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THE EFFECT OF PLASTICIZERS AND MOISTURE ON THE PRESSING PROCESS AND THE PROPERTIES OF CERAMIC PRODUCTS BASED ON ZIRCONIUM DIOXIDE

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An extensive application of zirconia ceramics in science and technology is determined by its unique properties, such as thermal stability, high hardness and chemical inertness. The latter property is widely used in the production of bioceramics [1]. Zirconia ceramics (ZC) due to its polymorphism does not exhibit high mechanical strength; therefore stabilizing [2] and strengthening [3] additives are introduced to improve it. In order to increase the mechanical strength, new composites are designed, for instance, $80ZrO_2$–$20Al_2O_3$ [4]. New potentials in improving the quality of ZC are offered by the use of nanopowders. The world leader in the production of the latter is Tosoh Corporation (Japan). Its initial products are used to manufacture fine-grained ZC with a density close to the theoretical value [5, 6]. The compacting pressure of 70 MPa, recommended by the manufacturer, is considerably lower than the minimal pressure, which could be provided by most laboratory compacting devices; therefore it is difficult to produce quality ceramics with them. At an unreasonably high pressure, there is an increase in the wall pressure and internal stresses in the bulk of the compact. A large amount of gases is observed inside it. All these factors give rise to fracture of the compacts and cracking of the ceramics during its sintering.

The wall pressure can be reduced by lubricating the press molds or by introducing microadditives [7, 8] or plasticizers, such as epoxy resin, into the raw powder material [9]. There are available data on a positive influence of moisture on the characteristics of optical ceramics made of aluminum-yttrium garnet [10] and on the production of alumina-silicate ceramics using semidry molding of compacts [11, 12]. There are practically no results on the investigation of the influence of the above factors on the manufacture and properties of high-density zirconia ceramics reported in the literature for the initial zirconium dioxide nanopowder.

In the present work, for the partially stabilized zirconia (PSZ) we study the influence of lubrication of the press-mold surfaces and introduction of plasticizing agents and moisture on the quality of the ceramics manufactured by sintering of the powder compacts formed by the method of uniaxial static pressing at a pressure of 120 MPa.

EXPERIMENTAL PROCEDURE

The initial powder feedstock was commercial PSZ-nanopowders of yttria stabilized zirconia (3% Y_2O_3) of a TZ-3Y-E grade (Tosoh, Japan). The powder compacts in the shape of pellets measuring 9 mm in diameter and 2.5–3 mm in thickness were fabricated using a PGr-10 laboratory compacting device at a pressure of 120 MPa. The inner surfaces of the press mold were lubricated with a PMS-100 methyl silicone oil (MSO) and a black-lead lubricant of the

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TABLE 1 Characteristics of Compacts and Zirconia Ceramics vs. Content of Moisture, EDP-4, and PMS-100 in Mold Powder

Additive	Content of additive in mold powder, wt.%			
	0	7.6	9	11.1
Compact density, g/cm^3				
Distilled water	2.94±0.05	3.21±0.03	3.22±0.08	3.25±0.03
EDP-4		3.26±0.02	3.25±0.01	3.38±0.04
PMS-100		3.22±0.04	3.24±0.09	3.26±0.11
Relative density of sintered ceramics, %				
Distilled water	98.3±0.05	98.39±0.06	98.61±0.08	97.59±0.06
EDP-4		97.92±0.07	97.53±0.05	98.02±0.06
PMS-100		93.13±0.09	93.53±0.1	91.07±0.08
Total porosity, %				
Distilled	1.71±0.11	1.57±0.09	1.34±0.10	3.38±0.08
EDP-4		2.07±0.10	2.99±0.11	2.02±0.08
PMS-100		6.85±0.31	6.43±0.25	8.93±0.28

3ton grade. The plasticizer was an EDP-4 epoxy resin without a hardener and PMS-100 MSO. The powder moisture was regulated by adding distilled water into its volume. Sintering of the ceramics was carried out in a SNOL 12/16 sintering furnace at a temperature of 1400°C for 1h. The ceramics density was determined by the method of hydrostatic weighing on the Shimadzu AUW-220D high-precision analytical balance. The total porosity of the ceramics was estimated from the data of the X-ray diffraction analysis and the porosity data determined experimentally. The ceramics microhardness was measured in a Zwik microhardness tester (Germany). The ceramics microstructure was examined by the method of scanning electron microscopy in a Hitachi TM-3000 microscope. The grain size was determined by the intercept method.

EXPERIMENTAL RESULTS

The lubrication of the press mold with PMS-100 MSO resulted in a decrease of the wall friction but did not rule out layering of the compacts. The best result was obtained with the 3ton lubricant. However, despite the visual integrity of the compacts, sintering of the ceramics was accompanied by cracking of the specimens. The latter can be accounted for by the presence of gases in the compact and its non-homogeneous packing. For the sake of minimizing these factors, EDP-4 and PMS-100 were separately added to the mold powder. Also, the method of dry compaction was used as an alternative to the introduction of a plasticizer. Table 1 presents the data on compact density and relative density and total porosity of the ceramics vs. the content of moisture, EDP-4, and PMS-100 in the mold powder.

It is clear from Table 1 that an increase in the content of plasticizer or moisture in the mold powder results in an increased density of the compact. Note that there is no direct dependence of the finished ceramic density on the compact density. Figure 1 presents the plots of dependence of microhardness H_v of the ceramics on the content of the plasticizer and moisture in the TZ-3Y-E nanopowder.

