INVESTIGATION OF THE INFLUENCE OF MGO AND CAO CONTENT ON THE QUALITY OF TECHNICAL CERAMICS

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
In this paper, the influence of MgO and CaO content on the quality of technical ceramics (which originally represents the Al_2O_3 - SiO_2 - CaO - MgO system) has been investigated. Therefore, quality tests were performed on samples where the contents of CaO and MgO were taken as variable values. Based on the obtained test results and their analysis, certain characteristics of ceramics are defined with the different percentages of individual oxides content in 98.2 - 99% Al_2O_3.

KEYWORDS: MgO, CaO, Technical ceramics

INTRODUCTION

Ceramic materials are inorganic non-metallic materials. They consist of metallic and non-metallic elements, interconnected by ionic and / or covalent bonds. In Anglo-Saxon languages, the term "ceramics" includes glass, enamel, glass - ceramics and inorganic binders (lime, cement). Ceramic materials are formed at room temperature, from dry mass. The final properties are achieved after firing at high temperatures (sintering).[1] In ceramic technology, the molding process occurs before the heat process, while during heat treatment the ceramic shrinks (volume changes). Only after sintering, ceramics get their real characteristics, ceramic material is formed.[2] Research in the field of materials for the last 15 years has been strongly focused on the development of technical ceramics. By studying the composition, structure and technology of shaping, they want to improve some unfavorable properties of classical ceramics; fragility, unpredictability of behavior in complex load conditions, susceptibility to cracking, resistance to heat stroke and heat shocks. At the same time, the field of application expands, from the working conditions where technical ceramics were primarily used; resistance to various aggressive media and high temperatures, high hardness requirements, to additionally mechanically or tribologically loaded parts.

Despite large investments in research, a number of serious problems remain that prevent the even wider application of ceramics for typical structural parts. The principles of construction with ceramics are significantly different from those of metallic materials, and the behavior under the action of impact and variable mechanical load has not yet been fully explained - such as how to consume excess energy without breaking. Furthermore, due to the significant influence of the quality of the raw material and technological parameters of shaping on the final properties of ceramic products, there is a large variation in the value of properties from nominal and generally different quality of similar parts.

THEORY

The production of technical ceramics takes place in several steps. It is these steps in the production process that affect the underlying properties. In addition to the molding and sintering processes, the selection of powder for production also plays an important role in the structure or properties of ceramics. In Figure 1, the factors that influence the microstructure of ceramic materials can be seen.

In the whole complex production process, a certain powder, shaping and sintering process together influence the creation of a crucial microstructure and thus the desired properties of the product.[13]

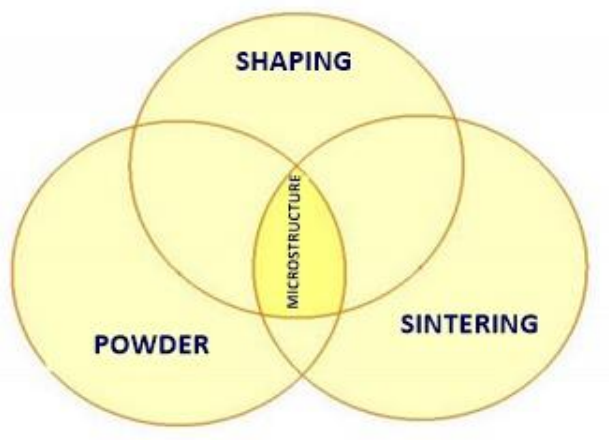

Figure 1. Effects on the microstructure of ceramic materials

EXPERIMENTAL

The aim of the experimental part of this paper was to examine the influence of MgO and CaO content on the quality of technical ceramics, which originally represents the Al_2O_3 - SiO_2 - CaO - MgO system. Therefore, quality tests were performed on samples where the contents of CaO and MgO were taken as variable values. Based on the obtained test results and their analysis, certain characteristics of ceramics are defined when we have different percentages of individual oxides content in 98.2 - 99% Al_2O_3.

The experimental part is divided into three phases, as follows:

- Preparation of powders (ceramic materials) for making samples,
- Sample production (powder pressing, machining and sintering),
- Quality control of prepared samples.

