

Microstructure and properties of 3Y-TZP ceramic fabricated using PEG temporary binder

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Abstract. 3Y-TZP ceramics prepared with uniaxial pressing technology followed by free sintering were investigated. Polyethylene glycols (PEG) with different molecular weight were used for the granules preparation. Green and sintered samples with different granulated powders were analyzed. The forming uniaxial pressure was 100 MPa. Sintering of samples was performed at 1520 °C during 5 hours of soaking. Microstructural investigation was carried out by scanning electron microscope. Obtained relative green and sintered densities for all sample series are equal (50 % and 95 %, corresponding). Fracture surfaces of green samples are uniform and do not contain defects as large pores. Microstructural investigation of sintered samples revealed large cracks with a size in the range between 20 and 40 μm . The average grain size is about 0.7 μm . The average microhardness for all series is about $1150 \pm 25 \text{ HV}_{0.5}$. The minimum strength was obtained for a samples series prepared using PEG 1500 and PEG 6000 mixture. All other series show a flexure strength on one level ($880 \pm 50 \text{ MPa}$). It is determined, that usage of polyethylene glycols with 400-6000 molecular weight as temporary organic additives is an effective for the 3Y-TZP ceramic production.

1. Introduction

The dry pressing technology followed by free sintering have a wide area of application in production of modern dense high-strength ceramics for different purposes [1]. As usually, the high strength of sintered ceramics is achieved by means of using finely dispersed powders as a raw material. At the same time submicron powder pressing leads to nonuniform distribution of pressure and formation of macrodefects in the compacts. This is due to the low technological properties and tendency to aggregating of submicron powders.

The negative effects of compacting can be reduced by granulation of raw powders (preparation of conglomerates with controlled shape, size and properties). Strength and the ability of granules to deform plastically affect their rearrangement in the press-form on initial pressing stage, as well as on destroying during final stage. This leads to the uniform distribution of pressure and elimination of large defects in compacts. The usage of various binders and plasticizers as organic additives is an effective method of controlling the granulated powder behavior. Typically, high molecular weight polymers are used as binders, and low molecular weight polymers are used as plasticizers.

The main parameters that determine the choice of polymer additives are dissolubility in water or alcohol media, the glass transition temperature (T_g) and the thermomechanical behavior [2]. The molecular weight (M_w) of the polymer significantly effects on the described parameters. It is known that the increase of molecular weight results in increasing of the glass transition temperature and



melting temperature as well as plateau of viscous-flow state changing. Besides, in case when T_g is higher than the pressing temperature the polymer ductility is limited and its granule strength is higher than the pressure in the press-form. For example, the granules obtained by using only polyvinyl alcohol (PVA) deform during compaction but practically do not destroy.

At the stage of sintering, the processes promoting the reduction of the residual porosity take place. The intensity of these processes depends on the activity of the raw powders. In this case, large defects (for example, surfaces and junctions of unbroken granules) partially retained and lead to a decrease of mechanical properties of ceramics [3, 4]. Y-TZP shows a limited ability to reduce porosity during ceramics sintering [5]. Thereby, temporary organic additives choice should be made in the way that if fully allows eliminating of macrodefects formation at the pressing stage. The purpose of this research is to estimate the usefulness of polyethylene glycols (PEG) with different molecular weight application for the manufacturing of 3Y-TZP ceramics with high mechanical properties by uniaxial pressing followed by free sintering technology.

2. Materials and experimental procedure

The submicron powder 3Y-TZP (PSZ-5.5YS, Stanford Materials) with an average particle size $d_{50}=0.5-1\ \mu\text{m}$ was used as a raw material for preparation of the experimental materials. Dispersing of water suspension was carried out by using ultrasonic treatment (plant power 2 kW). Deflocculation agent Dolapix CE 64 was used for preventing particles agglomeration.

The suspension granulation was performed with a Mobile Minor 0.8 (GEA Niro) spray dryer. Before the granulation stage 2 wt. % of organic additives was introduced into the suspension. PEG $M_w=400$ ($T_g\sim-50\ ^\circ\text{C}$), 20 wt. % water solution of PEG 1500 ($M_w=1500$, $T_g\sim-28\ ^\circ\text{C}$), 20 wt. % water solution of PEG 6000 ($M_w=6000$, $T_g\sim-17\ ^\circ\text{C}$) and their mixtures were used as organic additives [6]. Granules size was 15–30 μm for all experimental series. The press-powder moisture was 0.5–0.7 % depending on the composition of the used organics. To exclude moisture difference influence, all press-powders were saturated with water to moisture about 1 %.

