Advances in Materials
2024, Vol. 13, No. 1, pp. 10-15
https://doi.org/10.11648/j.am.20241301.12

Research/Technical Note

The Influence of the Green Density on the Quality of ZTA Zirconia Toughened Alumina Plungers

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Abstract

The purpose of this study is to investigate the effect of the green density (ρ_g) on the sintered density (ρ_s), shrinkage according height and diameter (HS, DS), relative density, porosity and hardness of ZTA ceramic plungers. Zirconia toughened alumina is characterized by excellent properties of hardness, toughness, thermal and chemical resistance, which make composite material interesting for multiple applications. Some of the significant applications of ZTA ceramics are in the production of biomedical implants, cutting tools, parts for pumps and others. The material is composed of high purity alumina 90% and 10% of zirconium oxide. This material successfully compensate fragility of the alumina and zirconium oxide price. After 24 hours of milling in a ball mill (Dorst, Germany) slurry with a specific surface 25 832 cm^2/g was transferred into a mixer with addition of binders (PVA + soap based binder) through a vibrating sieve (British and Foreign Patents). Solid content (%) of the slurry in amount of 69.16 was confirmed by thermogravimetric and differential gravimetric analyzes. The 1000 kg of the powder dried by spray drying (Spray dryer Niro) contains 2.6% of binders and 0.2% of moisture. Three sets of plungers with outer diameter of 3.6 cm, inner diameter of 2.0 cm and height of 7.6 cm were produced by cold isostatic pressing (CIP) using different pressures. The first set marked as 'A' was pressed by pressure of 80 MPa, the second set marked as 'B' was pressed by pressure of 100 MPa, and third set marked as 'C', was pressed by pressure of 150 MPa. According to statistical data processing, comparison and analysis of the results it is concluded that the quality of the ZTA plungers, in specific presented case, significantly depends on the green density (ρ_g).

Keywords

Zirconia Toughened Alumina, Green Density, Quality

1. Introduction

Ceramics can be defined as a solid compounds that are formed by the application of heat and sometimes heat and pressure, comprising at least two elements provided one of them is non – metal or metalloid. The other element (s) may be a metal (s) or another metalloid (s). Kingery defined ceramics on simpler way " the art and science of making and using solid articles, which have as their essential component, and are composed in a large part of inorganic, non-metallic materials". In other words, what is not metal or a polymer, is a ceramics [1]. All materials properties, including ceramic materials depend on their microstructure. Selection of the raw materials, process parameters and technique of production as

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Received: 18 January 2024; **Accepted:** 2 February 2024; **Published:** 28 February 2024

a result have specific microstructure of material. Producing of composite materials have purpose to attempt to eliminate negative characteristics and to take advantage of good characteristics of each material. Composite ZTA material presents promising material, dependently of mass fraction of ZrO_2, because of its mechanical properties, biocompatibility and aesthetic criteria [2]. Zirconia toughened alumina spray dryed granules were sieved on sieves (Endecot, Italy) in five size fraction ranging: < 80 µm, from 80 µm to 105 µm, from 105 µm to 150 µm, from 150 µm to 180 µm, from 180 µm to 220 µm and > 220 µm to determinate the granule size distribution (according to the ASTM E11-20). The ceramic green body can be directly fabricated to the final shape, before sintering. The desired shapes can be easily formed due to the low mechanical strength of weakly bonded ceramic powders in green body phase. Pressing is the most widely used shaping technique for advanced ceramics. Desired shapes can be produced by pressing under uniaxial or isostatic pressure. The external heat may be applied at the same time, in order to further enhance densification [3]. Green density is defined as the total mass of a body divided by the green volume [4, 13]. For a green body the green volume includes the volume of solid particles, the volume of any temporary additives and liquid present, and the volume of empty pore space. Many American Society for Testing and Materials (ASTM) methods for determining bulk (green) density are described but this methods are mostly based volume displacement by Archimedes principle. That is acceptable for glasses and refractory materials but for green ceramics this method is not suitable. For green body ceramics, mercury pycnometer is recognized as the benchmark for measuring bulk density of a body, but mercury is significant health hazard. Some of the different methods for bulk density determining (according ASTM C914 – 95) are: mercury method, water displacement of bodies coated with wax or water repellent spray, mineral oil and powder pycnometer methods. All of this methods have their advantages and disadvantages, according to that, in this work green density was determined by mass – volume measurement method [4]. Thirty samples with different range of green densities were analyzed. The average green density of samples marked as 'A' is 2.290 g/cm^3, and the average green density of the samples marked as 'B' is 2.318 g/cm^3. Samples marked as 'C' have average green density 2.471 g/cm^3. Value of green density provides information needed to control quality of the ceramics piece (after sintering) [4]. Sintering is most common way for ceramic powder consolidation. The process is irreversible and due to the heating the particles connect between each other and densification was performed. The sintering temperature is temperature lower than melting temperature. The green piece is high temperatures affected which causes thermal activation of mechanism of substance transport. The main goal is to achieve improvement of properties and density closest to relative density [5]. The advantage of application ZTA plungers, pistons and other ceramic pieces in pumps is related to their wear and corrosion resistance, and extending work life of pumps. Ceramic components in pumps are used in chemical, petrochemical industry, paper industry, cement production and others [6]. The satisfactory quality of ZTA plunger is defined in table 1 according to basic parameters which are discussed in this study. Basic parameters of quality for ZTA plungers are density 3.980 g/cm^3 and Vickers hardness 15 GPa. Required surface quality is ≤ 0.2 µm.