MATERIALS AND METHODS

Aluminum oxide ceramics on which the test was performed was made in the company Almatis from Germany, and the preparation of powders (ceramic materials) for the experiment was done in the Factory of car spark plugs and industrial ceramics Enker d.d. from Tešanj. Determination of the chemical composition of the starting material of aluminum oxide was performed by the manufacturer of raw materials (Almatis, Germany) and the results of chemical analysis of prepared powders (ceramic materials) were obtained in the laboratories of the quality management department of the spark plugs factory Enker d.d.

Chemical composition of prepared powders (ceramic materials):

• SiO_2	0.0093%
• CaO	0.0270%
• Na_2O	0.06%
• Fe_2O_3	0.0225%
• B_2O_3	0.0129%
• Al_2O_3	99.86%

Powder (ceramic material) is prepared by weighing the components in a mill, where it is ground for 24 hours. When the grinding operation is completed, the ceramic material is transferred to a mixer, where additives are added and mixing is performed. Finally, from the mixer, the ceramic material - "*schliker*" is pumped to the dryer where it is dried and powder is formed. After cooling, the powder goes to further technological processing. For conducting experimental tests, three powders of different composition were prepared, as follows:

- Powder 1 (P1): 98.5% Al_2O_3; 0.417% CaO; 0.40% MgO; 0.40% SiO_2
- Powder 2 (P2): 99.1% Al_2O_3; 0.21% CaO; 0.20% MgO; 0.40% SiO_2
- Powder 3 (P3): 98.2% Al_2O_3; 0.62% CaO; 0.60% MgO; 0.40% SiO_2

Two cassettes / sagers (118 PCS) of ceramic parts of the car spark plug, ie insulators, were prepared from each powder. Since MgO and CaO show their influence in the Al_2O_3 - SiO2 - CaO - MgO system at different sintering temperatures, the samples were sintered at two temperatures, 1550°C and 1600°C.

PRODUCTION OF SAMPLES

After the powders are prepared, the next operation in the technological process of production of samples, ie insulators for the production of car spark plugs, is pressing, then molding.

The most efficient method of mass production is isostatic pressing and shaping of ceramic molding by profile grinding. The grinding unit is located within the press itself and is interconnected by a conveyor belt. Isostatic pressing means even pressure on the ceramic material from all sides.

This significantly reduces the problems of unevenness due to pressing and allows even compaction of larger volumes of ceramic material, including shapes with a large ratio of length to diameter. Raw ceramic insulators are stacked in refractory packaging (cassettes - sagers) and then sent for sintering operation.

Sintering, ie densification of the molding, is basically the removal of pores between particles (followed by shrinkage) of the ceramic material.

Figure 2. Ceramic part of the car spark plug (before and after sintering)

SAMPLE ANALYSIS

Determination of density

Determination of the density of the tested samples was done in the factory of spark plugs and industrial ceramics Enker d.d. on apparatus from which the density of ceramic samples is read directly after sintering. 10 samples were analyzed from each sager cassette.

Thermo test

The thermal test is performed by immersing the top of the tested sample (insulator) in molten tin to a depth of 7 mm. At a temperature of 625°C, for a period of 20 s, the ceramic part immersed in molten tin must not show cracks. Since up to 625°C there was no cracking of the insulator from any of the three prepared materials, the test was performed until the cracking of the samples occurred. The temperature was increased by 25°C.

Hardness

The hardness of ceramics is determined by the Vickers method, on the device of the control sector in the factory of spark plugs and industrial ceramics Enker d.d Tešanj. The basic principle, as with all common measures of hardness, is to observe a material's ability to resist plastic deformation from a standard source. The basic condition for successful analysis and correct results is that the sample is representative and well prepared. The techniques involved in preparing the sample are as follows: cutting the sample, watering the sample with polymeric material, grinding, polishing, corrosion.

Porosity

The porosity of the prepared materials is determined using an optical microscope, on the same samples on which the hardness of the prepared materials was determined. Closed porosity is determined by microscopic analysis, and the results are read directly on the device. Closed porosity represents pores that are not interconnected. Closed porosity ceramics in different percentage values, depending on the conditions, are most often used in the refractory industry and thermal insulation.

