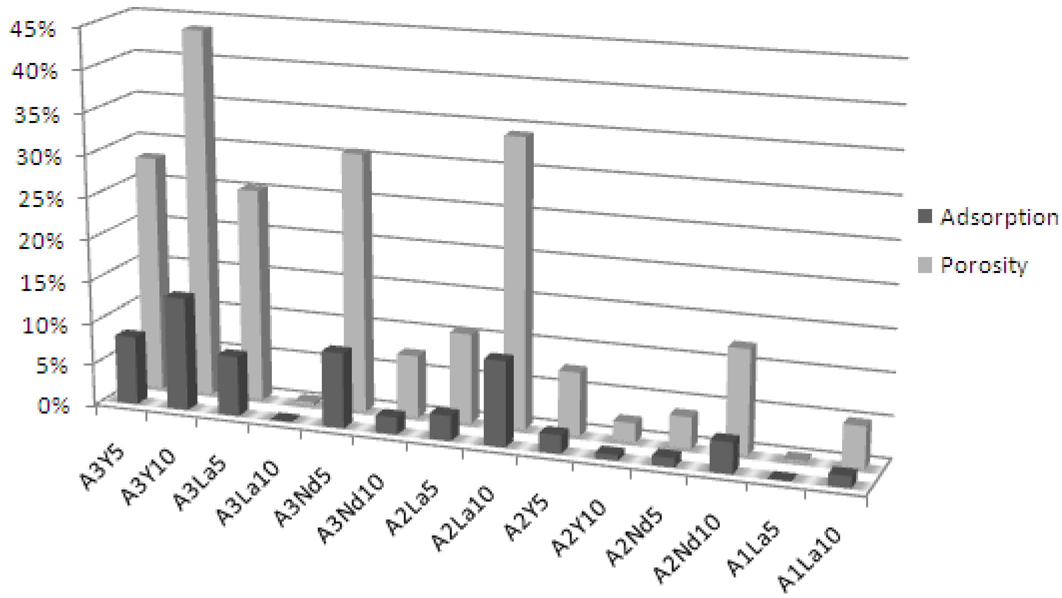

Figure 3 – Variation of adsorption and porosity with composition for T=1815 ˚C / *Variaţia absorbţiei şi a porozităţii la T=1815 °C.*

tering involving different sintering aids might be different for different oxides and different sintering temperature.

In the case of heating in cold plasma, where the heat transfer mechanism from source to material is completely different from that of the previous traditional ways, the results are obtained for the first time in Romania, so there were no previous data concerning the sintering behaviour and the values of ceramic properties to be obtained. These results, as one can see from fig. 4, are generally larger than those from traditional firing and therefore showing a more porous microstructure (this aspect will be confirmed by micro structural SEM determinations). However, the lowest values for adsorption and porosity have been found in the case of A3La5, composition that has also a good behaviour in the other sintering conditions.

When studying of ceramic properties for different sintering conditions (i.e. different sintering temperature) the following aspects have been found. As it can be seen from Fig. 5, the best adsorption behaviour (minimum values) is given by composition A3Y10. The same composition is also behaving the best in the case of porosity (see Fig. 6), for firing at 1500 °C and 1815°C, respectively.

