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The Effect of Acrylate on the Properties and Machinability of Alumina Ceramics

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Abstract:

Effect of methyl methacrylate (MMA) as a binder and heating treatment were investigated to improve green alumina compacts machinability. Properties of green compacts and their corresponding sintered samples prepared with and without MMA were compared. Investigation of green and sintered properties was performed on samples compacted at applied pressures up to 150 MPa. After pressing, samples with MMA were thermally treated at 115^{o}C. The intention was to enhance the polymerization of MMA at a temperature a little higher than the glass transition temperature (T_g = 103^{o}C) of poly (methyl methacrylate). Green compacts with MMA had higher green density values than those without MMA. Sintered samples with MMA had lower values of sintered density and higher values of total porosity; after sintering, relative linear shrinkage was around 15 % for the whole range of applied pressures. The possibility of easily machining the green compacts with MMA produces great possibilities for application in many fields.

***Keywords**: Alumina ceramics; Acrylic binder; Thermal treatment; Machining.*

1. Introduction

The machining process of ceramics is applied to achieve high precision of complex-shaped ceramic parts which is unachievable with traditional ceramic forming methods. Ceramic machining can be divided into two categories: machining of green bodies and machining of sintered ceramics. Machining of green parts is used to produce complex forms that have great potential for application in many fields of medicine and technology [1-6].

Green properties depend on the properties of the binders present in the green sample [7-11]. Likewise, the polymers glass transition temperature (T_g) of the organic binder is one of the most important parameters controlling binder performance because it affects the green density and green strength of dry pressed ceramics. In the case when ceramic powders are compressed at a temperature below the T_g of polymer binder, a tendency to form a heterogeneously distributed density rises by reducing the green density in ceramics [10,12-15]. Polyvinyl alcohol (PVA) is an important organic binder for the synthesis of ceramic powder. Moreover, PVA as a binder is commonly used for dry pressing and machining green and sintered parts [2,5,16-17].

Many authors studied the effects of some acrylic compounds as binders on machining and properties of green and sintered parts. Technological advancement of additives like

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acrylics provides sufficient strength of the compacts for machining and leads to formulations containing high solids contents in systems. They have useful and unique characteristics such as plasticization and controllable cross linking. Also, it was found that acrylate binders provide chip resistance of green bodies that can be machined without cracking and had exhibited compacts with good surface finish [7,9,11,18-19]. Due to hydrophobic nature of acrylates, during water evaporation, the groups of alumina particles are formed which under the optimal machining conditions contribute to the successful forming of complex shapes of ceramics [2-3,17-18].

In this work, the influence of methyl methacrylate (MMA)on the green density and machining of the complex shaped green compacts were studied. Machining by turning, milling, and drilling was performed on green compacts previously thermally treated at 40, 95, and 115^{o}C. It was found that machining of green bodies prepared with MMA can produce complex alumina forms with great possibilities of commercial application [7,19].

2. Materials and Experimental Procedures

2.1 Materials

Standard alumina powder (CT 3000 SG, Alcoa, USA) was used in this work. Averageparticle size of the powder was 0.6–0.8 μm with a specific surface area of 6–8 m^2/g. Methyl methacrylate (MMA) (Galenika, Serbia) with boiling temperature (T_b) of 100 ^{o}C, petroleum wax water suspension (Mobil Oil, New Zeland) andpolyvinyl alcohol (PVA) (Alkaloid, North Macedonia) with molecular mass (M_w) of 94000, glass transition temperature (T_g) of 47^{o}C were used as binders. PVA was dissolved in warm water before use. Glycerin (Zorka–Pharma, Serbia) and magnesium stearate (Galenika, Serbia) were used as additives for lubricationof the powder, whereas distilled water and ethanol (Zorka–Pharma, Serbia) served as solvents.

2.2 Preparation of alumina powder

Powder mixture for pressing was prepared in several steps. Firstly, alumina powder (100 g) was mixed with: binders – PVA (0.04 g) and petroleum wax water emulsion (4 g), lubricants – glycerin (6 g) and magnesium stearate (0.4 g), as well as solvents – distilled water (80 ml) and ethanol (20 ml), by using a ball mill for 6 h. Secondly, the mixture was kept still for 16 h at room temperature, then stirred for another 6 h and dried for about 36 h at 60^{o}C. Finally, the powder was ground and passed through various sieves yielding a homogeneous powder with a particle size smaller than 250 μm.