RESULTS AND DISCUSSION

Test results of density of prepared materials

The results of measuring the density of the prepared samples are given in Tables 1, 2 and 3.

Table 1. Values of density of material samples P1

Material	Sample number	γ (g/cm^3) (Ts = 1550°C)	γ (g/cm^3) (Ts = 1600°C)
P1	1	3.770	3.855
	2	3.771	3.853
	3	3.780	3.857
	4	3.776	3.850
	5	3.778	3.852
	6	3.790	3.857
	7	3.776	3.855
	8	3.781	3.851
	9	3.760	3.852
	10	3.766	3.854

Table 2. Values of density of material samples P2

Material	Sample number	γ (g/cm^3) (Ts = 1550°C)	γ (g/cm^3) (Ts = 1600°C)
P2	1	3.669	3.850
	2	3.691	3.853
	3	3.675	3.859
	4	3.688	3.850
	5	3.671	3.852
	6	3.645	3.857
	7	3.776	3.855
	8	3.662	3.856
	9	3.669	3.852
	10	3.661	3.855

Table 3. Values of density of material samples P3

Material	Sample number	γ (g/cm^3) (Ts = 1550°C)	γ (g/cm^3) (Ts = 1600°C)
P3	1	3.752	3.854
	2	3.770	3.853
	3	3.774	3.854
	4	3.688	3.859
	5	3.725	3.852
	6	3.645	3.853
	7	3.726	3.855
	8	3.595	3.856
	9	3.669	3.856
	10	3.668	3.855

The results show that the sintering temperature T = 1550°C is not sufficient to achieve quality, ie density corresponding to the density of the material with 98.2 - 99% Al_2O_3. The sintering temperature T = 1600°C is sufficient to achieve a certain quality of the material. For materials above 98.5% Al_2O_3, the minimum density is 3.82 g/cm^3.

Results of thermal shock of prepared materials

Tables 4, 5 and 6 give the results of thermal shock of prepared ceramic materials.

Table 4. Results of thermal shock for material P1

Material	Ts = 1550 (°C)	Test temperature (°C)			Ts = 1600 (°C)	Test temperature (°C)		
	Sample number	750	850	900	Sample number	750	850	900
P1	1	✓	-	-	1	✓	✓	✓
	2	✓	-	-	2	✓	✓	✓
	3	✓	-	-	3	✓	✓	✓
	4	✓	-	-	4	✓	✓	✓
	5	✓	-	-	5	✓	✓	✓
	6	✓	-	-	6	✓	✓	✓
	7	✓	-	-	7	✓	✓	✓
	8	✓	-	-	8	✓	✓	✓
	9	✓	-	-	9	✓	✓	✓
	10	✓	-	-	10	✓	✓	✓

Table 5. Results of thermal shock for material P2

Material	Ts = 1550 (°C)	Test temperature (°C)			Ts = 1600 (°C)	Test temperature (°C)		
	Sample number	750	850	900	Sample number	750	850	900
P2	1	✓	✓	-	1	✓	✓	✓
	2	✓	✓	-	2	✓	✓	✓
	3	✓	✓	-	3	✓	✓	✓
	4	✓	✓	-	4	✓	✓	✓
	5	✓	✓	-	5	✓	✓	✓
	6	✓	✓	-	6	✓	✓	✓
	7	✓	✓	-	7	✓	✓	✓
	8	✓	✓	-	8	✓	✓	✓
	9	✓	✓	-	9	✓	✓	✓
	10	✓	✓	-	10	✓	✓	✓

Table 6. Results of thermal shock for material P3

Material	Ts = 1550 (°C)	Test temperature (°C)			Ts = 1600 (°C)	Test temperature (°C)		
	Sample number	750	850	900	Sample number	750	850	900
P3	1	✓	-	-	1	✓	✓	-
	2	✓	-	-	2	✓	✓	-
	3	✓	-	-	3	✓	✓	-
	4	✓	-	-	4	✓	✓	-
	5	✓	-	-	5	✓	✓	-
	6	✓	-	-	6	✓	✓	-
	7	✓	-	-	7	✓	✓	-
	8	✓	-	-	8	✓	✓	-
	9	✓	-	-	9	✓	✓	-
	10	✓	-	-	10	✓	✓	-

The results show that the samples that were sintered at T_S = 1550°C, resistant to thermal shock up to 750°C, while the samples that were sintered at T_S = 1600°C, except for material P3, at a temperature of 900°C have shown cracks, which shows that this ratio of oxides in the material has the lowest resistance to thermal shock.

