The Influence of Thermal Treatment on the Properties of TiO_2 Ceramics Obtained by Extrusion

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Abstract. **In this paper, various titanium dioxide (TiO_2) ceramic properties (density, microstructure and electrical resistance) were investigated after thermal treatment in air and under high vacuum conditions. In the present research, cylindrical-shaped samples were used, which were obtained from the plastic TiO_2 ceramic mass by extrusion method. When the temperature of thermal treatment in the air is increased from 1100 to 1350 °C, sintering degree, ceramic density and grain size also increase, while porosity decreases. The density of the obtained ceramic samples reaches 82% of the theoretically possible. It has been found that during the process of sintering mainly open porosity decreases. Thermal treatment in air influences electrical resistivity of titanium dioxide ceramic samples; after thermal treatment under high vacuum conditions electrical resistivity of samples significantly decreases, and it has been observed that the samples with the highest density and the biggest grains have the lowest electrical resistivity.**

Keywords: **TiO_2, ceramics, microstructure, electric properties**

I. INTRODUCTION

Because of its properties – low absorption coefficient, high dielectric constant and high biocompatibility – titanium dioxide (TiO_2) ceramics is widely used in various technical fields, for example, in photocatalysis, biomaterials and different self-cleaning elements [1]. TiO_2 ceramics are also widely used in electronics, for example, in varistors and capacitors [2].

TiO_2 is a dielectric material with the band gap width ~ 3.2 eV; it is a poor electrical conductor, but similarly to SnO_2, TiO_2 can be relatively easily reduced [3]. If TiO_2 is thermally treated in a reducing environment, defects like oxygen vacancies are formed in its crystal lattice, and non-stoichiometric compounds are formed, which can be described with a general formula Ti_nO_{2n-1} or TiO_{2-n} [4]. Due to creation of oxygen vacancies, electrons, which were connected with O^{2-} ions, are liberated in TiO_2 crystal lattice; as a result, local energy levels are created in the forbidden zone, and electrical conductivity of the obtained oxide materials significantly increases. Even slight deviations from stoichiometric TiO_2 result in significant increase of electrical conductivity of the compound [5]. Non-stoichiometric titanium oxides are used as photocatalysts, photoelectrodes in the water photoelectrolysis, gas sensors, etc [6].

In the reduced TiO_2 crystal lattice, mainly point defects like doubly charged oxygen vacancies and Ti^{3+} or Ti^{4+} interstitials exist. At the same time, if a large oxygen deficit exists in the TiO_2 structure, share of crystallographic planes occurs in the crystal lattice and the so-called Magneli phases are formed [7]. Magneli phases are a range of non-stoichiometric titanium oxides with the general formula Ti_nO_{2n-1}, where n is between 4 and 10. These oxides are obtained by reducing titanium dioxide in high temperatures, in H_2 environment. As a result, ceramic materials with high electrical conductivity similar to that of graphite are obtained. Because of its excellent corrosion resistance, ceramics obtained by this method can be used as an electrode material in electrolysis processes [8]. Titanium oxide ceramics obtained by thermally treating TiO_2 undere high vacuum conditions, also demonstrate high electrical conductivity [9]. In the scientific articles [10, 11], possibilities of using ceramics obtained by this method in water electrolysis processes are studied.

Electrical properties of ceramics containing titanium oxides are affected by the ceramic microstructure [12]. Its electrical properties are significantly influenced by grain size, grain boundary area and porosity [13].

The present paper studies the influence of thermal treatment in the air and high vacuum conditions on TiO_2 ceramics obtained by extrusion method.

II. MATERIALS AND METHODS

Cylindrical-shaped TiO_2 ceramic specimens used in the present research were prepared from plastic TiO_2 ceramic mass by extrusion, using a *Dorst Vacuum Extrusion Press V10 SpHv.* Plastic ceramic mass was obtained by mixing the required components (see Table 1) in the kneader-mixer *Aachener Misch und Knetmaschinenfabrik IIIU 8/IV.* Mixing-kneading was carried out for 4 hours.