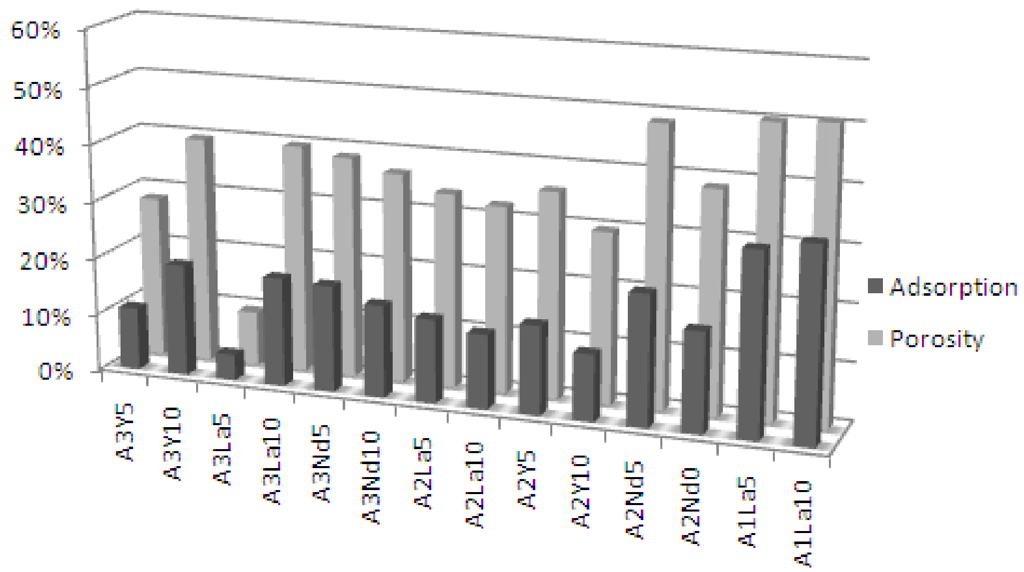

Fig. 4 - Variation of adsorbtion and porosity with composition for cold plasma-plasma sintering / *Variația absorbției şi a porozității în plasmă rece.*

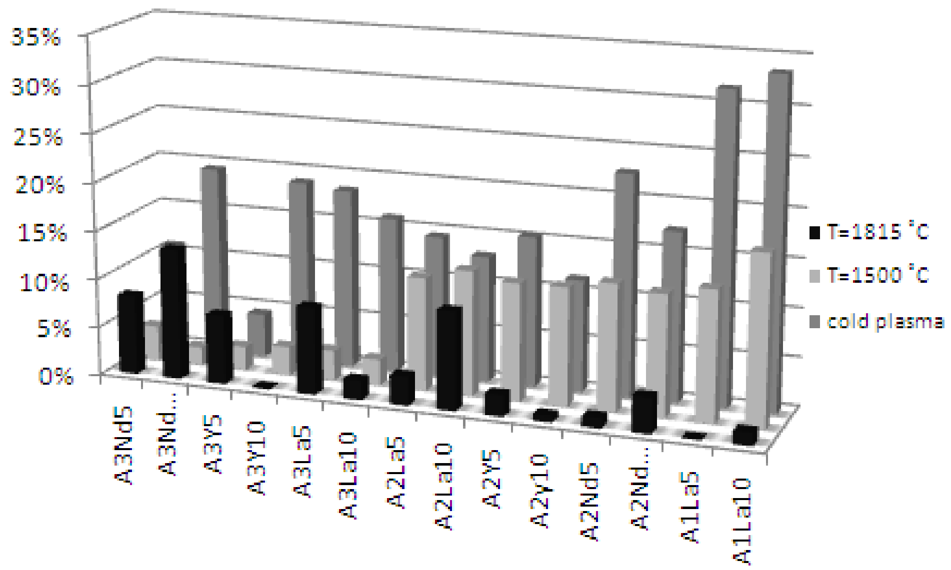

Figure 5 – Variation of adsorption with composition and sintering temperature / *Variația absorbției în funcție de compozitie şi temperatura de sinterizare.*

Cold plasma heating presents the same approach, e.g. high adsorption or porosity for almost all compositions.

A way to assess the sintering degree of a ceramic material is given by density values of the sintered specimens. In fig. 7 there are given the density values for all studied compositions and for all sintering approaches used in the present project. As expected the highest values have been found for the samples fired at 1815 °C (almost all composition show values above 3 g/cm^3) but there are also high values for certain samples fired at 1500 °C for the A3 type alumina and for all sintering aids and all used concentrations of the sintering aids.