Hardness test results of prepared ceramic materials

Tables 7, 8 and 9 give the results of hardness measurements (HV 5) for prepared ceramic materials.

Table 7. Display of hardness (HV 5) results for material P1

Material	Ts = 1550°C		Ts = 1600°C	
	Sample number	Hardness HV 5	Sample number	Hardness HV 5
P1	1	1303	1	1524
	2	1283	2	1648
	3	1314	3	1486
	4	1346	4	1552
	5	1303	5	1524
	6	1283	6	1486
	7	1304	7	1684
	8	1245	8	1369
	9	1303	9	1346
	10	1225	10	1314

Table 8. Display of hardness (HV 5) results for material P2

Material	Ts = 1550°C		Ts = 1600°C	
	Sample number	Hardness HV 5	Sample number	Hardness HV 5
P2	1	1379	1	1449
	2	1225	2	1369
	3	1303	3	1346
	4	1225	4	1283
	5	1225	5	1245
	6	1021	6	1303
	7	1060	7	1606
	8	1379	8	1369
	9	1303	9	1552
	10	1283	10	1225

Table 9. Display of hardness (HV 5) results for material P3

Material	Ts = 1550°C		Ts = 1600°C	
	Sample number	Hardness HV 5	Sample number	Hardness HV 5
P3	1	1225	1	1606
	2	1303	2	1552
	3	1346	3	1684
	4	1060	4	1552
	5	1103	5	1314
	6	1379	6	1369
	7	1303	7	1486
	8	1245	8	1524
	9	1225	9	1606
	10	1162	10	1314

Porosity test results of prepared ceramic materials

The percentage of closed porosity was determined by microscopic analysis of the examined samples, which is shown in the report. For the material sample (1), sintering temperature T = 1600°C, a closed porosity of 1.36% was determined, the microscopic view is shown in the figure 3. On samples sintered at temperature T = 1550°C, the measured closed porosity was 16.2%.

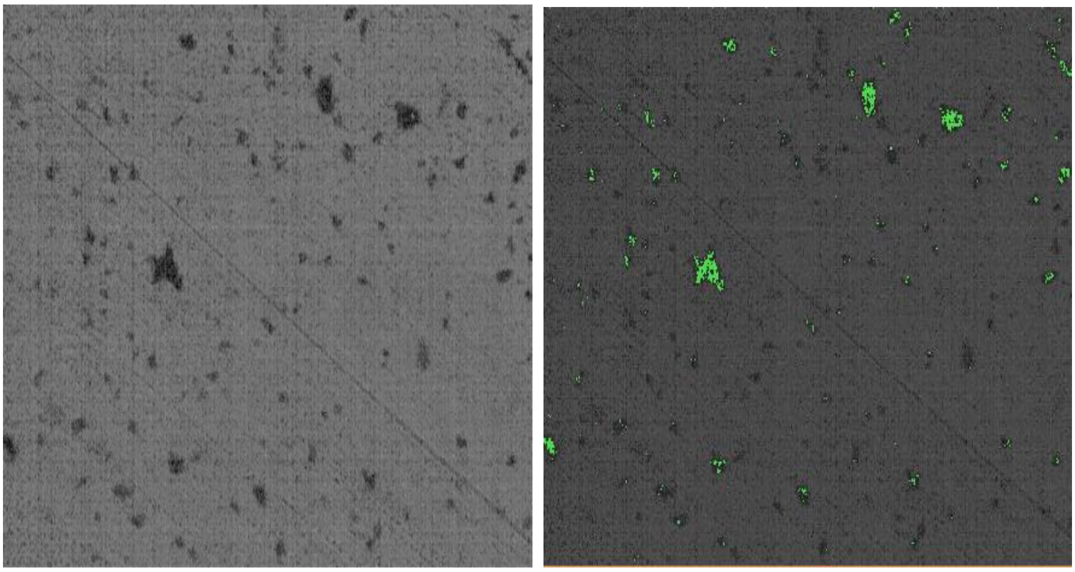

Figure 3. Original (a) and microscopically processed (b) image of the material sample surface (P1)

Figure 4 shows the number of grains in areas of certain sizes for the analyzed sample.