Table 1. *Quality parameters of ZTA plunger.*

Properties	Value
Density (g/cm^3)	3.980
Hardness (GPa)	15
Roughness Ra (µm)	≤ 0.2

2. Materials and Methods

2.1. Materials

This research (selection of the materials, preparation of ceramic powder, analyzing of the powder and machining of the green and sintered ZTA plungers) was entirely done in the Factory of spark plugs and industrial ceramics Enker D.D. in Tesanj, Bosnia and Herzegovina. Aluminium oxide is only thermodynamically stable in form of $\alpha - Al_2O_3$, and it is classified commercially according purity, grain size, morphology, content of α- alumina [1, 7]. In this study, ceramic powder was prepared from high purity Al_2O_3 (Almatis, Germany), average grain size (d50) 1.5 µm and zirconia oxide ZrO_2 average grain size (d50) 0.6 – 0.7 µm. According producers specification content of Al_2O_3 is 99.86 % and CaO, Fe_2O_3, B_2O_3, SiO_2, Na_2O were confirmed. Table 2 presents chemical composition of alumina.

Table 2. *Chemical composition of alumina.*

Sample	wt.%					
	CaO	SiO_2	Fe_2O_3	B_2O_3	Na_2O	Al_2O_3
Al_2O_3 powder	0,019	0,0056	0,0143	0,0110	0,05	balance

Aluminium oxide has fracture toughness 4 – 6 MPa $m^{1/2}$ and when initial crack appears, it can't be stopped by plastic deformation, the result is cracking of the ceramic piece. On the other hand, zirconia oxide has high toughness and when they join together, they formed material with excellent properties [2, 8]. The table 3 presents chemical composition of ZrO_2.

Table 3. *Chemical composition of zirconia.*

Sample	wt.%					
	$ZrO2 + HfO_2$	SiO_2	Fe_2O_3	B_2O_3	Na_2O	TiO_2
ZrO_2 powder	99,9	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1

2.2. Methods

For all sintered samples green density, shrinkage (according height and diameter) and sintered density were determined. With caliper (Mitutoyo, Japan) height (H, mm) and outer diameter (D, mm) were measured. Internal diameter was measured with micrometer (Mitutoyo, Japan). Mass of the green bodies was measured by analytical balance (Shimadzu, Japan). The green volume (V, cm^3) was obtained by relation:

$$V = (D^2 - d^2) \cdot \frac{\pi}{4} \cdot H, \ (cm^3) \quad (1)$$

Where D is average value outer diameter of plunger (mm), d is average value internal diameter of plunger (mm) and H is average value height of plunger (mm).

The green density was obtained by relation:

$$\rho_g = \frac{m}{V}, \ (g/cm^3) \quad (2)$$

Where ρ_g is green density of plunger, m is mass of green plunger and V is a volume of the green plunger.

The shrinkage according height (H, mm) was obtained according relation:

$$HS = \frac{Hg - Hs}{Hg} \cdot 100, \% \quad (3)$$

Where is H_g average height of the green plunger and H_s is average height sintered plunger.

The shrinkage according diameter (D, mm) was obtained according relation:

$$DS = \frac{Dg - Ds}{Dg} \cdot 100, \% \quad (4)$$

Where D_g is average diameter of the green plunger and D_S is average height sintered plunger.

Sintered density was evaluated using the Archimedes method (Radwag, UK), according to ASTM C373 – 88.

The relative density (ρ_R) was obtained by relation:

$$\rho_R = \frac{\rho_s}{\rho_t} \cdot 100, \% \quad (5)$$

Where ρ_R is relative density, ρ_s is sintered density and ρ_t is a theoretical density. Value of theoretical density is 4.1719 g/cm^3.