This last behaviour has drawn the attention upon the nature of the alumina's precursor. In fig.8 there are presented the density values for all tree alumina types doped with the same concentration of La_2O_3 and fired in different conditions. As expected, the results have confirmed these assumptions observed even in some previous determinations. Again, the highest density value was obtained for A3La10 composition that has been already emphasized as behaving well at sintering.

Micro structural determinations have been performed using SEM Shimadzu equipment. The micrographs have confirmed many of the assumptions used to explain sintering behaviour

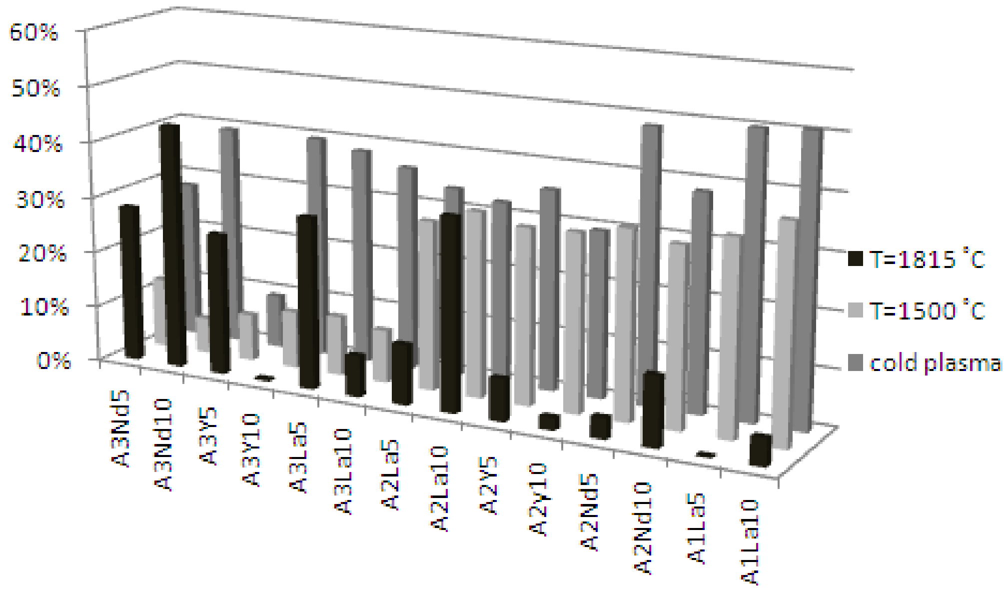

Fig. 6 - Variation of porosity with composition and sintering temperature / *Variația porozității în funcție de compoziție şi temperatura de sinterizare.*