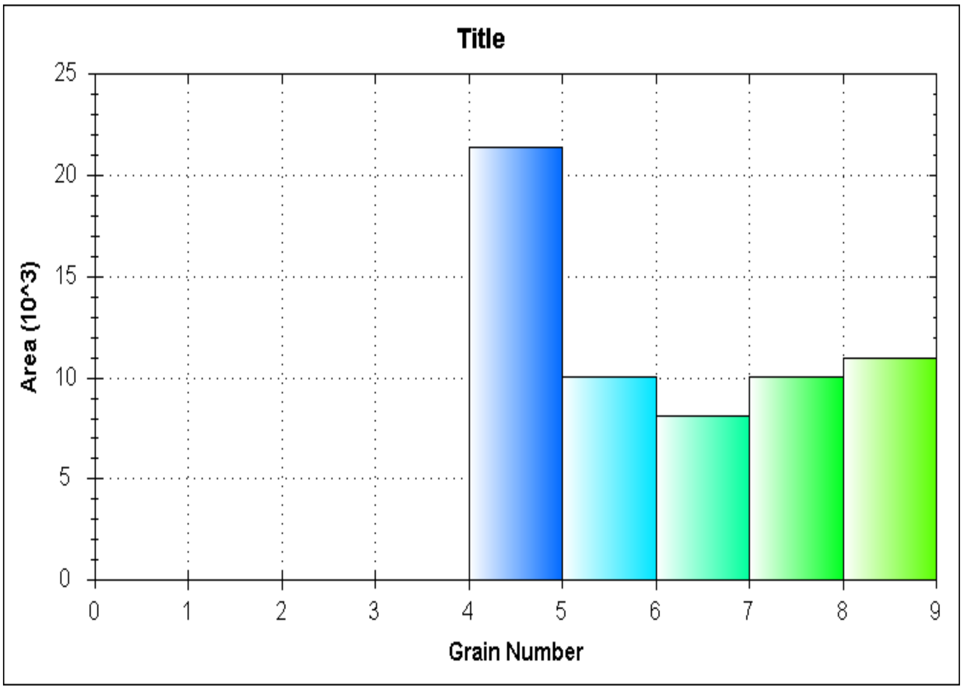

Figure 4. Grain size distribution for material P1, Ts = 1600°C

For material (P2), sintering temperature T = 1600° C, the percentage of closed porosity is 12%, the microscopic view is shown in Figure 5. On samples sintered at a temperature T = 1550°C, the closed porosity is 24%.

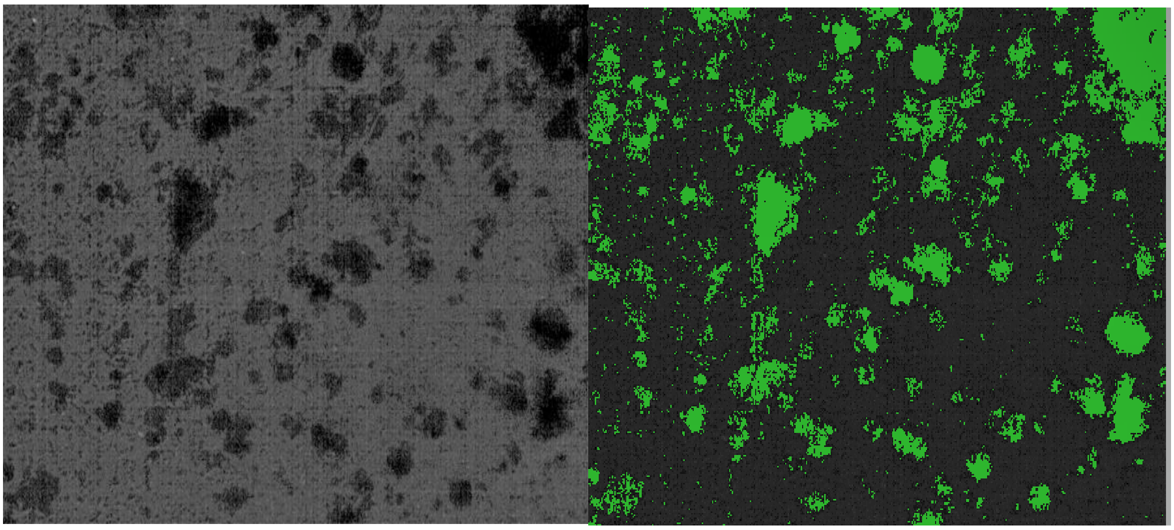

Figure 5. Original (a) and microscopically processed (b) image of the material sample surface (2)

