RIGA TECHNICAL UNIVERSITY
Faculty of Materials Science and Applied Chemistry
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PREPARATION OF EXTRUDED TITANIUM OXIDE CERAMICS, CHARACTERIZATION OF STRUCTURE AND PROPERTIES

Summary of Doctoral Thesis

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THE DOCTORAL THESIS IS SUBMITTED FOR AWARD OF DOCTORAL DEGREE IN ENGINEERING SCIENCES AT RIGA TECHNICAL UNIVERSITY

The Thesis for the doctoral degree in engineering sciences is to be publicly defended on June 5th, 2013 at 14^{oo} at Riga Technical University, Faculty of Materials Science and Applied Chemistry, Riga, Azenes 14/24, room № 272.

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CONFIRMATION

I confirm that I have developed the present Doctoral Thesis, which is submitted for consideration at Riga Technical University for scientific degree of the doctor of engineering sciences. The Doctoral Thesis has not been submitted at any other university for the acquisition of a scientific degree.

Agnese Pūra: .....

Date: .....

The Doctoral Thesis is written in Latvian language; it contains Introduction, Review of Literature, Description of Experiments, Results and Discussion, Conclusions, List of References, as well as 96 illustrations and 10 tables, altogether 141 pages. 128 references are given in List of References.

ACKNOWLEDGMENTS

I would like to thank my scientific supervisor professor Līga Bērziņa-Cimdiņa for hiring me to be a part of Rudolfs Cimdins Riga Biomaterials Innovation and Development Centre with my wonderful co-workers, for support in writing this Thesis, as well as for chance to gain new experiences and contacts in international conferences.

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OVERVIEW OF THE DOCTORAL THESIS

Current situation

TiO_2 ceramics is one of the most researched metal oxide materials, as it has several high value properties. The physical and chemical properties of TiO_2 ceramics are dependent on the production and processing technologies, and can be made suitable for use in various industries. TiO_2 ceramics are used in electronics, energetic, construction, and medicine.

Extrusion is widely used for production of technical ceramics as method for shaping materials. Extrusion has several advantages for use in production of materials that have novel applications.

There is no systematic research in scientific literature about production of non-stoichiometric TiO_2 ceramics using extrusion. Therefore experimental work encompasses research of both material properties and production technology. And as a result of this work an original composition of ceramic paste suitable for extrusion has been developed. Cylindrical samples have been extruded and thermally treated in air and in vacuum environment. The uses of obtained ceramics have been also researched.

The aim of the Doctoral Thesis

To develop optimal extrusion paste composition and process and parameter set for thermal treatment technology suitable for production of conducting TiO_{2-x} technical ceramics.

Tasks set for the Doctoral Thesis

1) To develop extrusion paste composition for successful extrusion process and production of high-quality extruded green bodies;
2) To develop technological process for recycling production waste (waste products incorporated into extrusion paste);
3) To determine plasticity of extrusion paste and its dependence on composition;
4) To determine the influence of composition of extrusion paste on extrusion process and relative density of extruded green bodies;
5) To optimize thermal treatment conditions (for both thermal treatment in air and under vacuum) and to assess the influence on phase composition, microstructure, porosity, shrinkage, and mechanical properties of ceramics;
6) To determine electrical resistance and thermoelectric properties after thermal treatment under vacuum;
7) To evaluate the possibility of use of obtained ceramics as electrodes and thermoelectric materials.

Scientific significance and novelty of the Doctoral Thesis

A systematic research of has been conducted to evaluate the interconnection of extrusion paste composition, extrusion parameters and quality of extruded green bodies.

The influence of thermal treatment conditions of extruded green bodies on the structure, the morphology, and on physical, electric and thermoelectric properties of obtained ceramics has been determined.

It has been ascertained that TiO_2 ceramic samples shaped using extrusion and after thermal treatment in air (1100 - 1400 °C) and additional thermal treatment in vacuum (1250 °C) contain $TiO_{1.95}$ crystalline phase.

Practical significance of the Doctoral Thesis

A set of technological processes and parameters to obtain extrusion paste have been developed. Depending on the application of TiO_2 ceramics, thermal treatment parameters have been adjusted for ceramics intended for use as electrodes or as thermoelectric materials.

Statement to defend

1. After development of original extrusion paste preparation technology (TiO_2 77.3-79.2 weight %, water 19-20.9 weight % and additives 1.8 weight %), it is possible to obtain extruded green bodies with more than 50 % of volume taken by anatase powder particles. Obtained particle packing ensures low (less than 1.5 %) shrinkage upon drying extruded green ceramic bodies. This invention has been patented.

2. The thermal treatment of extruded green bodies (first in air, then in vacuum conditions) affects conductive properties of non-stoichiometric TiO_2 technical ceramics. The electrical conductivity of non-stoichiometric TiO_2 ceramics is caused by formation of oxygen vacancies in TiO_2 crystal lattice and reduction of Ti^{4+} to Ti^{3+}, giving the material a n-type electrical conductivity that is utilized in thermoelectric materials and in electrodes.

3. The highest values of thermoelectric power factor are obtained, if TiO_2 ceramics are thermally treated in air at 1100-1200 °C and additionally under vacuum at 1250 °C. This ensures ceramics with comparatively lower density, high Seebeck effect coefficient values and electrical conductivity. For use as electrodes the extruded TiO_2 green bodies are thermally treated in air at 1300-1400 °C and additionally under vacuum at 1250 °C – ceramics formed under these conditions have low specific electrical resistance and comparatively high density.

Approbation of the Doctoral Thesis

The results of scientific research for this Thesis have been reported in international scientific conferences, 7 full-text publications and 14 peer-reviewed conference proceeding abstracts. 1 patent has been granted for invention described in this work in the Republic of Latvia.

SHORT OVERVIEW OF THE THESIS CONTENTS

In **Introduction** current situation and importance of this subject is described, the aims and tasks set for this work are given, practical and scientific importance of research results are listed, and Statement to Defend is given.

First chapter is **Review of Literature**, in which information about structure and properties of TiO_2, factors influencing TiO_2 phase conversion, TiO_2 non-stoichiometry and its formation are given. Scientific literature concerning electric and thermoelectric properties of TiO_2 ceramics is analyzed.

In scientific literature TiO_2 ceramics obtained using pressing (in form of pellets) or TiO_2 thin films obtained by sol-gel or sputtering methods are discussed. As there is no information on obtaining non-stoichiometricTiO_2 ceramics using extrusion, in the literature review general information about preparation of extrusion paste, extrusion technology and thermal treatment of ceramic materials is discussed.

Second chapter is **Description of Experiments**, in which technologies used to produce TiO_{2-x} ceramics and methods used to research obtained products are described. Third chapter is **Results and Discussion.**

DESCRIPTION OF EXPERIMENTS

Technology to produce TiO_{2-x} ceramic samples

Schematic representation of processes used to obtain ceramics described in this work can be seen in Fig. 1. Besides main stages, additional stages clarifying how low-quality products are recycled are shown.

Main raw materials used are – TiO_2 (I) anatase powder (*HOMBITAN LW-S, Sachtleben Chemie GmbH*, Germany, average particle size 300 nm), recycled TiO_2 (II) rutile powder (<125 μm), distilled water, additives – oil (*PRODUKT KP 5144, Zschimmer & Schwarz GmbH)* and binder (*Zusoplast C93, Zschimmer & Schwarz GmbH).*

To obtain paste for extrusion, first ceramic slurry (part of necessary TiO_2 powder, water and additives) was prepared using a dissolver (*Dispermat® CA 40)*. The prepared ceramic slurry and the remaining TiO_2 powder was made into a homogeneous paste using a mixer/kneader device (*AMK III U 8/IV)* and aged

for at least 72 h before extrusion. During the aging of the extrusion paste moisture is equalized throughout the paste volume.

The plasticity of ceramic paste ready for extrusion was determined using a penetrometer (*AFG 100N)*. The plasticity is given as penetration resistance against sensor penetration into paste per area unit (mN/mm^2).

The ceramic paste was shaped using an extruder (*DORST V 10 SpHV)* with a round-shaped die (Ø13 mm) to obtain cylindrical rods.