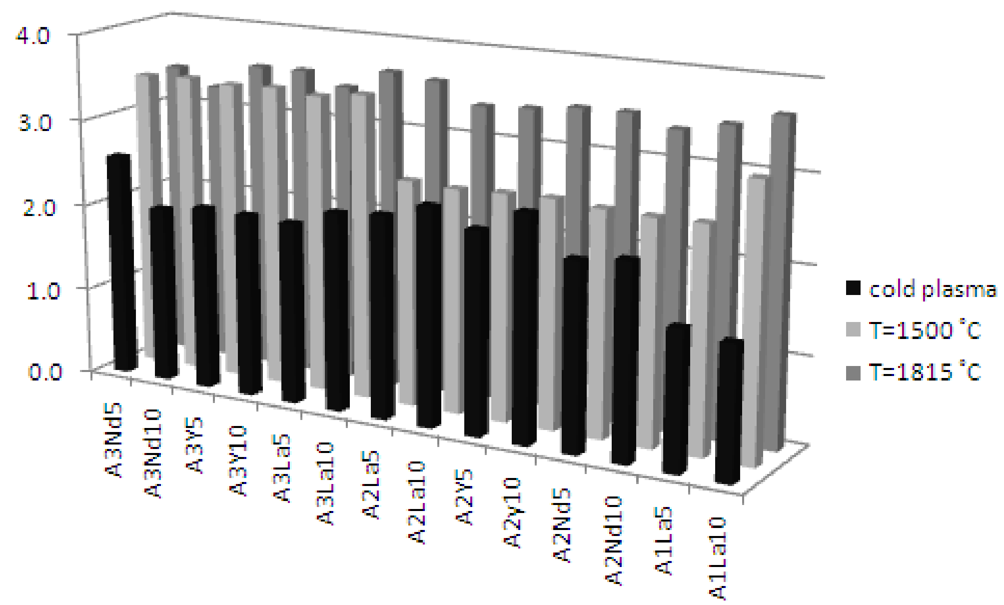

Fig. 7 - Variation of density with composition and temperature / *Variația densității în funcție de compozitie şi temperatura de sinterizare.*

following ceramic properties. Only few examples will be given in order to have a global image of the sintering. In Fig. 9, is presented composition A1La10 fired at 1500^{o}C. It can be noticed the small grain microstructure (average grain size is about 2 μm) and highly porous. The same composition fired at 1815°C (see Fig. 10) exhibits very well developed crystals having an average grain size over 10 μm, with well defined developed crystallization planes. However, inside the crystalline plane there clearly seen micro pores having a diameter around 1 μm and that might be a consequence of the sintering mechanism and the action of the sintering aid. To elucidate this aspect further study is required.

Fig. 11 shows the microstructure of the same alumina composition A1La10 sintered in cold plasma. In agreement with ceramic property determinations, the microstructure is a very porous one, with submicron grain size, exhibiting a pattern similar with sol-gel microstructures.

In order to see the effect of the nature of the sintering aid, in Fig. 12 there are presented the micrographs of the samples containing the same alumina (A3 type) and similar concentration of different dopants (La, Nd and Y) fired at 1815 ^{o}C. In all cases micro-pores are observed within well grown crystals of Al_2O_3. So far, we cannot provide an explanation of the micro-pores presence at this high sintering temperature.

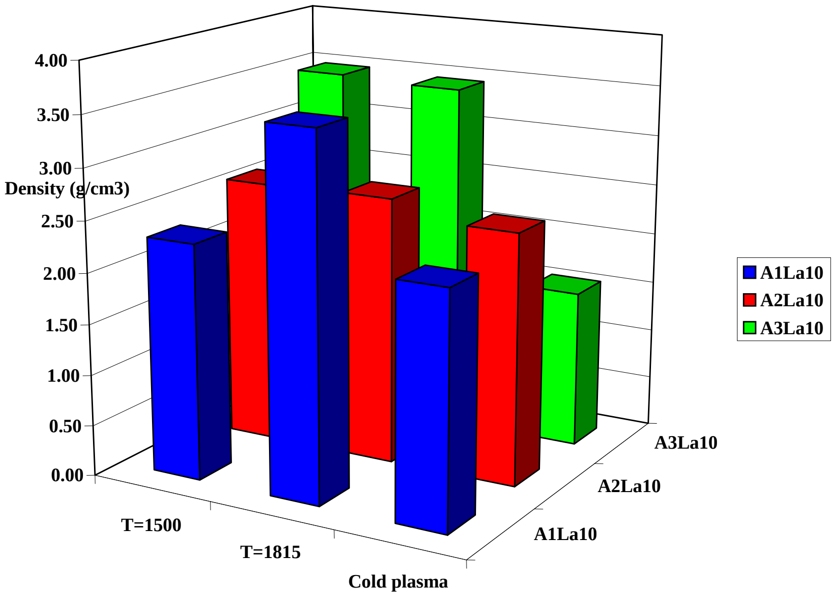

Fig. 8 – The effect of the precursor's nature on alumina sintering / *Efectul precursorului asupra materialului*