Penetrant test was obtained according to ISO 3452 – 1. The samples were totally immersed in fluorescent penetrant solution. Checking of samples is conducted by UV lamp test. The methodology used for the determination of hardness, was in accordance with ASTM C1327-99. Three Vickers impressions had been carried through in the surfaces of each sample, which already were polishing, using an applied load of 49 N during fifteen seconds. After the diagonal length measurement, the values of the Vickers hardness (GPa) were calculated, by the following equation:

$$HV = 0{,}0018544 \cdot \frac{P}{d^2} \quad (6)$$

Where *HV* is Vickers hardness (GPa), P is applied load (N) and d (mm) is arithmetic mean of the two diagonal lengths [9].

3. Results and Discussion

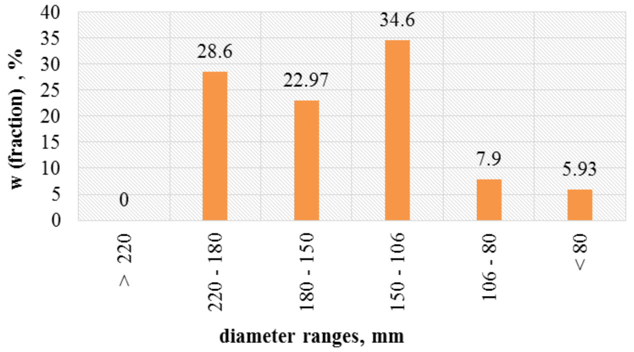

Figure 1. *Particle size distribution of the spray – dried alumina granules.*

Particle size distribution, that follows normal distribution (figure 1) shows that 94% of particles are in the range of 80 µm to 220 µm. Particle's shape and size distribution are important properties of the powder because of ensuring the proper filling the mould in the process of green body production [10, 11].

Figure 2 shows the dependence of the sintered density on the green (raw) density. As expected, as the green density increases, the sintered density also increases. Dense, uniform particle packing geometry in a green ceramic powder compact is the primary criterion in achieving high end point density body with desired microstructure and this is always the goal to be achieved by the relevant researchers and manufacturers [12].

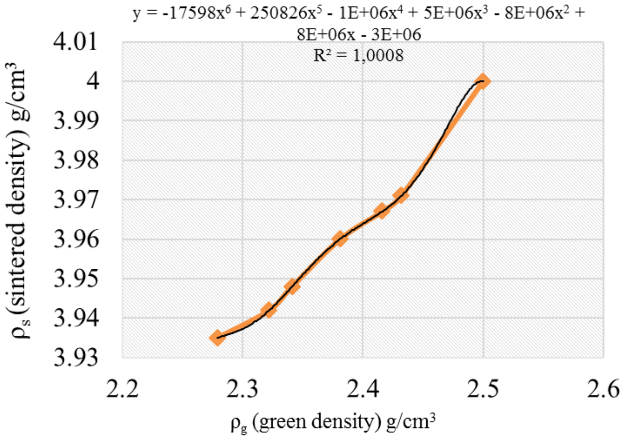

Figure 2. *Dependence of the sintered density on the green density.*

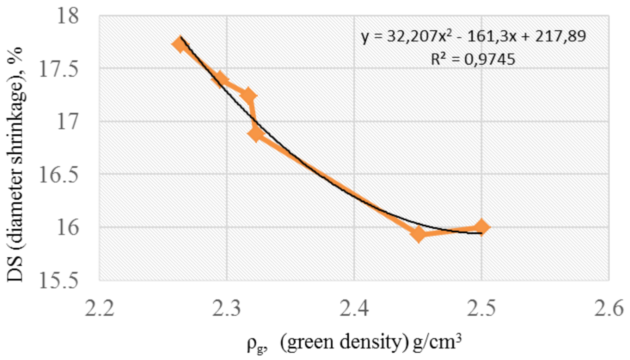

Figure 3. *Diameter shrinkage dependence on green density.*

The dependence of the shrinkage (by height and diameter) is significant. For the green sample with a green density (g/cm^3) 2.264 the shrinkage (%) is 17.71. For the green density (g/cm^3) 2.511, the shrinkage (%) is 15.59 (figure 3). The samples 'A' have the lowest value of green density and the samples 'C' have the highest value of the green density. The average shrinkages for the samples 'A', 'B', 'C' are presented on the figure 4.