The acrylic powder mixture was prepared by adding liquid MMA to the already prepared alumina powder. Homogenization of the prepared alumina powder with 2 wt.% of MMA was performed in a ball mill for 30 min. After drying, the synthesized powder was sieved through the sieve with 250 μm wide openings [7].

Thermal stability of both alumina powder mixtures, without and with MMA was investigated by thermo-gravimetric analysis (TG) in the air (Fig. 1) with the heating rate of 7^{o}/min by using TG Stanton Red croft model STA 1000 thermo balance [7].

2.3 Pressing

Both final powder mixtures, prepared with and without the addition of MMA, were uniaxially pressed in the form of pellets. Thirteen different pressures ranging from 30–150 MPa, were applied. The powder was pressed in the mold with 10 mm diameter on the

universal tensile testing machine (Mohr and Federhaff AG), adapted as a press, holding the peak pressure for 30 seconds. The mass of all samples was 2 g.

Forming pressure for powder pressing of 60 MPa was determined from diagrams, representing the dependence of green density on the applied pressure (Fig. 2).

After pressing, the samples with MMA were thermally treated at 115^{o}C for 3 h, at a temperature a little higher than T_g (103^{o}C) of poly (methyl methacrylate), since the results showed that the green compacts pressed with acrylate exhibit better mechanical properties and better machinability after heating at a temperature in the vicinity of T_g of the used MMA acrylate binder [10].

2.4 Pre-sintering and sintering process

The pre-sintering process was performed with the heating rate of 30 ^{o}/h up to 1000^{o}C, then holding for 1 h at 1000^{o}C. After wards, these samples were sintered with a heating rate of 240 ^{o}/h up to 1620^{o}C for 2 h.

2.5 Characterization of green compacts and sintered samples

2.5.1 Characterization of green compacts

The samples green density was calculated as a weight to volume ratio of the pressed samples by using a micrometer. Axial and radial compressive strengths were measured using the green cylindrical samples of 2 g with a diameter of 10 mm and 10 mm in height by using an 1185 Instron (High Wycombe, UK) type testing machine at room temperature. Measuring was performed on 10 samples at a loading rate of 1 mm/min with 0.35 mm thick cardboard to minimize sample friction by an automatic device. Rudnik et al. [20] investigated the application of thick cardboard in determining compressive strengths. Radial compression method can be used to determine tensile strength of brittle materials like alumina [21].

The compressive strength (σ) and Young's modulus (E) were calculated for the samples pressed at 70 MPa. The compressive strength was calculated using the following equation $\sigma=2P/\pi De$ where P, D, and e are a load applied at fracture, diameter, and thickness of the sample, respectively. Young's modulus (E) was calculated using the following equation $E=\sigma/\varepsilon$ where ε is an axial strain in the linear elastic region of a material.

2.5.2 Characterization of sintered samples

The density, open and total porosity of the sintered samples were calculated using results derived by the Archimedes method. The relative linear shrinkage of the samples was determined by measuring dimensions of samples by using a micrometer before and after the sintering of the samples. The observed surface appearance and microstructure of the sintered samples were examined by employing optical microscopy, Carl Zeiss, and JEOL 5800 scanning electron microscope. Prior to the examination of the microstructure, the samples were polished and covered with gold.

2.6 Test of machining of green compacts

Machining was performed on cylindrical samples and samples shaped as rectangular plates which were both pressed on 60 MPa. Cylindrical samples of 86 g had an outer diameter of 36 mm, an inner diameter of 17 mm and were 45 mm in height. Rectangular plate weighed 100 g, had a length of 60 mm, width of 60 mm and were10 mm in height. Before being green

machined by turning, milling and drilling, pressed samples with 2 wt.% MMA were thermally treated up to 115°C (Section 3.4) [7,19].

Cylindrical green compacts were treated with Potisje PA 501M lathe. The sample with outer and inner standard metric screw thread was made. The outer screw thread was machined with 60 rpm rotation with a 3 mm pitch and 3.9 mm deep slot. The inner screw thread was machined with 20 rpm rotation, 1.5 mm pitch and a 2 mm deep slot. Outer and inner rectangular pockets were also machined by turning. The cutting speed was 220 rpm rotation with 0.040 mm/° pitch and 3 and 5 mm deep slots. Pockets were 4 and 8 mm wide. Both outer and inner frontal edges were chamfered by turning. Tools used during the turning process were as follows: the process tools for longitudinal treatment, facing tool, pocketing tool and chamfering tool 45 ° lead angled. All of the tools used were of the vidia P10 quality.