Figure 6 shows the number of grains in areas of certain sizes for the analyzed sample.

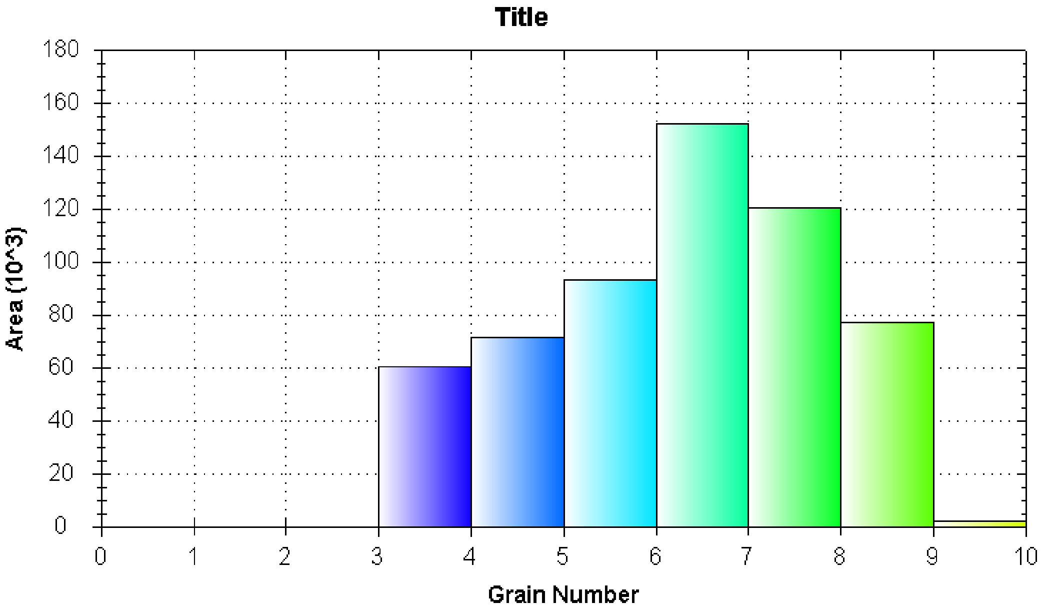

Figure 6. Grain size distribution for material P2, Ts = 1600°C

For material (P3), sintering temperature T = 1600°C, the percentage of closed porosity is 6.5%, the microscopic view is shown in the figure 7. On samples sintered at temperature T = 1550°C, the closed porosity is 18%.