It is evident from Table 1 and Fig. 1 that the best combination of density and microhardness is observed in the case where 9 wt.% of water is added, while with EDP-4 this is observed at its content of 11.1 wt.%. The use of semidry compaction and an introduction of EDP-4 do not reduce the density of the ceramics and give rise to an increase in its microhardness. The use of PMS-100 resulted in a 5% decrease in the relative density compared to the ceramics manufactured from the raw feedstock and a simultaneous 10% decrease in its microhardness. We attribute this effect to the fact that PMS-100 contains about 33 % silicone oxidized to SiO_2 during sintering, which according to the literature data [13] results in a decrease in the density and the microhardness of the zirconia ceramics. The electron microscopy examination followed by processing of the SEM images by the intercept method have demonstrated that the least grain

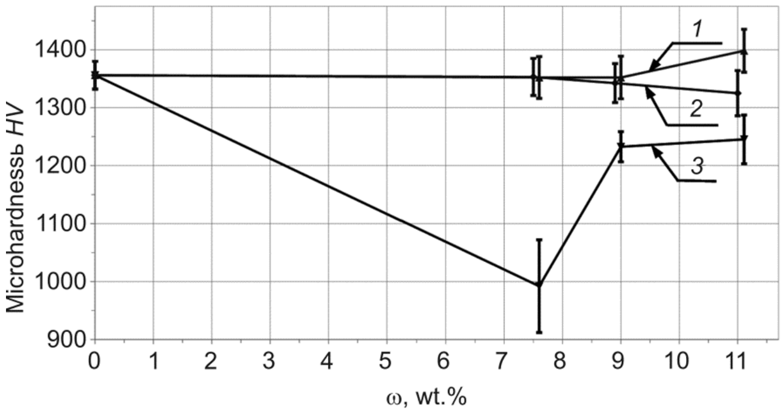

Fig. 1. Dependence of the microhardness of zirconia ceramics on the content ω of plasticizer and moisture in the TZ-3Y-E nanopowder: *1* – distilled water, *2* – EDP-4 epoxy resin, *3* – PMS-100 methyl silicone oil.

size ((290±20) nm) is observed in the ceramics sintered from the mold powder with the distilled water fraction of 9 wt.%. An addition of EDP-4 (11 wt.%) did not practically affect the grain size ((322±22) nm) compared to the ceramics without any additives ((329±21) nm). The ceramics manufactured from the initial nanopowder and the ceramics formed by the method of semidry compaction have homogeneous surfaces, while the ceramics with an EDP-4 additive exhibits a clear system of microcracks.

CONCLUSIONS

For the TZ-3Y-E PSZ nanopowder (Tosoh, Japan), the influence of lubrication of the surfaces of press molds, plasticizing additives and moisture on the quality of ceramics manufactured by sintering the powder compacts produced by uniaxial static pressing at a pressure of 120 MPa has been studied. The following conclusions have been made:

1. The use of semidry compaction and an EDP-plasticizer in combination with lubrication of the walls of press molds allows ruling out layering the specimens in the stage of compaction and cracking of the ceramics during sintering.
2. In the course of semidry compaction, at a moisture content of 9 wt.% in the mold powders the density and porosity achieved in the ceramics are close to the theoretical values.
3. The use of an EDP-4 plasticizer for implementation of 3D-technologies makes it possible to manufacture ceramics with good mechanical characteristics; however, the probability of formation of defects in the form of microcracks is quite high. In our further research we will focus on the ways to eliminate them.

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REFERENCES

1. R. G. Nazaryan and I. Yu. Lebedenko, Stomatologiya, **95**, No. 6-2, 61 (2016).
2. N. A. Toropov, V. P. Barzakovskii, I. A. Bondar, and Yu. P. Udalov, State Diagrams of Silicate Systems: reference book. 2-nd edition. Metal-Oxygen Compounds of Silicate Systems [in Russian], Nauka, Leningrad (1969).
3. H. P. A. Alves, A. C. S. Costa, and B. R. Carvalho, Mater. Lett., **270**1, A. 127689 (2020).

4. A. S. Klimov, A. A. Zenin, I. Yu. Bakeev, and E. M. Oks, Russ. Phys. J., **62**, No. 7, 1123–1129 (2019).
5. S. A. Ghyngazov, A. I. Ryabchikov, V. Kostenko, and D. O. Sivin, Russ. Phys. J., **61**, No. 8, 1513–1519 (2018).
6. E. S. Dvilis, O. L, Khasanov, and V. D. Paigin, Fund. Issledov., No. 12-2, 268 (2017).
7. N. Yu. Cherkasova, A. A. Bataev, S. V. Veselov, *et al*., Lett. Mater., **9**, No. 2, 179 (2019).
8. A. O. Zhigachev and V. V. Rodaev, J. Mater. Res. Technol., **8**, 6086 (2019).
9. Z. Di, S. Shimai, and J. Zhao, Ceram. Int., **45**, No. 10, 12789 (2019).
10. P. Gao, L. Zhang, and Q. Yao, Ceram. Int., **46**, No. 2, 2365 (2020).
11. V. A. Guryeva and A. V. Doroshin, Mater. Sci. Forum, **974**, 419 (2020).
12. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, Introduction to Ceramics, Wiley, N. Y. (1976).
13. S. A. Ghyngazov and S. A. Shevelev, Sist. Met. Tekhnol., No. 3(39), 159 (2018).