TABLE 1

CERAMIC MASS COMPOSITION

Component	Description	% of mass
TiO_2 (anatase) powder	Reagent purity 99,2 %; average grain size ~ 180 nm);	81
Distilled H_2O	-	17
Binder	Plasticizing additive based on cellulose derivative	0,2
Oil	Manufactured by Zimmer &Schwarz	1,8

Extruded samples were dried for 48 h at 20 °C temperature, with relative air humidity of 50 – 60%.

Dilatometric properties of the samples in the temperature range from room temperature to 1450 °C were determined with a heating microscope (HM) – *Hesse Instruments Heating Microscope - EM 201 (HT-16 (1600/80)).*

Dried samples were sintered in air at 1100, 1175, 1250, 1300 and 1350 °C temperature (heating rate 1 °C/min, dwell time 6h, cooling rate 1 °C/min), with a further thermal treatment under high vacuum conditions (2×10^{-3} Pa) at 1075 °C temperature (heating rate 5 °C/min, dwell time 3h, cooling rate 6 °C/min). After thermal treatment, samples were cut in 20 mm long cylinders for a more convenient measurement. Five specimens were produced for each thermal treatment condition.

The density ρ_m was determined by measuring the volume and weight of the samples. Afterwards, the measurements were related to the theoretical density of anatase or rutile TiO_2. Open and closed porosity of the samples after thermal treatment was determined using method based on Archimedes' principle [14].

Electrical resistance of the samples after thermal treatment in the air was measured with a Wheatstone bridge MO – 62 or with a tera-ohm meter *E6 – 13A*. To ensure high quality electric contact, sample ends were cleaned in glow discharge plasma and coated with copper, using a thermal evaporation in vacuum.

To characterize sample fracture surface microstructure, scanning electronic microscopy (SEM) *Tescan Mira/LMU* was used. Average diameter of the sample grains (d_a) was determined using *VEGA TC* software, measuring at least 200 ceramic grains in SEM photographs for each sample.

In order to determine the crystal phases, a *PANalitical X'pert PRO* model X-ray diffractometer (XRD) with a CuK_α radiation in the region $2\theta = 25 - 70°$ was used.

III. RESULTS AND DISCUSSION

Properties of ceramic materials are determined by their thermal treatment conditions. Impact of thermal treatment on the shrinkage of the sample obtained by extrusion process was evaluated using HM (Fig. 1). As it can be seen, cross-section field of the sample remains almost unchanged until 950 °C temperature.

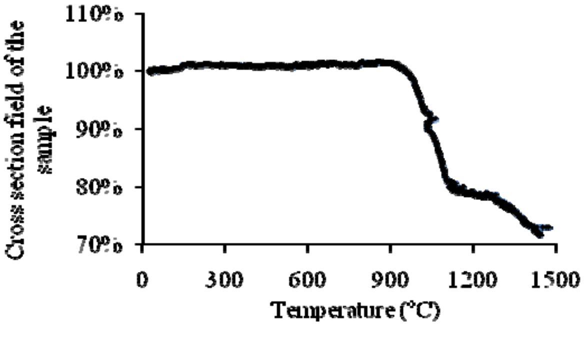

Fig. 1. Thermal shrinkage of the sample

A rapid shrinkage of the sample cross-section field is observed within temperature interval from 950 to 1100 °C. This observed shrinkage of cross-section field can be linked to both the ceramic sintering process and transformation of TiO_2 crystal modification from anatase onto rutile in the corresponding temperature [15].

Changes in the crystal structure of the samples during thermal treatment were verified by XRD (see Fig. 2). In the samples, which were not treated thermally, only anatase TiO_2 crystal phase was identified, while for samples which were thermally treated at temperatures from 1100 to 1350 °C, only rutile crystal phase was identified.

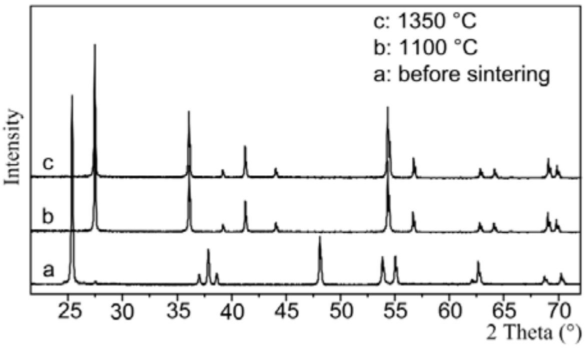

Fig. 2. XRD pattern of the samples after thermal treatment in air

Properties and possible uses of ceramic materials are determined by their density and porosity. After drying, the density of the obtained green body was on average 59% of theoretical TiO_2 density value. During thermal treatment at temperatures above 1100 °C (TiO_2 ceramic sintering occurs), density of samples significantly changes in comparison with the samples, which were not thermally treated (see Fig. 3).