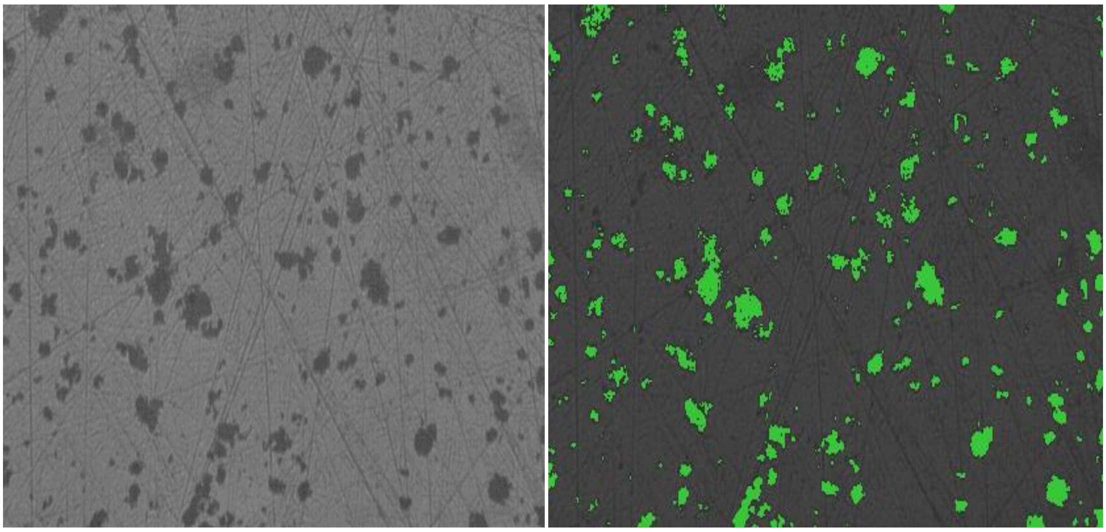

Figure 7. Original (a) and microscopically processed (b) image of the surface of the material sample P3

Figure 8. shows the number of grains in areas of certain sizes for the analyzed sample (P3).

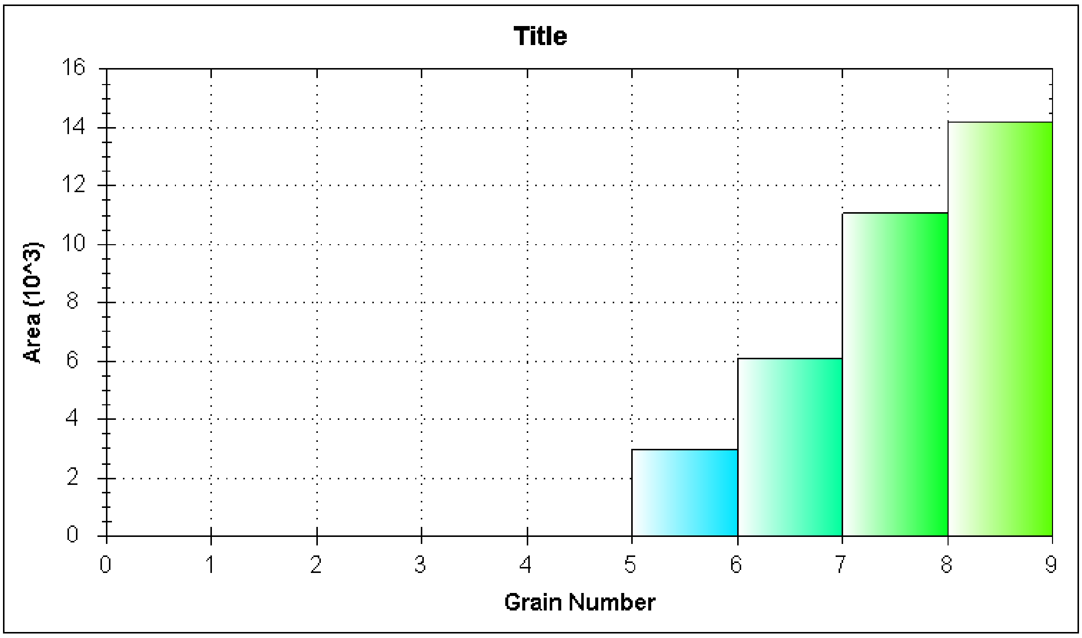

Figure 8. Grain size distribution for material (P3), Ts = 1600°C

CONCLUSION

The choice of raw material has a great impact on the end result. Each raw material has certain characteristics that in different processes of preparation, sintering, processing can show specificity in behavior.

It is necessary to know the action of raw materials, to know in which direction to go when developing new materials, or when determining the purpose of a particular finished material.

The analyzed materials, regardless of the changes in composition, which are not large, showed certain similarities but also certain differences in behavior. This means that when choosing materials for the production of ceramic segments, each of them can be a good choice, depending on the customer's requirements.

If the customer's desire is high resistance to abrasion, followed by withstanding elevated temperatures, according to these results we see that we can use the material P1 (because it met the requirement for hardness and thermal shock).

However, for applications where high resistance to thermal shocks (≥ 400 °C) is required, the choice will be a material with a higher percentage of porosity.