The outer rectangular milled pockets and groove on the pressed plate were obtained with vertical spiral milling machine ∅ 6 HSS, Progres MUG 2. The width of the milled pockets was 6 mm each. Speed of cutting was 220 rpm rotation with 14 mm/min pitch and 2 and 4 mm deep slots. Drilling of the compacts was also done on a vertical spiral milling machine ∅ 6 HSS, Progres MUG 2. A hole with a diameter of 6 mm was milled with the milling speed of 350 rpm rotation by gimlet ∅ 6 HSS.

Selected samples with MMA after machining and sintering are shown in Fig. 8.

3. Results and Discussion

3.1 Thermal stability of synthesized alumina powders

The shape of the TG curve of the sample without MMA is different from the shape of the TG curve of a thermally treated sample with MMA (Fig. 1). TG curve of the sample obtained without MMA shows two main stages of weight loss at the temperature ranging from about 30-140°C and 140-450°C. The sample with MMA shows one stage of weight loss at the temperature ranging from about 30-550°C [7]. Heating at around 100°C in the presence of MMA improved the thermal stability of the multicomponent mixture of alumina powders (will be explained in Section 3.4.).

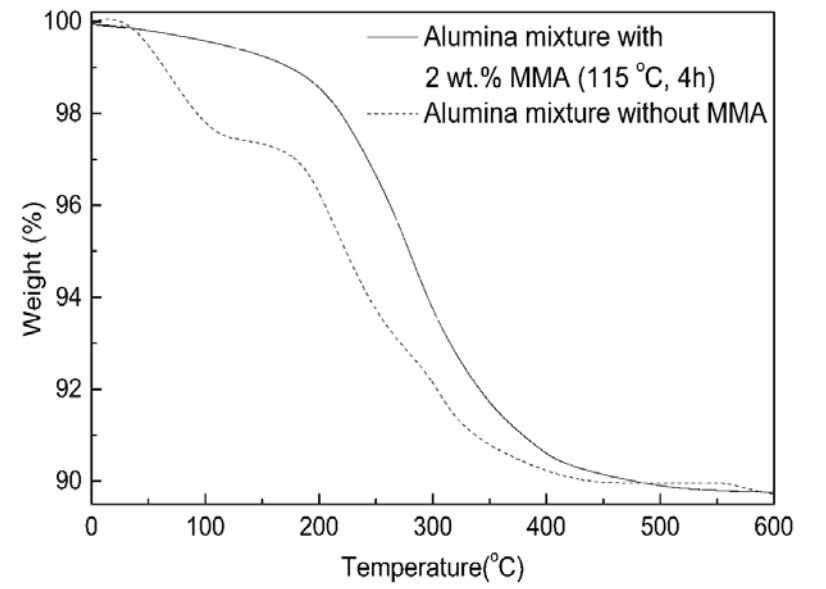

Fig. 1. TG of observed powder mixture without and with MMA thermally treated at 115°C for 4 h.

3.2 Properties of pressed samples

3.2.1 Green density

For samples without and with MMA, the dependence of the green density of pressed samples on applied pressure is shown in Fig. 2.

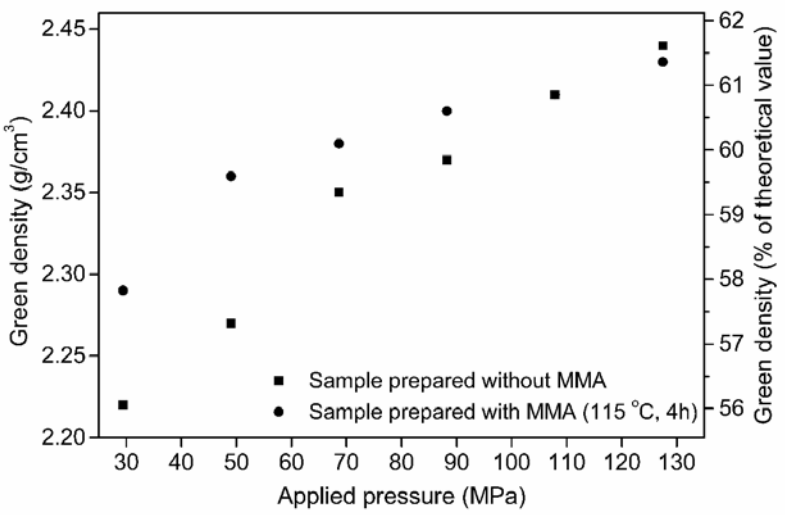

Fig. 2. Dependence of green density of pressed samples on applied pressure.