If temperature of thermal treatment is increased, density of samples increases, reaching about 82% of theoretical density of TiO_2 for samples sintered at 1350 °C. Successive thermal treatment of the samples under high vacuum conditions did not cause further changes of density. This can be caused by the temperature chosen for the thermal treatment (1075 °C), which is lower than the temperatures, at which the samples were treated under air conditions.

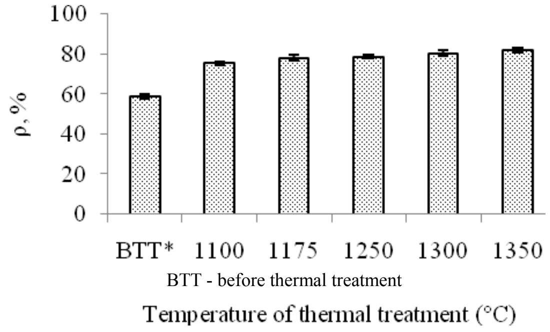

Fig. 3. Density of the samples after thermal treatment in air

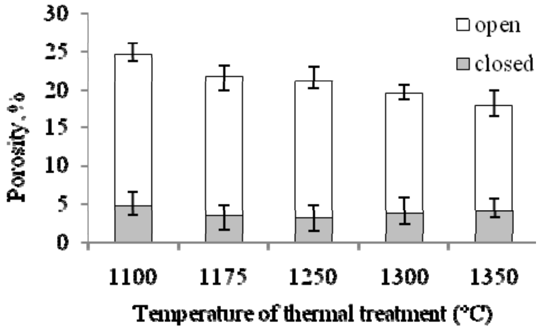

Fig. 4. Porosity of the samples depending on thermal treatment temperature

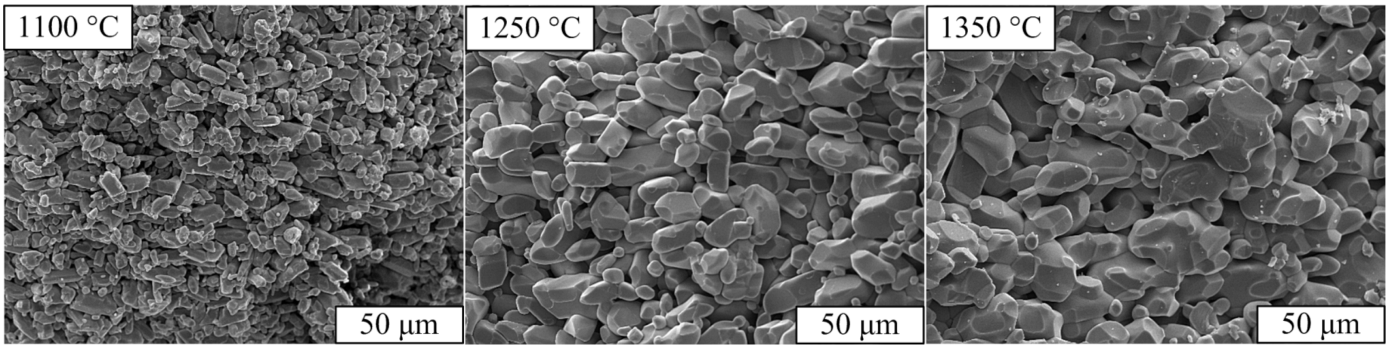

Fig. 5. SEM photographs of specimens after thermal treatment in air

Material sintering is related to decreasing of porosity. It can be seen that with a thermal treatment temperature in air from 1100 to 1350 °C and increasing sintering degree, total porosity of the samples decreases from about 24 to 18%. Evaluating changes of open and closed porosity, it can be concluded that during sintering of the samples, proportion of open porosity decreases, while amount of closed porosity remains in the range from 3.5 to 4.5% in whole range of chosen thermal treatment temperatures.