Bar-shaped samples of 5x5x50 mm size were prepared by uniaxial pressing on the Instron 3369 test machine. The forming uniaxial pressure was 100 MPa. Sintering of samples was performed in the LHT 02/17 (Nabertherm) laboratory furnace at 1520 $^\circ\text{C}$ during 5 hours of soaking [7].

Green and sintered samples were analyzed. Investigation of the samples after pressing was carried out based on geometric density measurement data and SEM images of fracture surface. The density of the sintered samples was determined using Archimedes' method. Microhardness and flexure strength were investigated to estimate the mechanical properties of the obtained ceramics. Microhardness was measured by the Vickers method on 402MVD semiautomatic instrument (Wolpert Group) under loading of 500 g. Three-point flexure strength tests were performed according to standard EN 843-1-2008 at the same equipment that was used at the pressing stage. Structural and fractographic studies of the samples were carried out with scanning electron microscope (SEM) Carl Zeiss EVO 50. Investigations were conducted at NSTU Materials Research Center.

3. Results and discussion

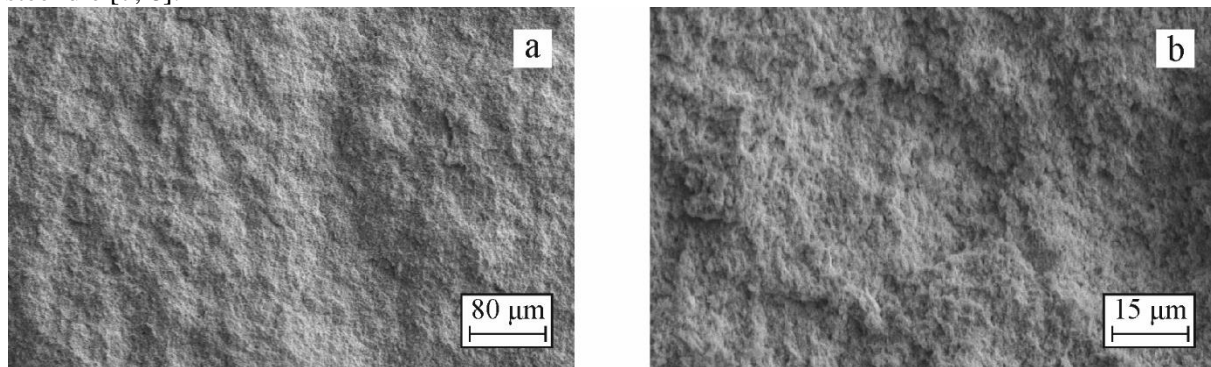
For research, four sample series of zirconia ceramics were obtained. The granulated powders with temporary organic additives of different molecular weight were used in the experimental series preparation (Table 1). The used polymers have the same molecular structure but different chain length. As a result, when two different binders were added simultaneously it was supposed that a homogeneous mixture of polymers with intermediate molecular weight is formed in suspension. Furthermore, in case of mixing two types of polymers the result physical and mechanical properties of binder are of an intermediate state between the initial components.

Green samples obtained from different granulated powders were analyzed. The density of all sample series are equal (Table 1). It can be assumed, that all press-powder granules have similar physical and mechanical properties and equal pressing behavior. The obtained density also suggest a low concentration of such macrodefect as pores in the samples.

Table 1. Green and sintered ceramic properties

Series N	Organic binder, (wt. %)	Relative green density, % of theoretic density	Relative sintered density, % of theoretic density	Flexure strength, MPa
1	PEG 1500 (2)	50 ± 1	96 ± 1	820 ± 50
2	PEG 6000 (2)	50 ± 1	95 ± 1	910 ± 50
3	PEG 6000 (1) + PEG 400 (1)	50 ± 1	95 ± 1	880 ± 50
4	PEG 1500 (1) + PEG 6000 (1)	50 ± 1	95 ± 1	530 ± 50

The fracture surfaces of the green samples are shown in figure 1. The analysis indicates that the fracture surfaces are homogeneous and do not contain such defects as large pores (Figure 1a). At the same time, a small content of granule boundaries is visible in figure 1b. It also should be noted, that large defects such as diagonal cracks are absent. The formation of these cracks is associated with the overpress effect. Similar defects occur in powder materials with high plasticity. Such materials do not have enough strength and the formation of overpress defect is caused by the elastic after-effect of the steel die [7, 8].