It is evident that with the increase of pressure, the values of green densities of pressed samples also increase, which is usual for systems in which rearrangements of particles take place. However, after applying pressure of about 60 MPa, this effect starts to relieve, reaching saturation at higher pressure. Therefore, the pressure of 60 MPa was selected as an optimum pressing pressure to avoid excessive energy input into the compacts, which could lead to failure during machining. Both groups of samples reached relatively high green density (Fig. 2), indicating good strength that could be developed during pressing at high pressures [7].Samples with MMA has higher values of green density than those without MMA at almost all applied pressures. The effect is more pronounced at lower pressures indicating better compressibility of samples with MMA since a similar level of green density is obtained at higher pressures. Obtained values from 56 % to 61.5 % of the theoretical density (3.96 g/cm^3) correspond to values ranging from 50 to 65 % [22].

3.2.2 Compressive strength and Young's modulus

Values of compressive strength (σ) and Young's modulus (E) for green samples pressed at 70 MPa are shown in Table I.

Tab. I Results of compressivestrength *(σ)* and Young's modulus (E) depending on the orientation of applied load.

Green samplepreparedd:	**Orientation of applied load:**			
	axially		radially	
	σ(MPa)	E(MPa)	σ(MPa)	E(MPa)
without MMA	2.52 ± 0.16	61.9 ± 6.15	0.34 ± 0.04	24.5 ± 3.98
with MMA (115^{o}C, 3h)	2.67 ± 0.41	69.3 ±15.4	0.43 ± 0.02	25.6 ± 1.61

For the sample with MMA, obtained values of σ and E determined under axially and radially oriented loads are slightly higher than for the sample without MMA. It is evident that the presence of MMA in the alumina mixture improved the strength of pressed alumina green samples.

3.3 Properties of sintered samples

3.3.1 Density and porosity

Dependence of the sintered density on applied pressure for investigated samples (Fig. 3) shows that the samples without MMA achieved higher sintered density values than those with MMA.

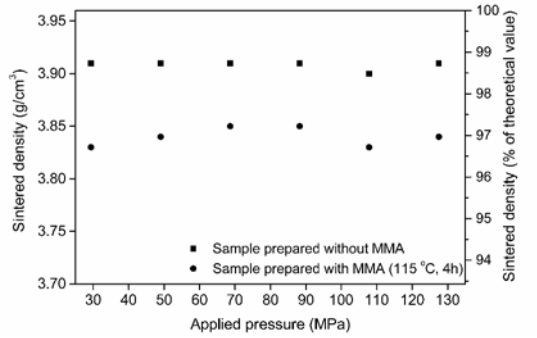

Fig. 3. Dependence of sintered density on applied pressure.

A diagram showing the dependence of total porosity on applied pressure is shown in Fig. 4. In the whole range of applied pressures, total porosity was higher in the samples with MMA, compared to the samples without MMA. The total porosity values were not significantly changed upon increasing the pressure up to 60 MPa in samples with MMA. In samples with MMA, higher total porosity values match lower values of sintered density for the same applied pressure. Dependence of open porosity on applied pressure is also given in Fig. 4. For both groups of samples (with MMA and without MMA), low values of open porosity are similar for the whole range of applied pressures. Therefore, pores effects on some mechanical properties and machinability of the composites could not be neglected.