The process of increasing density and reducing porosity of TiO_2 ceramics is simultaneously related to transformations of the sample microstructure, including ceramic grain size (see Fig. 5). As it can be seen, during thermal treatment growth of ceramic grains occurs. The most intensive growth of ceramic grains is observed in temperature range from 1100 to 1250 °C.

The average grain diameter increases almost twice, from 13 μm at 1100 °C to 25 μm at 1350 °C. It can be seen that grains are mostly elongated in shape.

After thermal treatment in air, electrical resistance of the samples was measured. Since the samples were sintered at various temperatures, their geometric sizes were different. To compare electrical resistance, a specific electrical resistance R_{sp} of the samples was calculated.

After thermal treatment in the air atmosphere, electrical resistance of the obtained ceramic samples achieves high values (3.5 – 5.8×10^3 Ω·m), characteristic of dielectric materials.

Thermal treatment of the samples under high vacuum conditions causes a dramatic decrease in sample electrical resistance (Fig. 6.). Reduced electrical resistance can be related to creation of oxygen vacancies and change of Ti^{4+} to Ti^{3+} ions in TiO_2 crystal lattice [4]. Creation of oxygen vacancies under high vacuum conditions, as well as TiO_2 thermal treatment in a reducing environment, significantly increases electrical conductivity [12]. A certain relation between descriptive parameters of material and its electrical resistance was observed. When the temperature of thermal treatment and average grain diameter increase, the density of the ceramic samples also increases, (see Fig. 6.), but electrical resistance decreases (from 0,9 Ω·m for a sample which has been thermally treated in air at 1100 °C before thermal treatment under the vacuum conditions, to up to 0,1 Ω·m for a sample which was thermally treated in air at 1350 °C before thermal treatment under high vacuum conditions).

It is possible that thermal treatment of TiO_2 at high temperatures with a following thermal treatment under high vacuum conditions causes an intensified creation of oxygen vacancies in TiO_2 crystal lattice. Possibly, with grain size increasing, grain volume starts to dominate in the electron transfer, with the electrons migrating from the grain surface into the volume [16].

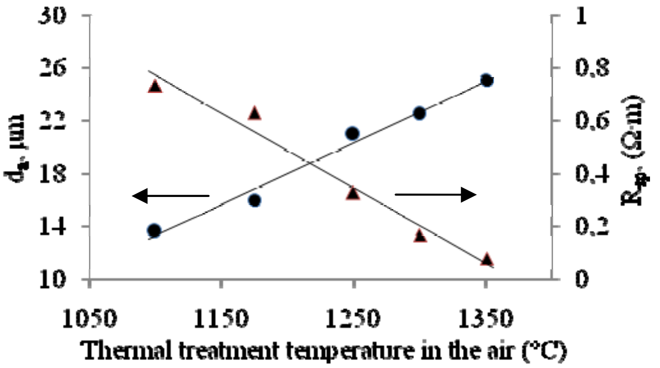

Fig.6. Average grain diameter, d_a and specific electric resistance R_{sp} of the samples depending on the temperature of the thermal treatment in air and the following thermal treatment under high vacuum conditions at 1075 °C.

IV. CONCLUSIONS

Temperature of thermal treatment influences the process of TiO_2 ceramic sintering. With the increase of thermal treatment temperature in the air atmosphere from 1100 to 1350 °C, density of ceramics also increases and porosity of the samples decreases, which proves the increasing of the sintering degree. Thermal treatment influences microstructure and electrical properties of titanium dioxide ceramics.

Thermal treatment of the samples under high vacuum conditions causes a dramatic reduction in the sample electrical resistance (from 5.8×10^3 Ω·m for a sample which has been thermally treated in the air at 1350 °C to 0.1 Ω·m after thermal treatment under high vacuum conditions at 1075 °C, for the same sample). A connection between the size of ceramic grains and electric resistance of the samples is observed.