After extrusion rods were dried in a separate room intended for this purpose. The moisture content in samples was determined every 24 h until it was constant. After drying the relative density and shrinkage of the samples were determined.

Thermal treatment conditions (maximum temperature, the rate the temperature was increased, time of thermal treatment) were chosen according to data available in scientific literature and data obtained using differential thermal analysis (DTA) using *BAHR Termoanalyse DTA 703* (to determine at what temperatures organic additives were burned-out) and heating microscopy/optical dilatometer (HM/OD) *EMO-1750/30-K* (to determine sintering temperature range), also X-ray diffraction (XRD) *PANalytical X`Pert PRO* and *Rigaku SmartLab* with a monochromator (to determine TiO_2 polymorphs and detect changes in crystal lattice).

Thermal treatment of ceramics was done in muffle furnace *Nabertherm LH 15/14* (for thermal treatment in air) and vacuum furnace *СГВ - 2.4.2/15 И3* ($6{,}6 \cdot 10^{-3}$ Pa). After thermal treatment the relative density, porosity, shrinkage and mechanical properties (three point flexural strength) of TiO_2 and TiO_{2-x} ceramics were determined. The microstructure of obtained ceramics was observed using field-emission scanning electron microscopy (SEM) *Tescan Mira/LMU*. For TiO_{2-x} ceramics electrical resistance was determined and thermoelectric properties examined.

For TiO_2 and TiO_{2-x} ceramics phase composition and structure was additionally examined using X-ray diffractometer *Rigaku SmartLab* with a monochromator, Fourier transform infrared spectroscope (FTIR) *Varian 800* and Raman spectroscope *Renishaw inVia micro-Raman.*

After extrusion, drying, and thermal treatment (in air and under vacuum) the quality of samples was assessed by visual observation. The samples must be without visible defects – that is – without deformations, cracks or pores. Low-grade samples were milled and the obtained powder sieved to obtain TiO_2 rutile (TiO_2R) particles with particle size <125 μm. TiO_2R powder was recycled as additive in some compositions of ceramic paste for extrusion.

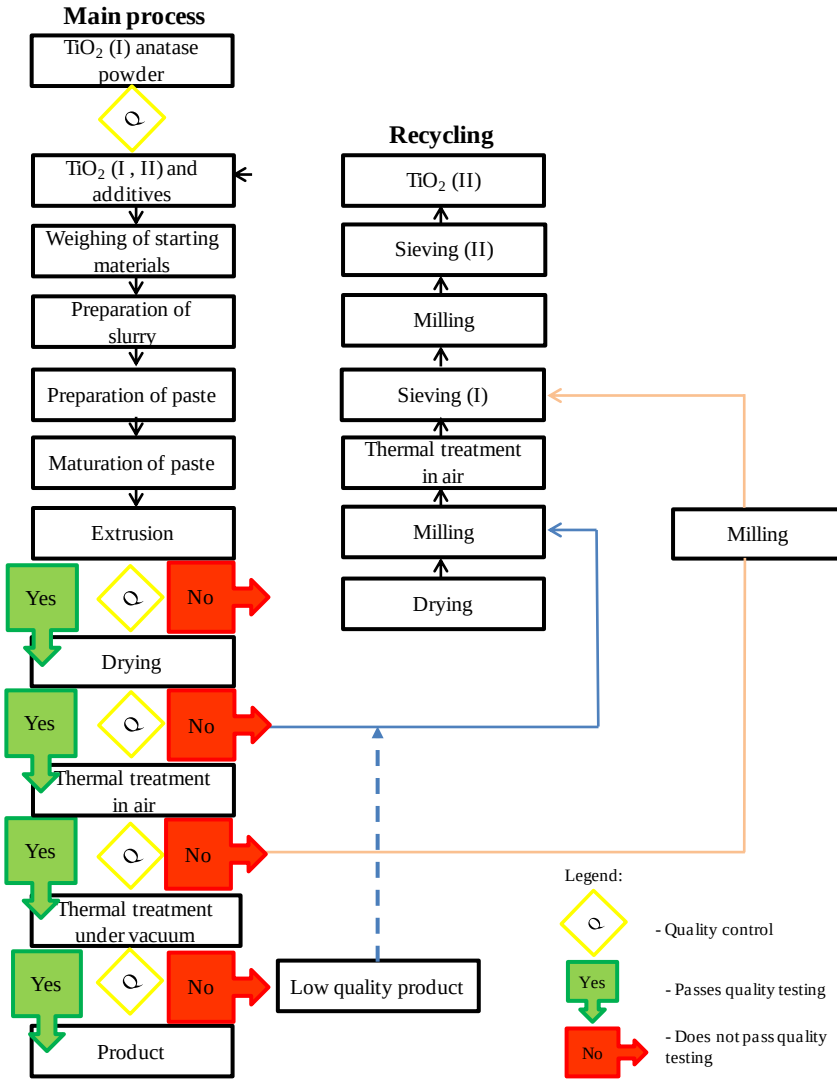

Fig.1. Schematic representation of technological processes used to obtain TiO_{2-x} ceramic samples

Several criteria were taken into account during development of ceramic paste compositions: 1) paste must be able to experience plastic flow at constant pressure during extrusion and it must be possible to shape the extruded paste with a die; 2) after extrusion the product must retain shape during further handling In Table 1 four series of extrusion paste compositions are given. The series were prepared after analyzing the results of previous series (plasticity of extrusion paste, pressure in press cylinder during extrusion, visual appearance of extruded green bodies, and relative density after drying).

Table 1

Composition of extrusion pastes

	Series 1				**Series 2**			**Series 3**			**Series 4**		
Paste	P-14	P-13-12	I-O	P-15	P-17	P-18	A6M	A4	A6	A5	A6-2M	A7	A8
TiO_2, weight %	73.95	75.45	75.85	76.15	76.25	76.4	77.3	78.6	79.2	79.7	71.25	63.88	41.45
TiO_2R_s, weight %											6.95	15.32	41.75
H_2O, weight %	23.1	21.6	21.2	20.9	20.9	20.9	20.9	19.6	19.0	18.5	20	19	15
Binder,, weight %	1.35	1.35	1.35	1.35	1.25	1.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Oil, weight %	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6

RESULTS AND DISSCUISON

Characterization of extrusion paste and extruded samples

To obtain high quality samples, extrusion paste must contain as small amount of additives as possible. If the amount of additives is too large, after thermal treatment the burn-out of additives may create undesirable porosity and microstructural defects. This would increase amount of low quality samples.

For **Series 1** TiO_2 and water ratio is varied. The amount of TiO_2 powder is decreased from 76.15 to 73.95 weight % and the amount of water is increased from 20.9 to 23.1 weight %.

In Fig.3 (a) it is shown that decreasing water content has an effect on plasticity of the extrusion paste – the extrusion paste is more viscous (the penetration resistance of penetrometer sensor increases from 27 to 45 mN/mm^2). This has a significant effect on pressure in press cylinder. During extrusion of paste P-13-12 and paste P14 separation of liquid from paste is observed (at the press cylinder).

In Fig.3 (b) it is shown that, if the water content is decreased in extrusion paste (relative to TiO_2 powder content), it is possible to obtain more dense samples. If the water content is decreased to 20.9 weight % (P-15), the relative density (RD) of the samples in increased by 1.3 % (if compared against paste P-14 which contains 23.1 weight % of water).

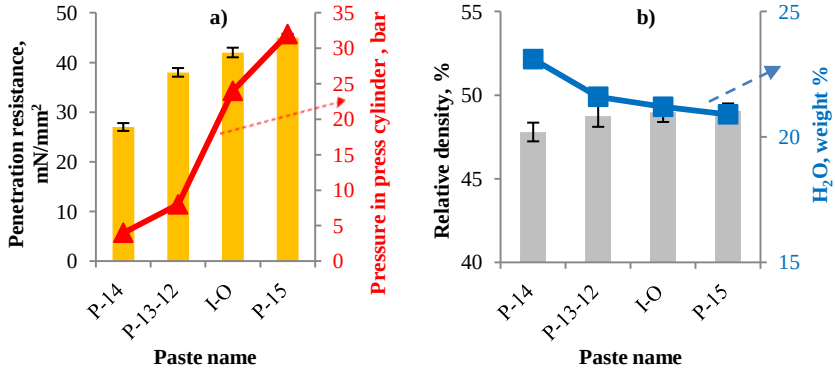

Fig.3. Series 1: plasticity of extrusion paste and pressure in press cylinder (a) and the relative density of samples (b) depending on water content

For **Series 2** the ratio of TiO_2 and binder was varied. The amount of TiO_2 was increased from 76.25 to 77.3 weight % and the amount of binder was decreased from 1.25 to 0.2 weight %. The water content was chosen after analysis of results for samples from Series 1.