To achieve the prescribed values of specific weights and that for materials with ≥ 98% is a minimum of 3.82 g /cm^3, from the obtained results it can be seen that the temperature of 1550 °C is insufficient. A temperature of 1600 °C is sufficient to achieve specific weights, even when there is a change in the content of magnesium and calcium oxide. The most important ratio in the material is the oxide ratio (SiO_2:MgO, SiO_2:CaO) as well as the content of the basic oxide (Al_2O_3).

For materials above 98% Al_2O_3, it is best to determine empirically the ratio of SiO_2:MgO:CaO oxides, which will give the best results when tested for the intended purpose.

When determining resistance to thermal shock, for material P1 samples with sintering temperature of 1550 °C are resistant up to 750 °C, while samples with sintering temperature of 1600 °C, except for material P3, all passed the test. Considering these results, we can conclude that ceramic materials with ratios as in materials P1 and P2 at a sintering temperature of 1600 °C have higher resistance to thermal shock and such materials can be recommended for future research of this type.

Satisfactory values for hardness were shown by samples of materials P1 and P3, because they had an average value of hardness HV5 ≥ 1500 on testing.

Materials with higher specific gravity have lower porosity. The production of materials with a higher percentage of porosity (open and closed) is on the rise, because these materials are characterized by better resistance to thermal shocks, and some to the influence of aggressive media. This is one of the better ways to know the influence of certain oxides, such as CaO and MgO, on the formation of a material with a higher percentage of porosity, if the need for that material arises.

For 98.5 to 99% Al_2O_3 material, the minimum sintering temperature is 1600 °C. For materials up to 95% Al_2O_3 by changing the content of the tested oxides (CaO, MgO, SiO_2) it is possible to lower the sintering temperature below 1550 °C.

REFERENCES

[1] Tomislav Filetin, Franjo Kovačićek i Janez Indof: Svojstva i primjena materijala

[2] Filetin, T.; Kramer, I.: Tehnička keramika, Fakultet strojarstva i brodogradnje, 2005.

[3] Musikant, S.: What Every Engineer Should Know About Ceramics, Marcel Dekker. Inc., New York, 1990.

[4] M.W. Barsoum, M.W.: Fundamentals of ceramics, McGraw- Hill, 1997.

[5] M.W. Barsoum, M.W.: Fundamentals of ceramics, McGraw- Hill, 2003.

[6] M.N. Rahaman.: Ceramic Processing and sintering, second edition; Department of Ceramic Engineering, University of Missouri, U.S.A.

[7] BOUGARD, E. 2003. Ceramic in the Upper Palaeolithic, Prehistoric Pottery, People, pattern and purpose, Prehistoric Ceramics Resarch Group:Occasional Publications No. 4, BAR International Series, Oxford, 29-35.

[8] GRGIĆ, J., et al. 2007. Svijet minerala, katalog izložbe, Pomorski povijesni muzej Hrvatskog primorja, Rijeka - Pula.

[9] GRIMSHAW, R. W. 1971. The Chemistry and physic of clays and allied cheramic materials, London, reprint.

[10] HORVAT, M. 1999. Keramika, Tehnologija keramike, tipologija lončenine, keramički arhiv, Razprave Filozofske fakultete, Ljubljana.

[11] Ćurković, L. : Prezentacija Keramika, beton i drvo I. dio, Zagreb, 2008./2009.

[12] J.H. Edgar; Research interest: Bulk Aluminum Nitride Crystal Growth

[13] Casellas, D.; Nagl, N. M.: Growth of Surface Indentation Cracks in Alumina and Zirconia Toughened Alumina, Key Engineering Materials, 127-131, 895-902 (1997).

[14] Kolemen, U.: Analysis of ISE in microhardness measurements of bulk MgB2 superconductors using different models, J. Alloys Compd. 425, 429-435 (2006).

[15] Sahin, O.; Uzun, O.; Kolemen, U.; Ucar, N.: Vickers microindentation hardness studies of -Sn single crystal, Mater. Characterization, 58, 197-204 (2007).

[16] http://www.nonmet.mat.ethz.ch/education/courses/Materialwissenschaft_2/brevier.pdf

[17] Mellor's Modern Inorganic Chemistry, Revised and edited by G.D. Parkes, M.A.,D.Phil, New York, 1952.

[18] Richerson W., David: Modern Ceramic Engineering, New York, 1982.

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