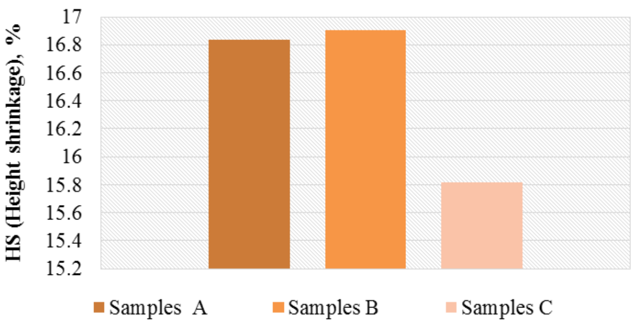

Figure 4. *Height shrinkage of 'A ', 'B', 'C' samples.*

The average and standard deviation of diameter (D), height (H), green density (ρ_g) and sintered density (ρ_s) are shown in the table 4.

Table 4. *Dimensions, green and sintered density (average value and experimental standard deviation.*

Properties	Samples A	Samples B	Samples C
ρ_g, g/cm^3	2.290 ±0.014	2.318 ±0.046	2.471 ±0.031
ρ_s, *g/cm^3*	3.934 ±0.002	3.948 ±0.007	3.987 ±0.010
DS, *mm*	17.456 ±0.332	17.120 ±0.14	15.302 ±0.416
HS, *mm*	16.833 ±0.431	16.904 ±0.06	15.819 ±0.423

The table 5 presents the values of the relative density and porosity for samples A, B, C and standard deviation.

Table 5. *Relative density and porosity (average value and standard deviation).*

Properties	Samples A	Samples B	Samples C
ρ_R, %	94.313 ±0.0705	94.644 ±0.191	95.577 ±0.256
Porosity, %	5.686 ±0.0705	5.355 ±0.191	4.422 ±0.256

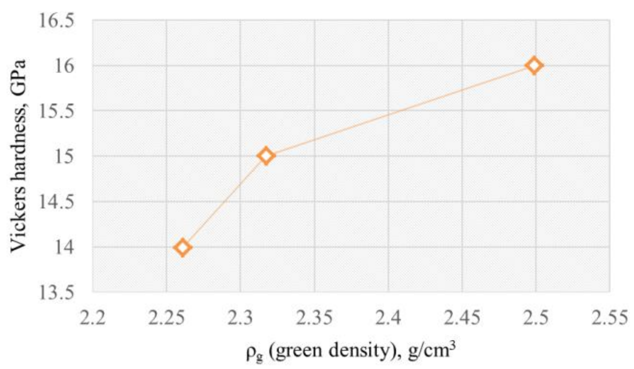

Figure 5. *Influence of the green density on the Vickers hardness.*

As expected, influence of the green density on hardness is obvious (figure 5). Moreover, plungers with green densities lower than 2.5 g/cm^3 have Vickers hardness lower than required. Penetrant test was conducted effectively and examined plungers don't have any cracks or open porosity. Surface quality was determined by appliance for roughness measurement (Mitutoyo, Japan). All samples have average roughness ≤ 0.2 µm.

4. Conclusions

The particle size distribution is in accordance to the prescribed values for ZTA spray-dried powder, which is an important characteristic for molding (cold isostatic pressing of the green body).

The sintered density is significantly dependent on the green (raw) density in the production process of ZTA plungers. By recording and analyzing the changes during pressing in the value of green density we have clear goal of green density to achieve the satisfied plunger quality.

According to expectation, it was obtained that the shrinkage according to height and diameter decreases with the increase of the green density of the plunger.

An increase of green density results an increase of relative density and thus decreases porosity.

The highest values of the Vickers hardness have the samples with the highest green density.

It is concluded that the overall quality of the ZTA plungers depends on the green density of the bodies.

An interesting step for further research would be to test the samples from sets "A", "B" and "C" in the real conditions of exploitation of the ceramic plunger in pumps in order to compare durability and working life.

Abbreviations

ZTA: Zirconia Toughened Alumina
V: volume
D: outer diameter
d: internal diameter
H: height
D_g: green diameter
H_g: green height
D_s: sintered diameter
H_s: sintered height
ρ_g: green density
ρ_s: sintered density
ρ_R: relative density
ρ_t: theoretical density
HS: shrinkage according height
DS: shrinkage according diameter
PVA: Poly Vinyl Alcohol
CIP: Cold Isostatic Pressing
ZrO_2: zirconium oxide
Al_2O_3: aluminium oxide
CaO: calcium oxide
Fe_2O_3: ferric oxide
B_2O_3: boric oxide
SiO_2: silicon dioxide
Na_2O: sodium oxide
TiO_2: titanium dioxide
HfO_2: hafnium oxide
UV: Ultraviolet
HV: Vickers Hardness
P: Load

Conflicts of Interest

The authors declare no conflicts of interest.

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