In Fig.4 (a) it shown that decrease of amount of binder affects plasticity of extrusion paste – the paste has higher plasticity (the penetration resistance of penetrometer sensor has decreased from 43 to 36 mN/mm^2 and wherewith the pressure at the press cylinder has decreased as paste flows more freely through extruder. The differences in this case are not as pronounces as in Series 1.

In Fig.4 (b) it is shown that, if the amount of binder is decreased (relative to amount of TiO_2), more dense samples are obtained. If the binder content is decreased from 1.25 to 1.1 weight % the increase of relative density is not significant (P-17 and P-18). In turn, if the amount of binder is decreased to 1/6 of original amount, the relative density is increased by almost 3% (A6M). In comparison to Series 1 samples with larger relative densities are obtained – 51.54 %.

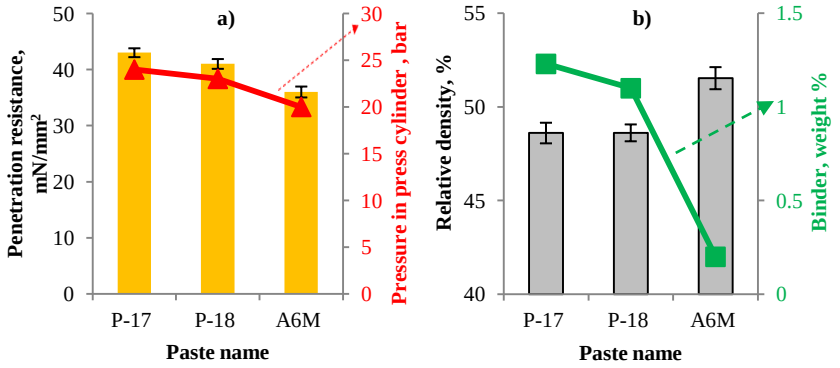

Fig.4. Series 2: plasticity of the paste and pressure in press cylinder (a) and relative density of samples (b) depending on the amount of binder added

The use of minimal amount of binder (0.2 weight %) facilitates not only extrusion process, densification of the samples and retention of extruded shape, but also reduces CO_2 emissions compared to previous experiments, where the amount of binder was more 6 times higher.

In **Series 3** (after evaluation of previous Series 2) the amount of binder was 0.2 weight % and the TiO_2 and water was varied. The content of water was reduced from 20.9 to 18.5 weight %.

In Fig.5 (a) it is shown that decrease of water content significantly affects plasticity of extrusion paste, compared to previous experiments – the paste is less plastic (the penetration resistance of penetrometer sensor has been increased from 50 to 63 mN/mm^2 and wherewith the pressure in press cylinder for extrusion paste A5 has increased several times – almost to 80 bar – which inconveniences extrusion process.

In Fig.5 (b) it is shown that decrease of water content affects relative density of the samples. Compared to Series 2 samples with the highest relative density (51.54%), in Series 3 relative density is increased by 2% (A5). But the extrusion process of A5 paste in this series is inconvenienced by comparatively low plasticity (related to water content in the extrusion paste). As a result the extruded green bodies were deformed – cracks were formed and samples bent.

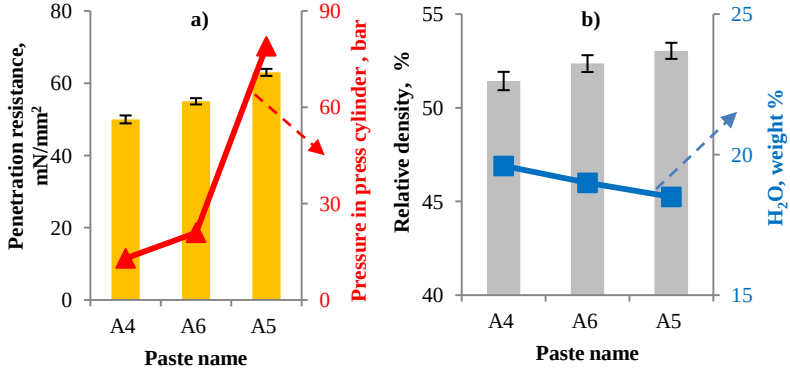

Fig.5. Series 3: plasticity of extrusion paste and pressure in press cylinder (a) and relative density (b) depending on water content

Samples extruded using extrusion pastes A6M and A6 had the highest density (TiO_2 anatase 77.3-79.3 weight %, water 19-20.9 weight %, binder 0.2 weight % and oil 1.6 weight %. For aforementioned extruded green bodies TiO_2 anatase powder particles take up more than 50% of volume. For cubic packing of spherical particles the volume taken by particles is 52.36 % [1].

In **Series 4** TiO_2 anatase and TiO_2R ratio is varied; the water content is also changed as the TiO_2R particles are larger and already sintered. In Fig.6 (a) it is shown that addition TiO_2R has not significantly affected the plasticity of the extrusion paste, if compared to previous experiments (penetration resistance of penetrometer sensor increases from 38 to 51 mN/mm^2), but pressure in the press cylinder is 10 bar. Therefore it can be concluded that the addition of TiO_2R ensures ease of flow in the extruder, even if water content is decreased from 19 to 15 weight %.

In Fig.6 (b) it can be seen that, if TiO_2R is added, samples with higher relative density can be obtained (53.05%) compared to previous experiments (except for A5 extrusion paste). If TiO_2R composition is increased twofold, the relative density increased by 1.5% (A7). In turn, if TiO_2R and TiO_2 anatase ratio is almost the same by weight, the relative density increases to 61.38 % (A8).

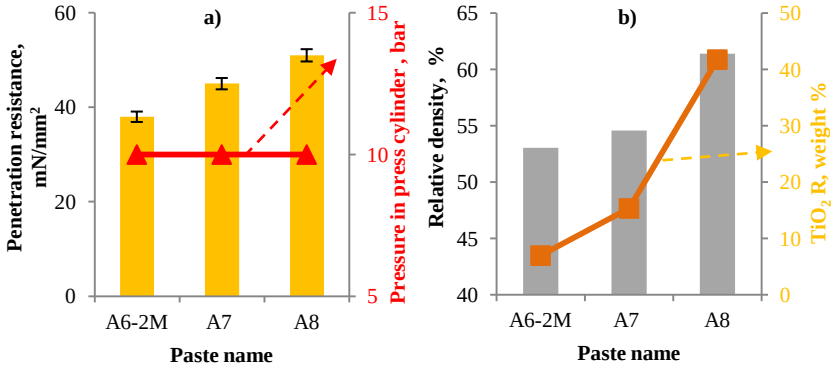

Fig.6. Series 4: plasticity of extrusion paste and pressure in press cylinder (a) and relative density of samples (b) depending on TiO_2R content

It was observed that green bodies extruded using A8 paste cracked upon drying; this can be explained by high TiO_2R content.

After evaluating all extrusion paste compositions (series), it was concluded that most promising extrusion paste compositions for extrusion process were A6M and A6 (TiO_2 anatase only), as well as A6-2M and A7 (recycled TiO_2R powder added).

The **dynamics of drying of extruded samples** were examined, and it was concluded than extrusion paste lost 0.7-2.05 % moisture in the vacuum chamber, which accounts for 4-10 % from initial amount of water in extrusion paste. The moisture level (0.20 %) in samples becomes constant after 5-8 days, and is dependent on composition of the extrusion paste. The shrinkage of samples upon drying is approximately 1.5 %.

The **thermal treatment regiment** was developed. Using **DTA** it was observed that the decomposition occurs at a temperature range 200-450 °C (exothermic process), and P-15 extrusion paste has increased exothermic effect than A6. The reason for aforementioned fact is that P-15 samples have the highest amount of additives – 1.35 weight %, but A6 – only 0.2 weight %.