**Figure 1.** Fracture surface of the green samples (1st series).

It is assumed that granules with low strength were formed using all considered organic binders. Using considered PEG the obtained granules strength is sufficient to avoid overpress defect. At the same time during the pressing process at the initial stage of the load application, the granules are destroyed without redistribution. As the result the quantity of such defects as granule surfaces and junctions in the green ceramic decreased, but a uniform pressure distribution in the compact is not achieved.

Microstructural investigations of sintered samples showed, that large cracks with a size in the range between 20 and 40 μm were observed (Figure 2a). This defect size is the equal to the diameter of the initial granules. It is assumed that due to the uneven pressure distribution the concentration of defects in green ceramic (the surface of undestroyed granule) is quite high. The average grain size is about 0.7 μm . Figure 2b also shows that the maximum grain size was up to 3.8 μm in the local areas.

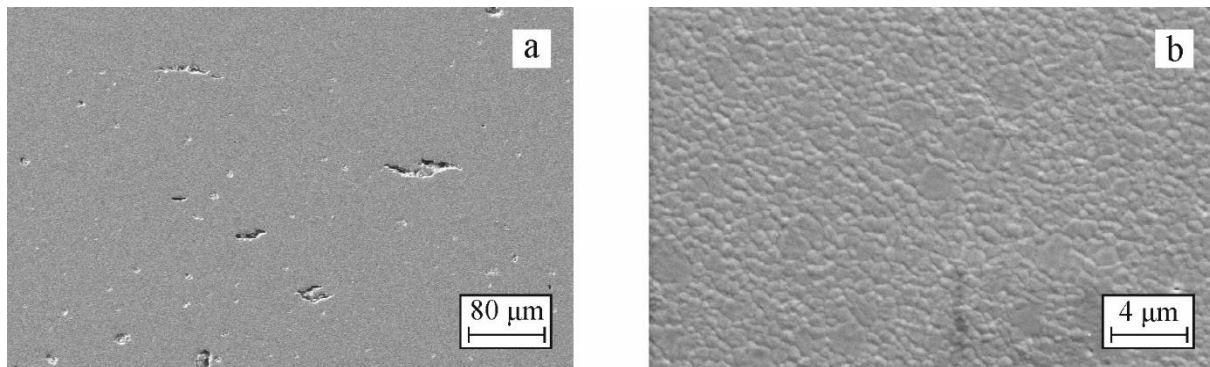


Figure 2. Typical defects (a) and microstructure (b) of the 1st samples series.

Although the fine-grained microstructure was obtained, the presence of large defects in sintered ceramic are affected on mechanical properties level. The average microhardness for all series is about $1150 \pm 25 \text{ HV}_{0.5}$. The minimum strength was obtained from the samples series prepared using PEG 1500 and PEG 6000 binder mixture. All other series show a flexure strength on one level ($880 \pm 50 \text{ MPa}$). This level corresponds to the properties of modern high strength zirconia ceramic obtained by such expensive technologies as cold and hot isostatic pressing. In particular, authors of [9, 10] showed that ceramics, obtained by cold isostatic pressing, have strength at the level of 600-1100 MPa. Moreover, according to [3] the usage of PEG as an organic binder for zirconia ceramic is more valid in comparison with polyvinyl alcohol when the samples strength was about 700 MPa.

The fracture surfaces of the sintered samples are shown in figure 3. It was stated that for all experimental series the origins of fracture were undestroyed granules. Figure 3a shows interface between undestroyed granule and the rest structure. It was assumed that the presence of almost spherical shape granules in sintered ceramic (Figure 3b) results from non-uniform pressure distribution. According to microstructure analysis, low flexure strength of the 4th experimental series samples were related with higher volume fracture these defects in comparison with other samples.