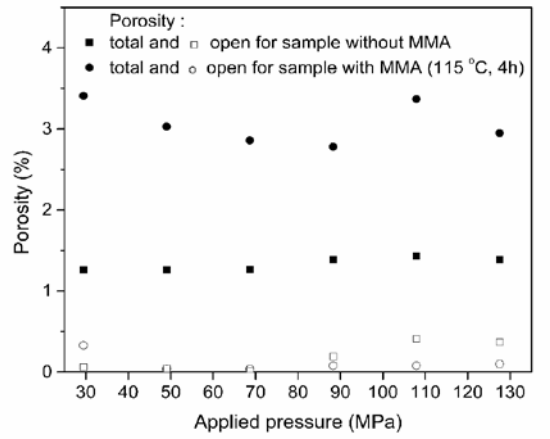

Fig. 4. Dependence of porosity of sintered samples on applied pressure; solid symbol – total porosity, open symbol – open porosity.

Also, density and porosity of sintered samples as functions of applied pressure (Fig. 3 and Fig. 4) illustrate that values of sintered density and porosity remain more or less unchanged with the increase of pressure for both samples.

3.3.2 Microstructural analysis

Fig. 5 and Fig. 6 shows surfaces of tested sintered samples by SEM analysis and optical microscopy, respectively.SEM analysis pointed out that the sample grains with MMA are more elongated and coalesced to each other compared to the form of grains sample without MMA (Fig. 5). It is evident that MMA affected grain growth, showing that grains grow faster in one direction.

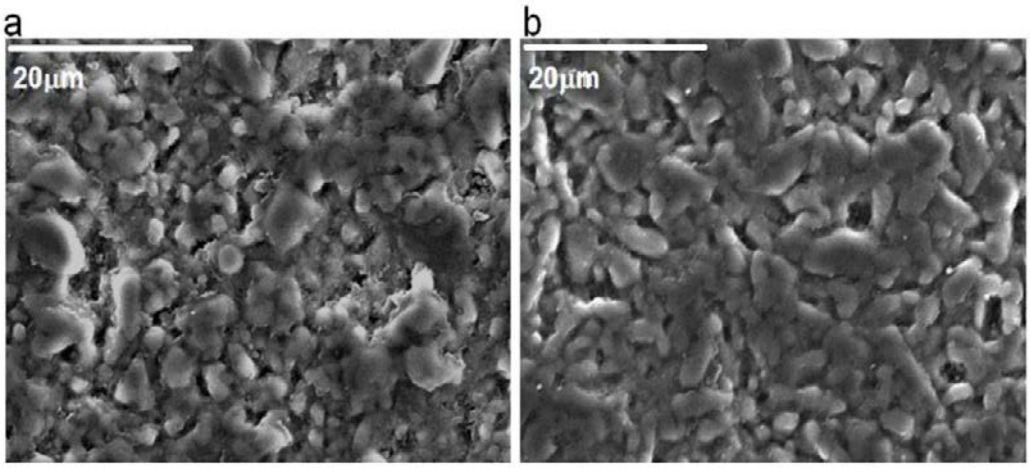

Fig. 5. SEM images of surfaces of sintered samples. The shape of grains for both investigated samples: a) without MMA and b) with MMA.

Optical microscopy confirmed that well-dispersed liquid MMA on the surface of ceramic particles had made many little gaps on the surface of the sintering sample prepared with MMA relative to the sample prepared without MMA (Fig. 6).

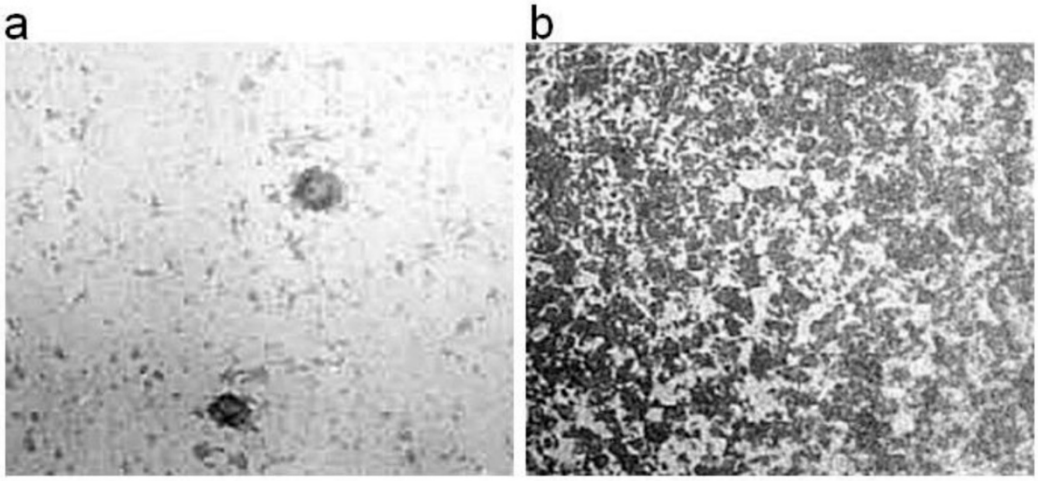

Fig. 6. The optical microscope of surfaces of sintered samples: a) without MMA and b) with MMA thermally treated at 115^{o}C for 4 h (200X).