Using **HM/OD** it was observed that in temperature interval room temperature 900 °C TiO_2 samples expand linearly, then the beginning of sintering occurs ($T_{b.sint.}$ = 900 °C), and if temperature is further increased to 1100 °C rapid densification occurs (5-7.5 %/100 °C), the sintering of TiO_2 anatase particles occurs, as well as phase change (anatase to rutile), and grain growth. Linear shrinkage at this stage is 10-13 %. When temperature rises further to ~1300 °C the shrinkage is slower (1-2.5 %/100 °C), and further linear shrinkage is 2-5 %.

Using **XRD** it was shown that for TiO_2 samples after thermal treatment at 1100 °C phase change from anatase to rutile is complete.

After summarizing DTA, HM/OD and XRD results, and the information found in the scientific literature the following thermal treatment parameters (heating rates, soaking times) were chosen – see Fig.7.

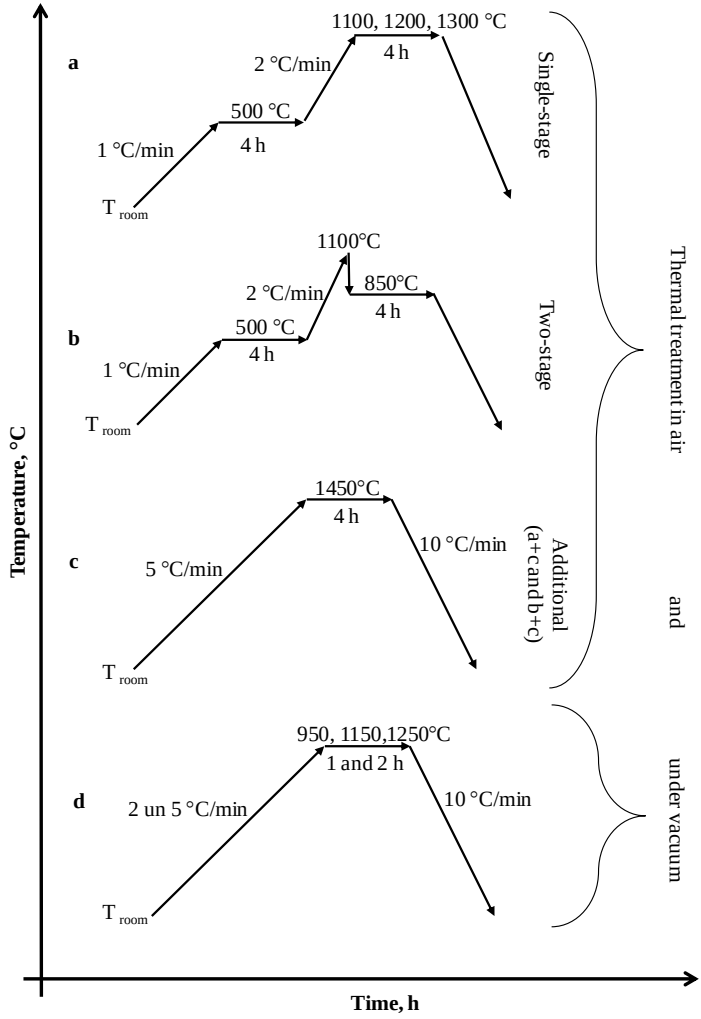

Fig.7. Thermal treatment conditions in air and in vacuum

After extrusion and drying sample quality was evaluated by both technological means and visually. As some extrusion pastes were not suitable to obtain quality samples, only green bodies extruded from extrusion paste (containing only TiO_2 anatase) A6M and A6 were processed further to evaluate how extrusion paste composition affects properties of the ceramics after sintering. Green bodies extruded from A6-2M, A7 and A8 extrusion pastes were also processed to evaluate how addition of recycler rutile powder affects properties of the ceramics. After thermal treatment in air and under vacuum, electrical resistance and thermoelectric properties were investigated for ceramic samples extruded from A6 and A7.

The influence of thermal treatment on microstructure of TiO_2 ceramics

After evaluation cross-sectional fracture SEM images of TiO_2 ceramics (Fig. 8), after **single-stage thermal treatment** of ceramics extruded from A6M, it is concluded that microstructure formed at temperatures 1100-1200 °C in non-homogeneous, as grains with distinct boundary surface have not formed. Bimodal porosity is observed – within the grains and amongst the grains. Size of isolated pores is 0.5-2.0 μm. Ceramic samples extruded from A7 after thermal treatment at 1100 °C have a very fine-grained microstructure. After thermal treatment at 1300 °C both kinds of samples have grains sized 7-20 μm and no significant differences are observed. Relative density of ceramic samples extruded from A6M after single-stage thermal treatment is larger compared to samples extruded from A7 (this is caused by addition of TiO_2R).

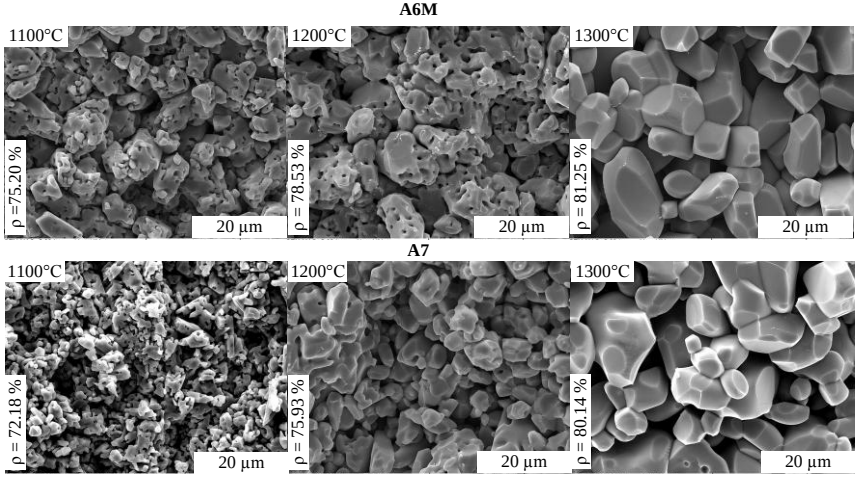

Fig.8. SEM images of fracture surface of ceramic samples extruded from A6M and A7 after single-stage thermal treatment at 1100, 1200 and 1300 °C

After evaluation of SEM images of fracture surface of TiO_2 ceramics after **two-stage thermal treatment at 1100-850 °C** (Fig.9), it is concluded that samples extruded from A6M and A6 have a microstructure consisting of needle-shaped grains. The width of the needle-shaped grains is 1-32 μm, length – 7-25 μm. No needle-shaped grains are observed for other samples. Most likely the addition of TiO_2R has interfered with formation of needle-shaped grains. For these samples the microstructure is very similar to that of samples after single-stage thermal treatment. After two-stage thermal treatment the relative density of ceramics is 1-3 % larger than for ceramics after single-stage thermal treatment.

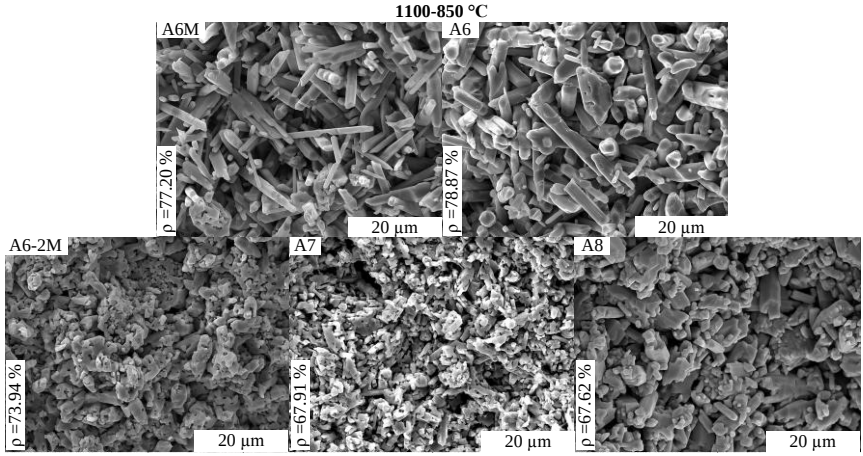

Fig.9. SEM images of fracture surface of samples after two-stage thermal treatment at 1100-850 °C

An **additional thermal treatment** was carried out at 1450 °C for samples previously thermally treated in a single-stage at 1100 °C and for samples treated in two-stages at 1100-850 °C. All such samples had no significant microstructural differences – in both cases grains sized 20-50 μm had formed, and the samples fractured both at grain boundaries and at grain volume. Relative density after additional thermal treatment is in air is 82-89 %.