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Kristaps Rubenis, Jurijs Ozolins, Agnese Pūra, Jānis Ločs, Madars Reimanis, Inga Narkevica, Līga Bērziņa-Cimdiņa. Termiskās apstrādes ietekme uz ekstrūzijas ceļā iegūtas TiO_2 keramikas īpašībām

Darbā pētīta termiskās apstrādes gaisa vidē un augstvakuuma apstākļos ietekme uz titāna dioksīda (TiO_2) keramikas blīvumu, mikrostruktūru, un elektrovadītspēju. Pētījumam izmantoti cilindriskas formas paraugi, kuri iegūti ar ekstrūzijas paņēmienu no plastiskas TiO_2 keramikas masas. Iegūtie paraugi termiski apstrādāti gaisa vidē 1100, 1175, 1250 un 1350 °C temperatūrā. Pēc termiskās apstrādes gaisa vidē, paraugi atkārtoti termiski apstrādāti augsta vakuuma apstākļos 1075 °C temperatūrā. Konstatēts, ka, pieaugot termiskās apstrādes temperatūrai gaisa vidē, palielinās iegūtās keramikas saķepšanas pakāpe, pieaug keramikas blīvums un graudu izmērs, savukārt porainība samazinās. Iegūto keramisko paraugu īpatnējais blīvums pārsniedz 82% no teorētiski iespējamā. Konstatēts, ka keramikas saķepšanas procesā galvenokārt notiek atvērto poru īpatsvara samazināšanās. TiO_2 keramikas paraugu elektriskā pretestība pēc termiskās apstrādes gaisa vidē sasniedz ievērojamas vērtības ($3{,}5 - 5{,}8 \times 10^3$ Ω·m), kādas raksturīgas dielektriskajiem materiāliem. Pēc atkārtotas termiskās apstrādes augsta vakuuma apstākļos, paraugu elektriskā pretestība būtiski samazinās. Novērota sakarība, ka paraugu elektriskā pretestība pēc termiskās apstrādes augta vakuuma apstākļos samazinās, pieaugot keramikas blīvumam un graudu vidējam diametram. Paraugu īpatnējā elektriskā pretestība samazinās vidēji no 0,9 Ω·m, paraugam, kurš gaisa vidē pirms termiskās apstrādes augsta vakuuma apstākļos termiski apstrādāts 1100 °C temperatūrā, līdz 0,1 Ω·m, paraugam, kurš gaisa vidē pirms termiskās apstrādes augsta vakuuma apstākļos termiski apstrādāts 1350 °C temperatūrā.

Кристапс Рубенис, Юрий Озолиньш, Агнесе Пура, Янис Лочс, Мадарс Реиманис, Инга Наркевица, Лига Берзиня-Цимдиня. Влияние термической обработки на свойства TiO_2 керамики, полученной экструзионным способом.

В работе исследовалось влияние термической обработки в воздушной атмосфере и в условиях глубокого вакуума на плотность, микроструктуру и электропроводность TiO_2 керамики. В экспериментах использовались образцы цилиндрической формы, полученные экструзионным способом из пластической керамической массы TiO_2. Полученные образцы термически обрабатывались в воздушной среде при температурах 1100, 1175, 1250, 1350^0C с последующей обработкой в условиях глубокого вакуума при температуре 1075^0C. Установлено, что с увеличением температуры термической обработки от 1100 до 1350^0C в воздушной среде возрастает степень спекания керамики, увеличивается плотность, размер зёрен и уменьшается пористость образцов. Удельная плотность полученных образцов достигает величин больших, чем 82% от теоретически возможного. В процессе спекания, главным образом, наблюдается уменьшение открытой пористости. Удельное сопротивление керамических образцов после термической обработки в воздушной среде достигает значительных величин ($3{,}5 – 5{,}8\times10^3$ Ω·m), характерных для диэлектрических материалов. После повторной термической обработке в условиях глубокого вакуума электрическое сопротивление образцов резко снижается. Найдена зависимость между уменьшением значений удельного сопротивления и увеличением плотности керамики и размеров зёрен. Удельное сопротивление снижается с 0,9 Ω·m, для образцов, полученных при 1100°C до 0,1 Ω·m, для образцов, предварительно термически обработанных при температуре 1350°C.