3.3.3 Relative linear shrinkage (%)

The percentage of relative linear shrinkage (Table II) is a valuable parameter for predicting and controlling precise dimensions of sintered samples [7].

Tab. II Percentage of linear shrinkage *(%)* of some vs applied pressure for sintered samples.

Pressure (MPa)	Percentage of linear shrinkage (%) of sintered samples prepared:	
	without MMA	with MMA (115^{o}C, 3h)
30*	18.1	14.4
50	18.2	15.2
60*	18.0	14.5
70	16.9	15.3
90*	17.4	15.6
110	16.5	15.1
130	16.4	15.2

In the case of samples without MMA, higher values of linear shrinkage were obtained. In this sample, relative linear shrinkage decreased from 18.2 % to 16.4 % with increased applied pressure. In samples with MMA, relative linear shrinkage was around 15 % in the whole range of applied pressures. This is an advantage since relative linear shrinkage higher than 16 % could pose a problem often leading to cracks or other types of failure during the sintering of complicated shapes. Higher green density (Fig. 2) indicates better particle packing and results in lower linear shrinkage during the synthesis [7]. Due to the additional presence of MMA in the compression mixture, these samples have higher porosity (Fig. 4) and better thermal stability (Fig. 1). The presence of MMA caused the onset of intensive decomposition of the mixture components to move to higher temperatures (Fig. 1). Better thermal stability at higher temperatures led to the formation of a more number of pores (Fig. 4) and less shrinkage of MMA samples than samples without MMA (Table II).

3.4 Strengthening of green compacts with MMA

Improving green machinability of the sample with MMA has been achieved by prolonged heating at 40, 95, and 115^{o}C, respectively. This way, the influence of binders was prolonged while pressed material was further reinforced.

The intention was to enhance the polymerization of MMA in the pressed parts with the reaction of pre-polymerization (40^{o}C, 16 h) and polymerization (95^{o}C, 4 h) to produce short MMA polymer chains with low molecular mass. Those short polymer chains have better contact with ceramic particles than long polymer chains with high molecular mass. According to Howard et al. [12], activation of chain groups of MMA polymer occurred at 115^{o}C after 4 h. The temperature of activation of MMA polymer groups of 115^{o}C is slightly higher than T_g of 103^{o}C of MMA polymer synthesized according to the proposed procedure [23].

3.5 Machining of green compact

MMA was used as an additive to improve the pressing of alumina powder and machining of the green compact. Green compacts of samples with MMA were very smooth and shiny after pressing. A similar appearance of the surface was observed under SEM, as reported [24]. Selected samples with MMA after machining and sintering are shown in Fig. 7.

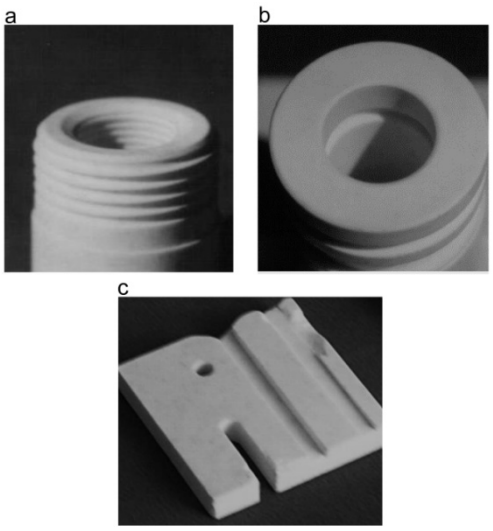

Fig. 7. Sintered machined green compacts prepared with MMA: a) outer and inner standard metric screw thread made by turning, b) outer and inner rectangular profile groove made by turning and c) pockets, groove and hole made by milling.