In SEM images of samples extruded from A6M show **cross-sectional inhomogeneities** after thermal treatment in air at 1100 °C. Approximately 2 mm from edge of cylindrical sample there is denser microstructure with smaller grains compared to that at the middle of the sample, see Fig.10. The formation of these microstructures might be caused by thermal treatment conditions, the sample preparation process (extrusion) – as sample is denser at the edges. As sample is less dense in the middle, the grains are able to shift more at high temperatures and form larger grains that at the sample edge surfaces. But after

thermal treatment at 1300 °C or at higher temperatures, a homogeneous microstructure has formed all over the sample cross-section.

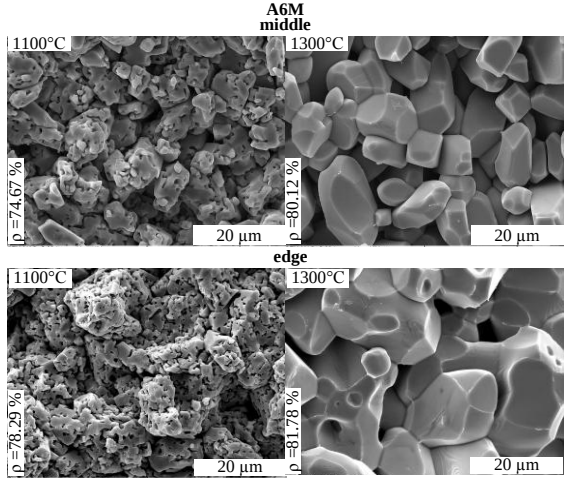

Fig.10. SEM images of A6M sample middle and edge after single-stage treatment at 1100 and 1300 °C

If microstructure of A6 ceramic samples in longitudinal direction and cross-section after thermal treatment at 1300 °C in air is compared (Fig.11), chaotically placed grains are observed.

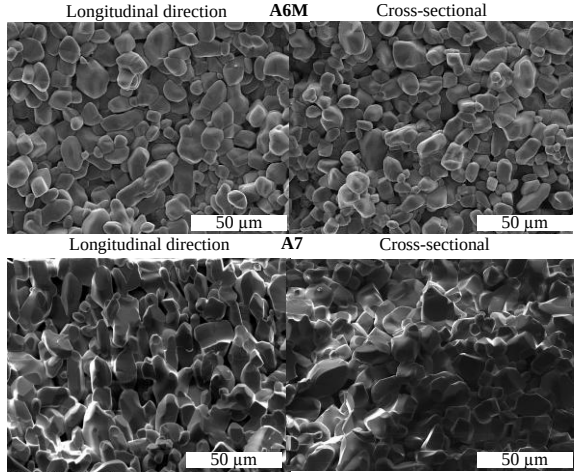

Fig.11. SEM images of ceramic samples extruded from A6M and A7 (in longitudinal direction and cross-sectional) after thermal treatment in air at 1300 °C

But ceramic samples extruded from A7 (extrusion mass contains 15.32 % TiO_2R) after thermal treatment at 1300 °C show **texturing of microstructure in longitudinal direction** (direction of extrusion).

The influence of thermal treatment on mechanical properties

Three-point flexural strength test results for TiO_2 ceramic samples after thermal treatment at 1100 °C are shown in Fig.12. For samples extruded from A6M and A6 extrusion pastes (containing only TiO_2 anatase phase) there are no significant differences in flexural strength (~ 22 MPa). Ceramic samples extruded from A6-2M (containing 6.95 % TiO_2R) also have similar flexural strength values (~25 MPa). Ceramic samples extruded from A7 and A8, (recycled TiO_2R added) flexural strength significantly lowered with increase of TiO_2R content (A7-15.32 %, A8-41.75 %). Correlation between flexural strength ad relative densities was observed.

Elastic modulus after thermal treatment in air at 1100 °C for A6M and A6 samples is approximately 18 GPa, but deformation 0.2 %. For other samples, if TiO_2R content is increased, elastic modulus decreases from 17 to 5 GPa, but deformation from 0.2 to 0.1 %.

After additional thermal treatment in air (at 1100 and 1450 °C) the textural strength of all tested TiO_2 ceramic samples is between 47 and 49 MPa. It was also observed that relative density between various sample series is not markedly different. This indicates that temperature of thermal treatment is also high enough (1450 °C) for samples containing rutile to sinter similarly.

The elastic modulus after additional thermal treatment in air is 20-28 GPa, but the deformation is 0.2 %.

Flexural strength of A6M sample series (thermally treated in air at 1100 °C and additionally thermally treated under vacuum at 1000 and 1250 °C). It was observed that thermal treatment under vacuum at 1000 °C does not affect flexural strength and it remains approximately 20 MPa (compared with flexural samples thermally treated only in air. But after thermal treatment under vacuum at 1250 °C flexural strength has increased almost four-fold, whereas relative density has increased only by approximately 3%.

Relative density of samples extruded from A6M after additional thermal treatment in air is larger (84.64 %) than of those additionally thermally treated under vacuum conditions at 1250 °C (81.13 %). Flexural strength of these samples is almost two-fold larger than for samples additionally thermally treated under vacuum conditions.

Elastic modulus after additional thermal treatment under vacuum at 1000 °C is 21 GPa, but deformation 0.2%. Whereas after additional thermal treatment under vacuum at 1250 °C elastic modulus is 21 GPa, but deformation 0.3%.

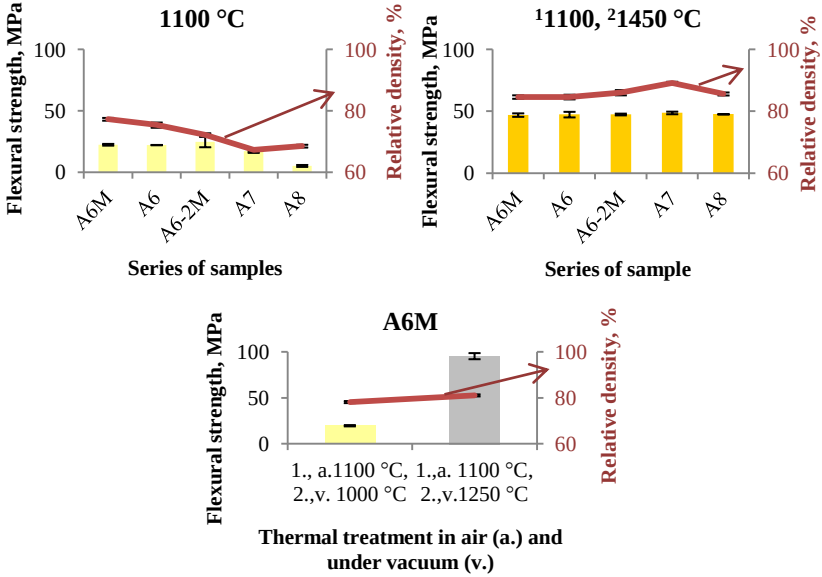

Fig.12. Flexural strength and relative density of TiO_2 ceramic samples after single-stage thermal treatment at 1100 °C and after two-stage thermal treatment at ^{1}1100, ^{2}1450 °C and for A6M sample series after additional thermal treatment under vacuum conditions at 1000 and 1250 °C

Analysis of phase composition and structure

After in-depth study of X-ray diffraction peaks (conducted using X-ray diffractometer with a monochromator *Rigaku SmartLab*) it was ascertained that **after thermal treatment in air at 1100 °C** TiO_2 ceramics consist of rutile phase (Fig.13). After study of individual diffraction peaks, for example (110) and (220) peaks, it can be seen that sample contains two separate TiO_2 rutile phases (data base numbers: 00-021-1276 [a] and 04-007-4874 [b]). Crystal lattice parameters differ for these rutile phases. For the first phase parameters are: a=4.591884 Å, b=4.591884 Å, c=2.960341 Å. But for the second phase parameters are: a=4.599978 Å, b=4.599978 Å, c=2.957185 Å. For both phases $\alpha=\beta=\gamma=90°$. This separation is connected to structural changes, for example appearance of oxygen vacancies and accordingly to formation of non-stoichiometric TiO_2 (TiO_{2-x}).