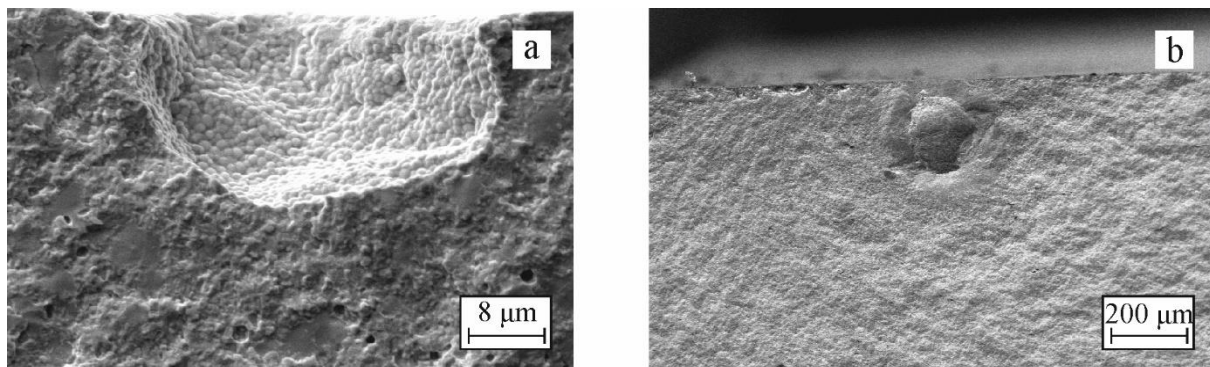


Figure 3. Typical fracture origin: an interface between undestroyed granule and the rest structure of the 1st samples series (a), undestroyed granule of the sample of the 4th series (b).

4. Conclusions

Consequently, usage of polyethylene glycols with 400-6000 molecular weight as temporary organic additives is an effective method for the production of 3Y-TZP ceramic by the axial pressing followed by free sintering technology. All studied samples series had a relative density about 95 % of theoretical value and a microhardness about $1150 \pm 25 \text{ HV}_{0.5}$.

The low strength of polymers leads to destroying of the most powders granules during the pressing stage. As a result, the volume fraction of such defects as surfaces and junctions of undestroyed granules was reduced and sintered ceramics strength increased. The highest flexure strength was obtained for ceramic samples with the injection of 2 wt. % PEG 6000 and was about 910 MPa.

At the same time, we expect that the low strength of temporary organics excludes the stages of granules redistribution and pressure equalizing in the green sample. Therefore, in areas with low specific pressure macrodefects are forming. Microstructural studies have shown that the major structural defect of all sintered ceramic samples is large cracks with a size from 20 to 40 μm .

Acknowledgments

This research was performed at Novosibirsk State Technical University under the financial support of the Ministry of Education and Science of the Russian Federation (contract No 02.G25.31.0144 on 01.12.2015).

References

- [1] Carter C B and Norton M G 2007 *Ceramic materials: science and engineering* (Springer Science & Business Media)
- [2] Taktak R, Baklouti S and Bouaziz J 2011 *Mater. Charact.* **62**(9) 912-6
- [3] Veselov S V, Stukacheva N S, Kuzmin R I, Cherkasova N Yu, Perepelkin M Yu and Myz A L 2016 *Science bulletin of NSTU* **4**(65) 207-17
- [4] Adolfsson E and Shen Z 2012 *J. Eur. Ceram. Soc.* **32**(11) 2653-9
- [5] Hwang S L and Chen I W 1990 *J. Am. Ceram. Soc.* **73** 3269-77
- [6] Faucher J A, Koleske J V, Santee Jr E R, Stratta J J and Wilson III C W 1966 *J. Appl. Phys.* **37** 3962-4
- [7] Belousova N; Veselov S; Kuzmin R and Melnikova E 2014 *Applied Mechanics & Materials* **698** 513-8
- [8] Carneim R D and Messing G L 2001 *Powder Technol.* **115**(2) 131-8
- [9] Li J, Liao H and Hermansson L 1996 *Biomaterials* **17**(18) 1787-90
- [10] Liang X, Qiu Y, Zhou S, Hu X, Yu G, Deng X 2008 *Journal of University of Science and Technology Beijing* **15**(6) 764-8