The sample with outer and inner standard metric screw thread is shown in Fig. 7a. Outer and inner rectangular pockets were also machined by turning (Fig. 7b). The outer rectangular milled pockets and groove on the pressed plate are shown in Fig. 7c. During the plate's milling, the proper pocket milling profile was obtained at the tool inlet, but the material cracked at the end of the pockets. These shapes of pockets and grooves were obtained by only one passage of the tool. Drilling of the compact was also done (Fig. 7c**).**It has been shown that the sample with MMA is easily machined as a „soft metal“.

3.5.1 Ceramic sealing set of rings used in pumps for transport of fluid–example for commercial products

A ceramic sealing set of rings used in pumps for transport of fluid (Fig. 8) can be successfully produced with subsequent minimal machining, leading to achieving predefined dimensions after sintering.

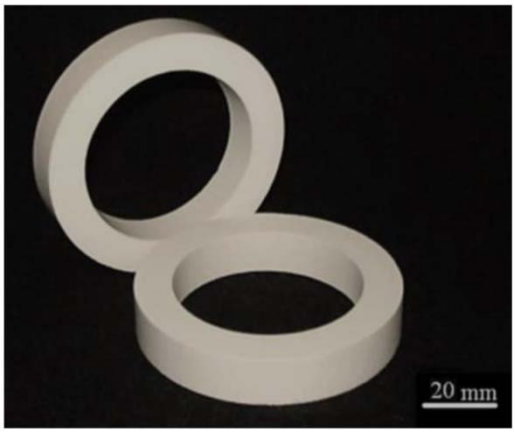

Fig. 8. Ceramic set of rings for sealing used in pumps for transport of fluid with outer and inner diameters of 63 mm and 51 mm, respectively.

Powder with MMA in the amount of 90 g was shaped using a mold with a hole with an outside diameter of 83.1 mm and an inner diameter of 59.9 mm. After thermal treatment up to 115^{o}C (Section 3.4), the green body was machined, which reduced its dimension to 77.6 mm and to 64 mm outer and inner diameter, respectively. These dimensions increased by the adopted % of linear shrinkage for this shape: the outer diameter increases by 20 % and the inner one by 18.5 %. Finally, for the sintered sample, the outer and inner diameters of 63 mm and 51 mm were successfully achieved by minimally using the milling machine (Fig. 8).

4. Conclusion

The presence of 2 wt.% of MMA in the multicomponent mixture of alumina powders and organic additives was used to improve the pressing of alumina powder and machining the green compact. The presence of MMA changed some green and sintered properties of alumina. The samples with MMA have higher values of green densities than samples without MMA. In the case of sintered samples with MMA, relative linear shrinkage was around 15 % for the whole range of applied pressures. The MMA was added as a supplementary additive in the alumina mixture, significantly changing the surface morphology of sintered alumina compared to the surface morphology of alumina prepared without MMA. After thermal treatment (40^{o}C, 16 h), (95^{o}C, 4 h), and (115^{o}C, 4 h), the green sample with MMA was smooth and shiny after pressing and well machined by turning, milling and drilling as a „soft metal“. It has been shown that machining green alumina with MMA can produce complex ceramics that can be commercially used.

Acknowledgments

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Сажетак: *Испитиван јеутицај метил метакрилата (ММА) као везива као и утицај термичког третманана машинску обрадивост испресака од алумине. Упоређена су својства како код испресака од алумине припремљених са и без ММА тако и код њима одговарајућих синтерованих узорака. Испитивање особина испресака и синтерованих узоракаизведено је на узорцима који су испресовани на притисцима до 150 МРа. Након пресовања, узорци са ММА су термички третирани на 115^{o}С са намером да ММА полимеризује на нешто вишој температури од температуре стакластог прелаза (T_g = 103^{o}С) поли(метил метакрилата. Испресци са ММА имали су веће густине од испресака без ММА. Синтеровани узорци припремљени са ММА имали су ниже синтероване густине и већу укупну порозност, анакон синтеровања, релативно линеарно скупљање је било око 15 % за цео опсег примењених притисака пресовања. Пробе машинске обрадљивости показале су да машинска обрада испресака са ММА има велике могућности за комерцијалну примену.*

Кључне речи*: алумина; акрилно везиво; термичкитретман,машинска обрада.*