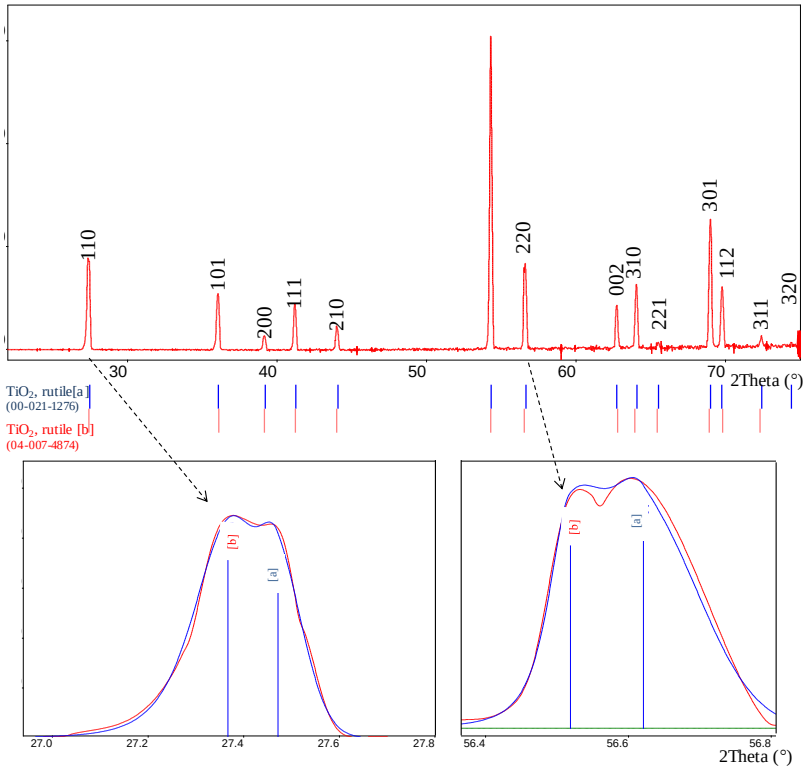

Fig.13. X-ray diffraction pattern and shapes of two individual rutile peaks - (110) and (220) for samples ceramic extruded from A6 after thermal treatment at 1100 °C

X-ray diffraction patterns of TiO_2 ceramic samples thermally treated in air at high temperature values (1200-1400 °C) and under vacuum **at 1250 °C**, see Fig. 14, match rutile structure. However three separate rutile phases can be observed – two TiO_2 phases (database numbers: 04-007-4874 [b] and 01-072-7374 [d]), and non-stoichiometric $TiO_{1.95}$ phase (01-073-1782 [c]). These phases also have different lattice parameters. Lattice parameters for phase [b] are: a=4.600702 Å, b=4.600702 Å, c=2.961479 Å; for phase [c]: a=4.591784 Å, b=4.591784 Å, c=2.956293 Å; for phase [d] a=4.625430 Å, b=4.625430 Å, c=2.956111 Å. For all phases $\alpha=\beta=\gamma=90°$.

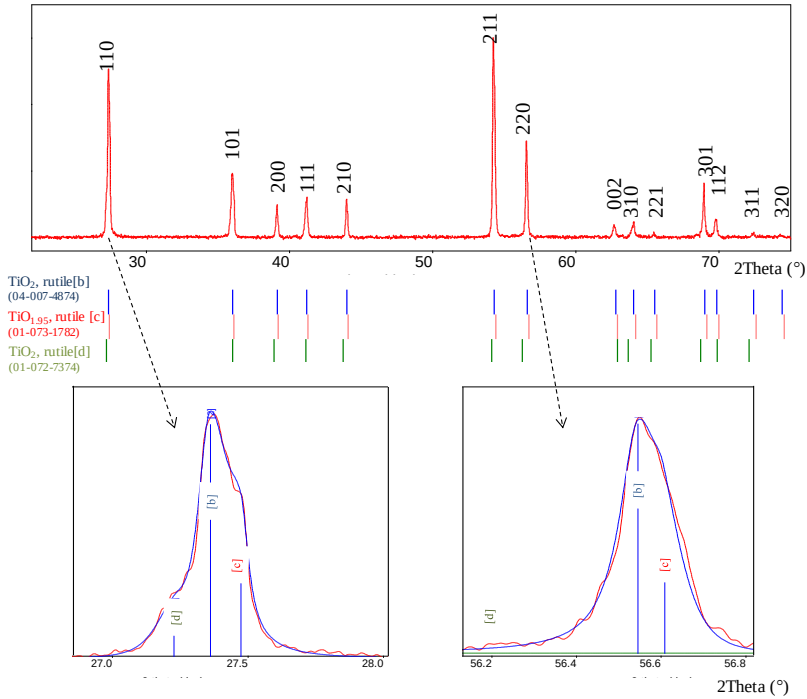

Fig.14. X-ray diffraction pattern and shapes of two individual peaks – (110) and (220) for ceramic samples extruded from A6 after thermal treatment in air and additional thermal treatment under vacuum conditions

Electric and thermoelectric properties of TiO_2 ceramic samples

All samples for which Seebeck effect was measured (after sintering in air and additional thermal treatment under vacuum conditions) were n-type semiconductors. This has been observed before in the works of other researchers investigating thermoelectric properties of "slightly" reduced TiO_2 [2, 3, 4].

For **Series 1** (extruded using A6) thermal treatment in air at several temperatures from 1000 to 1400 °C and additional thermal treatment under vacuum conditions at 1250 °C, temperature was increased at a rate 2 °C/min.

In Fig.15 the dependence of electrical conductivity on temperature for Series 1 is shown. It can be observed that, if the temperature for thermal treatment in air (sintering before thermal treatment in vacuum) is increased, the electrical conductivity also increases. It is possible that in these cases electrical

conductivity is caused by defects within grain volume (caused in turn by creation of oxygen vacancies within the TiO_2 crystal lattice and by reduction of Ti^{4+} to Ti^{3+} during treatment under vacuum)

The highest electrical conductivity at temperatures from 300 to 600 K is exhibited by sample A6-a.1400-v.1250-2 (~100-115 S/m).

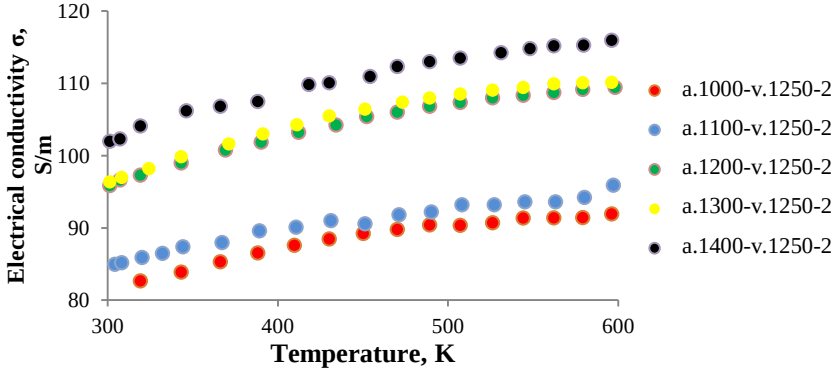

Fig.15. Electrical conductivity of ceramic samples prepared from paste A6 depending on the temperature

During construction of Arrhenius plot, the activation energy of electrical conductivity was determined. For all samples from Series 1 activation energy is in the 0.0053-0.0074 eV range and electrical conductivity is provided by vacancies.