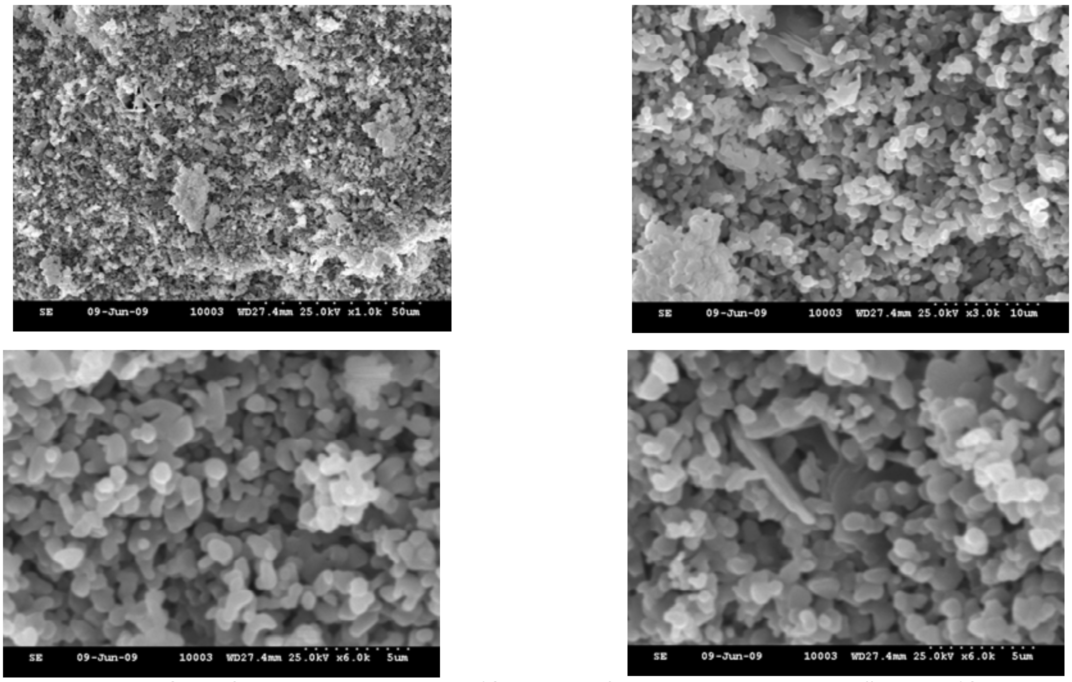

Fig. 9 - SEM of A1La10 sintered at 1500 ˚C / *Micrografia probei A1La10 sinterizată la 1500 ˚C*

In conclusion, several aluminas have been sintered using different sintering aids, for different concentrations. The sintering heat treatment has been performed following both traditional firing at two different temperatures and cold plasma heating.

5. Conclusions

Sintering behaviour of alumina is influenced by:

- nature of alumina precursors
- nature of doping elements as sintering aids
- ratio of sintering aids
- temperature of heat treatment
- nature of heat treatment (firing, cold plasma, microwave)

In this context, the values of the ceramic properties (porosity, adsorption and density) are directly influenced by the sintering temperature and by the manner in which the thermal transfer is carried out (gas sintering, cold plasma, microwave).