As Seebeck coefficient values are dependent on charge carrier concentration (Seebeck coefficient increases as charge carrier concentration decreases [5]), the samples with the highest Seebeck coefficient values (Fig.16) have lower electrical conductivity (Fig.15). Samples A6-g.1100-v.1250-2 and A6-a.1200-v.1250-2 (125-140 μV/K) have the highest Seebeck coefficients, but the sample A6-a.1400-v.1250-2 (85-100 μV/K) the lowest values.

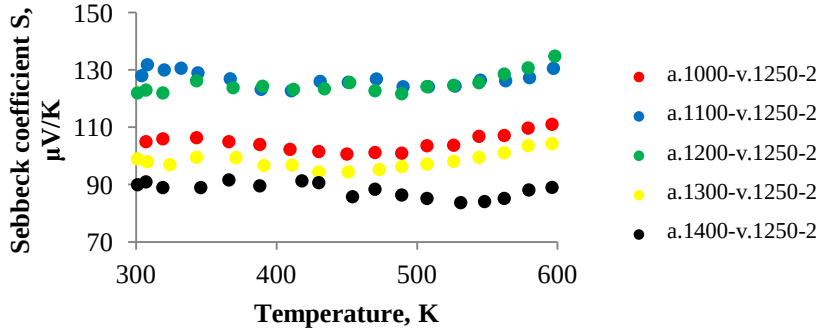

Fig.16. Seebeck coefficient for ceramic samples prepared from A6 depending on temperature

In Fig.17 the dependence of thermoelectric power factor ($S^2\sigma$) on temperature is depicted. Sample A6-a.1200-v.1250-2 has the highest Seebeck coefficient as well as thermoelectric power factor (1.2-2.0 $\cdot 10^{-6}$ $Wm^{-1}K^{-2}$), but sample A6-a.1400-v.1250-2 – the lowest thermoelectric power factor (0.7-0.9$\cdot 10^{-6}$ $Wm^{-1}K^{-2}$).

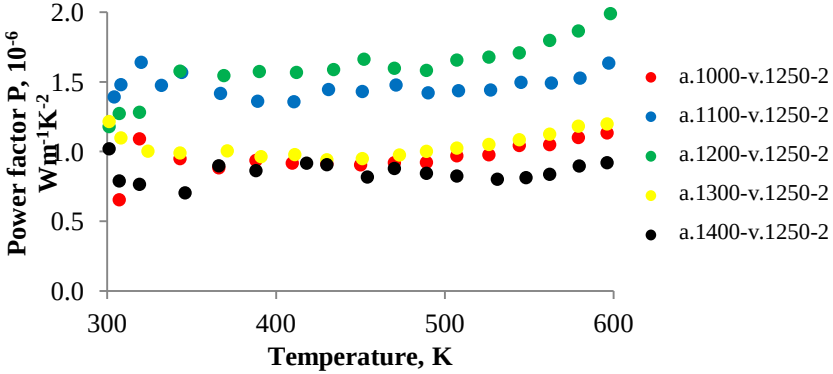

Fig.17. The thermoelectric power factor depending on temperature for ceramic samples prepared from A6

Thermal treatment of samples of **Series 2**, extruded from A6 paste was conducted at temperatures from 1000 to 1400 °C, further additional thermal treatment was done under vacuum at 1250 °C. In this experiment increase rate of temperature during treatment was 5 °C/min. In the following text the samples from Series 2 are denoted as A6-a.1000-v.1250-5... A6-a.1400-v.1250-5, etc.

In Fig.18 the dependence of electrical conductivity on temperature for samples from Series 2 is shown. The highest electrical conductivity is observed for sample A6-a.1300-v.1250-5, (78-85 S/m). However, in general all samples have ~20-25% lower electrical conductivity than samples in Series 1. It is possible, that this is because of shorter overall thermal treatment time under vacuum (it was longer for samples from Series 1 as heating rate was lower and total thermal treatment time longer). It may be that samples that are thermally treated for longer time have higher amount of defects and, therefore have higher electrical conductivity. Also the fact that samples from Series 1 were heated at a lower rate and therefore had higher relative density (which in turn insures higher electric conductivity) must be taken into account [2]. Samples from Series 1 were submitted to treatment under vacuum for twice as long, and therefore should have higher amount of defects along grain boundaries.

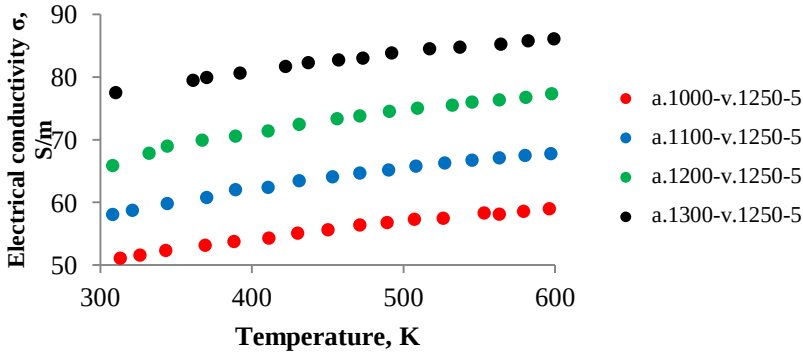

Fig.18. Electrical conductivity for ceramic samples prepared from A6 depending on temperature.

From Arrhenius plot it can be concluded that for samples from Series 2 at given temperature range charge carriers are vacancies. Activation energy was calculated for all samples from Series 2. The activation energy for samples from Series 2 was a bit higher than for samples from Series 1(0.0059-0.0086 eV).

Sample A6-a.1100-v.1250-5 has the highest Seebeck coefficient (170-190 μV/K) amongst samples from Series 2, but sample A6-a.1300-v.1250-5 has the lowest (90-120 μV/K). In general Seebeck coefficient values are lower for samples from Series 2 than for samples from Series 1. As samples from Series 2 have lower electrical conductivity, the charge carrier concentration is also lower and therefore Seebeck coefficient values rise.

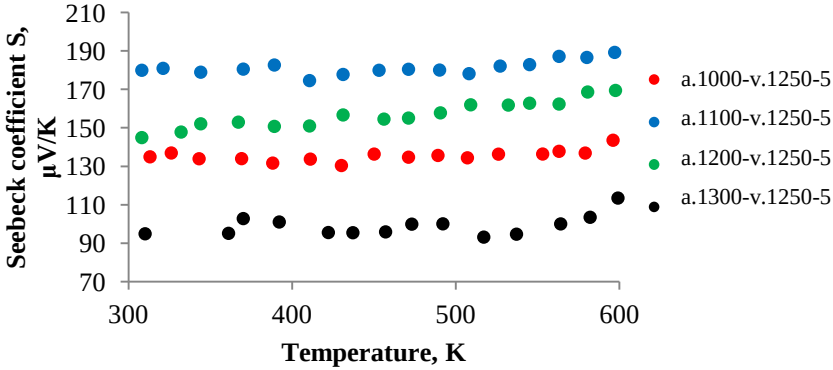

Fig.19. Seebeck coefficient for ceramic samples prepared from A6 depending on temperature

Thermoelectric power factor for samples from Series 2 depending on temperature is shown in Fig.20. Obtained results are very similar to those of samples from Series 1, as the comparatively lower electrical conductivity of samples from Series 2 in the case of thermoelectric power factor is compensated by higher Seebeck coefficient values. The highest thermoelectric power factor ($1.8\text{-}2.5 \cdot 10^{-6}$ $Wm^{-1}K^{-2}$) was calculated for sample A6-a.1100-v.1250-5 that was thermally treated in air at lower temperature. The lowest thermoelectric power factor ($0.7\text{-}1.0 \cdot 10^{-6}$ $Wm^{-1}K^{-2}$) was calculated for sample A6-a.1300-v.1250-5 that was thermally treated in air at a higher temperature.