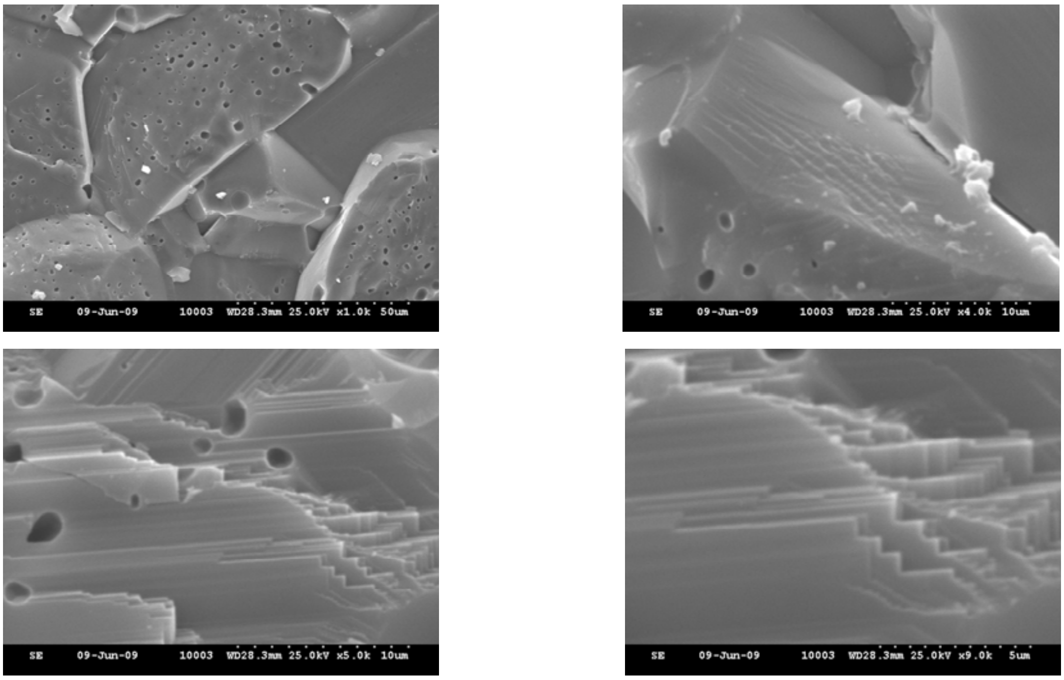

Fig. 10 - SEM of A1La10 sintered at 1815 ˚C / *Micrografia probei A1La10 sinterizată la 1815 ˚C.*

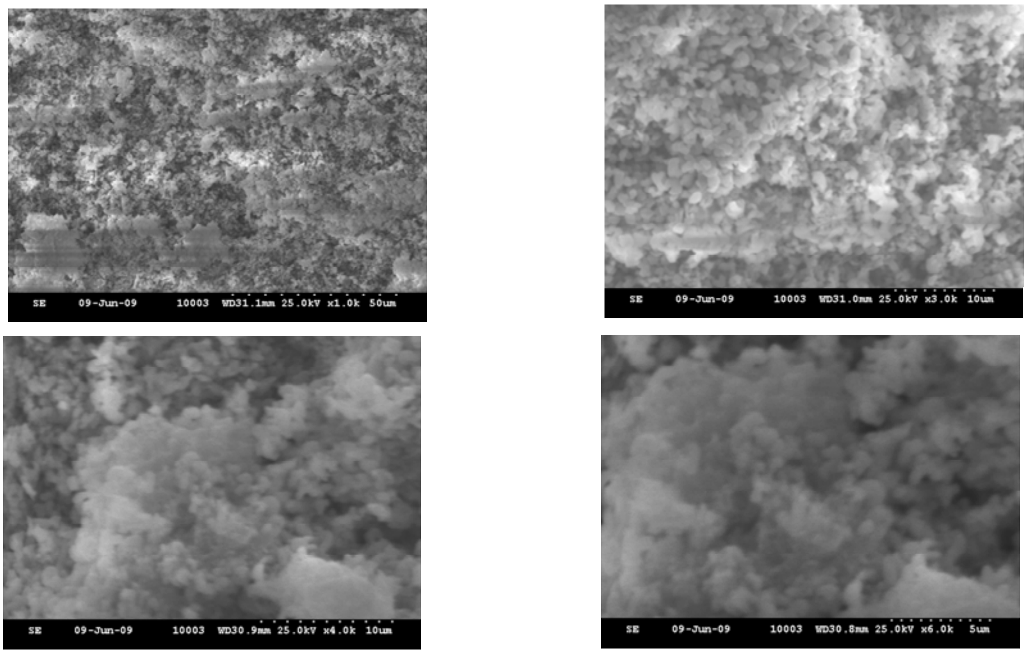

Figure 11 – SEM of A1La10 sintered in cold plasma / *Micrografia probei A1La10 sinterizată în plasmă rece.*

The adsorption and porosity reaches minimum values for all three types of aluminas, but for different dopants. Consequently, we can nominate for low and very low absorption and porosity the following compositions: A3La10, A2Y10, A2Nd5 and A1La5. This random behavior suggests that the sintering mechanism that implies different dopants could be different for different oxides and different sintering temperatures.

When using cold plasma, the heat transfer mechanism from the source to the material is completely different from the previously mentioned traditional cases (gas heating and electric heating). In addition, these results are a premiere, comparison data for this sintering technique, from the point of view of the work parameters and achievable ceramic properties being unavailable.

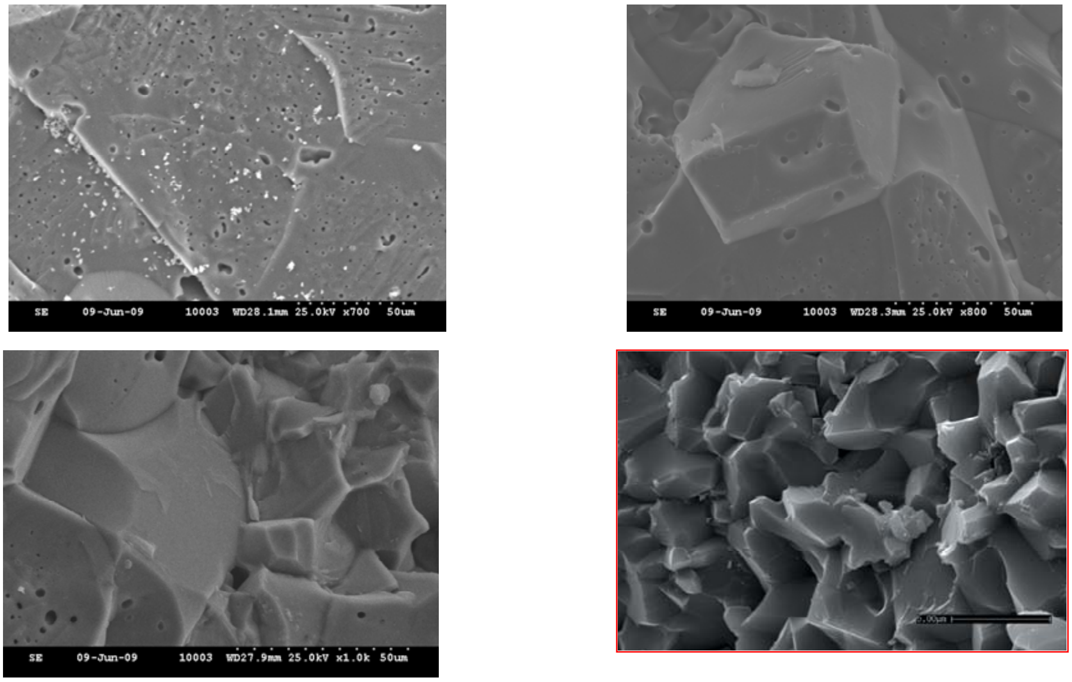

Fig. 12 - SEM's of different A3 samples (the picture from the bottom right corner is alumina taken from literature – for comparison purposes) with different additions (La, Nd, Y) sintered at 1815 ˚C / *Micrografiile unor probe A3 (figura din colțul dreapta jos este o micrografie a aluminei luată din literatură – pentru comparație) cu dopanți diferiți (La, Nd, Y) sinterizate la 1815 ˚C.*

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MANIFESTĂRI ŞTIINȚIFICE / SCIENTIFIC EVENTS

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