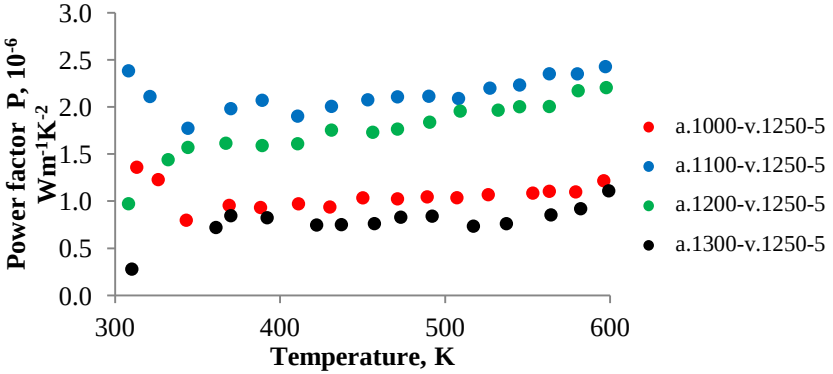

Fig.20. Electric power factor for samples prepared from A6 depending on temperature

Thermal treatment for samples from **Series 3** (paste A7) was conducted in air at two different temperatures 1000 and 1200 °C with further treatment under vacuum at 950 °C or 1150 °C temperature. Heating rate during thermal treatment in vacuum was 5 °C/min. The samples in further text are denoted as A7-a.1000-v.950-5... A7-a.1200-v.1150-5, etc.

The amount of generated defects in TiO_2 crystal lattice and therefore electric conductivity depends (oxygen vacancies, Ti^{3+} ions, etc.) on temperature of thermal treatment under vacuum. As samples in Series 3 were thermally treated under vacuum at lower temperatures (950 or 1150 °C) than samples from Series 1 and Series 2 (1250 °C), the electrical conductivity of samples from Series 3 is lower (Fig.21). Samples from Series 3 thermally treated under vacuum at 1150 °C have higher electrical conductivity than samples that are thermally treated under vacuum at 950 °C. Therefore electrical conductivity for samples A7-a.1000-v.1150-5 and A7-a.1200-v.1150-5 is 7-22 S/m, but for samples A7-a.1000-v.950-5 and A7-a.1200-v.950-5 lower by 1 S/m.

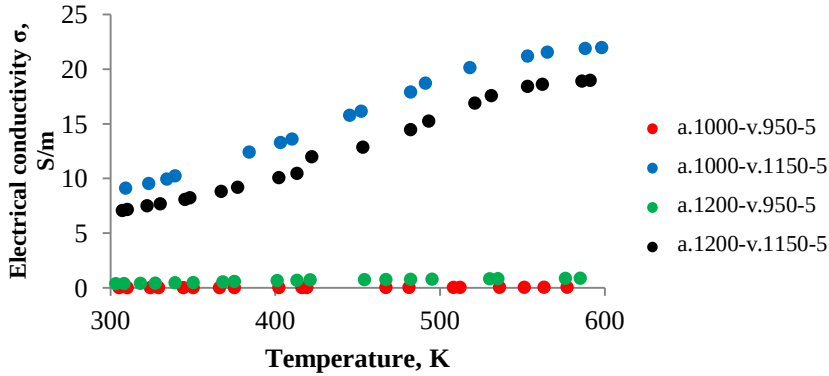

Fig.21. Electrical conductivity for ceramic samples prepared from paste A7 depending on temperature

From Arrhenius plot for samples from Series 3 it can be concluded that at lower temperature range charge is predominantly carried by vacancies, whereas at higher temperature range intrinsic conductivity predominates. The plot can be divided into two ranges – for first range (at lower temperatures) activation energy is 0,033-53 eV (depending on chosen thermal treatment), but for second range 0,043-0,102 eV.

As electrical conductivity for samples from Series 3 is lower (the charge carrier density is lower as well) than for samples from Series 1 and Series 2, the values of Seebeck coefficient are higher (Fig.22). For example, sample A7-

a.1200-v.950-5 has the highest value ~330 μV/K, but sample A7-a.1000-v.1150-5 the lowest value ~ 160 - 205 μV/K.

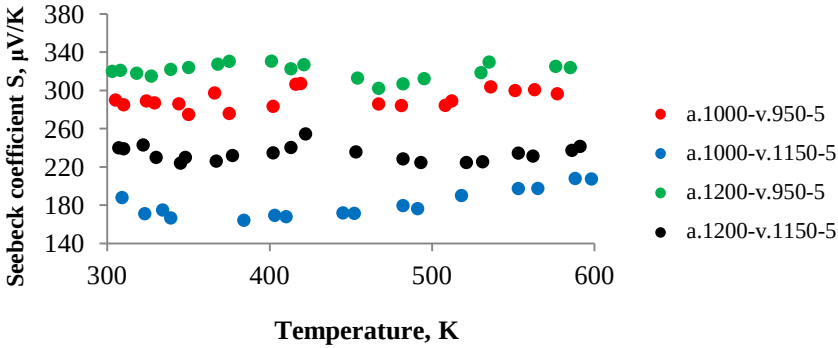

Fig.22. Seebeck coefficient for ceramic samples prepared from A7 paste depending on temperature

The thermoelectric power factor (Fig.23) for samples A7-a.1000-v.1150-5 and A7-a.1200-v.1150-5 is 0.3-1.1·10^{-6} $Wm^{-1}K^{-2}$.

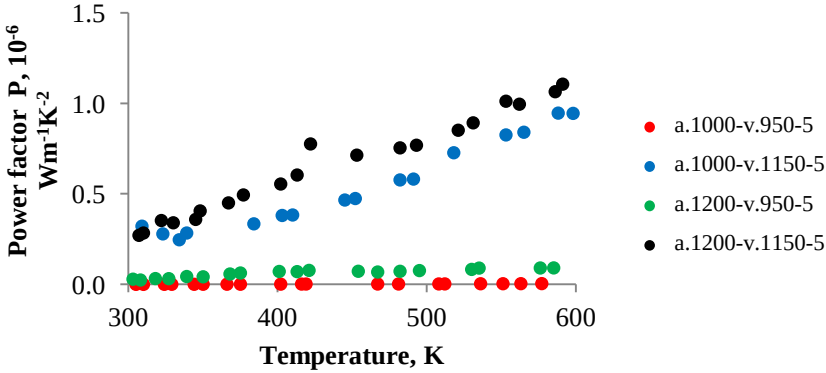

Fig.23. Thermoelectric power factor for ceramic samples prepared from paste A7 depending on temperature

From the obtained results it is concluded that both high Seebeck coefficient values and high electrical conductivity are needed. Optimal treatment conditions to obtain thermoelectric materials are the following: thermal treatment in air at 1100-1200 °C and under vacuum at 1250 °C.

However TiO_{2-x} ceramic samples sintered in air at 1300-1400 °C and additionally under vacuum at 1250 °C have higher electrical conductivity and therefore these materials have the potential to be used as electrodes [6-8].

CONCLUSIONS

1. An original extrusion paste was developed, containing TiO_2 (anatase) 77.3-79.2 weight %, water 19-20.9 weight %, binder 0.2 weight % and oil 1.6 weight %, where packing density of TiO_2 powder particles is larger than 50%. Using the developed extrusion paste, successful extrusion process can be conducted and the extruded green bodies are without defects.
2. A technology to recycle the production waste of manufacture of TiO_2 ceramics by using it as an ingredient for extrusion pastes. The paste utilizing recycled waste consists of: TiO_2 (anatase) 63.9-71.25 weight %, recycled TiO_2 (rutile) 6.9-15.3 weight %, water 19-20 weight %, binder 0.2 weight % and oil 1.6 weight %.
3. The addition of recycled low quality products (TiO_2 rutile powder) to the extrusion paste leads to texturized ceramic microstructure in the direction of extrusion; the texturation is most readily observed in ceramic green bodies thermally treated at 1100-1300 °C.
4. If extruded TiO_2 ceramics are thermally treated in air at temperatures over 1300 °C, there are no significant differences between microstructure, density and mechanical properties of ceramics extruded using pastes with different compositions.
5. After evaluating electric resistance, thermoelectric properties and phase composion of ceramics after thermal treatment under vacuum conditions, it was concluded that during thermal treatment under these conditions point defects are formed in TiO_2 crystal lattice.
6. It is possible to use extruded TiO_2 ceramic samples, which are thermally treated in air 1300-1400 °C and additionally under vacuum at 1250 °C as material for electrodes inteded for water treatment using electrolysis.
7. Extruded TiO_2 ceramic samples thermally treated in air at 1100-1200 °C and additionally under vacuum at 1250 °C can be used as n-type thermolelectric materials.

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