

The Influence of Air and Subsequent Vacuum Thermal Treatment on the Thermoelectric Properties of Extruded TiO₂ Ceramics

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Abstract. The thermoelectric properties of air sintered and vacuum annealed TiO₂ samples consolidated by the extrusion process have been studied. The samples were sintered in air at 1100, 1175, 1250 and 1350 °C and subsequently annealed under vacuum at 1075 °C. After both thermal treatments oxygen deficient phases were not observed and only a single rutile TiO₂ phase was present in the samples. The density and grain size of the samples increased with an increase in air sintering temperature, while the total porosity decreased. Electrical conductivity of the samples increased with an increase in air sintering temperature. The highest Seebeck coefficient (~410 μV/K) and thermoelectric power factor ($3,25 \times 10^{-6} \text{ W/m}^2\text{K}^2$) at 280 °C were obtained for the sample that was sintered in air at 1175 °C before the following annealing under vacuum.

Keywords: TiO₂, ceramics, microstructure, thermoelectric properties

I. INTRODUCTION

Approximately 90% of the world's power is generated by heat engines. Most heat engines use fossil fuel to provide heat, which is then converted to work. In the energy conversion process, a large fraction of the energy content is lost as waste heat (typical heat engines operate at 30–40 per cent efficiency, which means that more than half of the fuel energy is expelled as waste heat) [1].

One way to recover part of this waste heat is to use thermoelectric materials that can directly and reversibly convert heat to electrical energy. This process is based on the Seebeck effect, which describes the voltage induced by the temperature difference across a material. The voltage produced is proportional to the temperature difference across the material. The proportionality constant is defined as the Seebeck coefficient and is obtained from the ratio of the voltage generated and the applied temperature difference: $S = \Delta V / \Delta T$ [2]. The performance of thermoelectric material is driven by its figure of merit ZT , a parameter determining the efficiency of thermoelectric conversion and is defined as $ZT = S^2 \sigma T / k$, where S , σ , T and k are the Seebeck coefficient, electrical conductivity, temperature and thermal conductivity, respectively [3]. The product ($S^2 \sigma$) is called the power factor. It is commonly used to evaluate the performance of thermoelectric materials [2].

The challenge of research on the thermoelectric materials is to increase values for ZT . Figure of merit of the material can be increased by increasing the power factor $S^2 \sigma$ and/or decreasing the thermal conductivity k . These parameters in ZT vary with carrier concentration. Therefore, controlling carrier

concentration is an essential prerequisite for optimizing the ZT values [4, 5].

The most widely used commercial thermoelectric material is bulk Bi₂Te₃ and its alloys [6, 7]. Since tellurium is extremely rare found in the Earth's crust [8], it would be desirable to develop alternative materials that minimize the use of rare elements and involve cheaper and widely available elements.

Transition metal oxides have been attracting increasing attention owing to their good thermoelectric properties, innocuity and low costs [9]. Among the transitional metal oxides, TiO₂ might be considered one of the most promising thermoelectric materials [10, 11].

TiO₂ is a dielectric material with the band gap width ~ 3 eV and is used in a wide range of applications because of its non-toxicity, thermal stability, high oxidation resistance and controllable semiconducting properties [9]. TiO₂ occurs in three distinct polymorphs: rutile, anatase, and brookite, but only rutile and anatase are of technical importance.

For thermoelectric applications, the electrical conductivity of TiO₂ should be increased. It can be achieved by reduction treatment and impurity doping. If TiO₂ is thermally treated in a reducing atmosphere (gaseous, vacuum), various defects, such as oxygen vacancies and Ti³⁺ defects, 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} [12].

In stoichiometric TiO₂ crystal, the metal atom is in 3d⁰ (Ti⁴⁺) electronic configuration. During reduction, Ti⁴⁺ ions can receive electrons from reducing gases or lattice oxygen usually removed from stoichiometric TiO₂. As a result, Ti₂O₃ regions in TiO₂ lattice can be formed, in which the metal atom is in 3d¹ (Ti³⁺) configuration [13]. Due to such lattice defects, local energy levels inside the band gap of TiO₂ can be formed, and electrical conductivity of the oxide significantly increases [14]. Even slight deviations from stoichiometric TiO₂ can significantly increase its electrical conductivity [15]. If there is a large oxygen deficit in the TiO₂ structure, share of crystallographic planes occurs in the crystal lattice and the so-called Magneli phases are formed [16]. 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 can be obtained by reducing titanium dioxide at high temperatures in H₂ atmosphere. As a result, ceramic materials with high electrical conductivity similar to that of graphite are obtained. Magneli phase titanium oxides show relatively high thermoelectric performance [10, 17].

It is also known that electrical properties of ceramics containing titanium oxides can be affected by various microstructural defects (pores, grain boundaries, etc.) [18, 19].

In the present study, we investigate the influence of air and subsequent vacuum thermal treatment on the microstructure and thermoelectric properties of TiO₂ ceramics formed by extrusion, which is a cost-effective method to produce objects with a cross-sectional profile.

II. MATERIALS AND METHODS

To produce a paste for extrusion, commercial TiO₂ powder (*Sachtleben Chemie GmbH, Hombitan LW-S*) with purity greater than 99% and average particle size of 300 nm was mixed with 18 wt% water and 2 wt% additives (plasticizer, lubricant) in a kneader-mixer (*AMK, IIIU 8/IV*) at constant temperature of 20 °C and a rotor speed of 30 rpm. The paste was then transferred to a vacuum extrusion press (*Dorst, V10 SpHv*) and formed to cylindrical green bodies with a diameter of 13 mm and length of about 100 mm. The consolidated green bodies were first dried at room temperature for 3 days in order to remove residual water and prevent crack formation. After drying the green body compacts were pressureless sintered in air at 1100, 1175, 1250 and 1350 °C for 5 h with a heating and cooling rate of 3 °C/min. In order to increase free carrier concentration, after sintering the samples were annealed under vacuum (2×10^{-5} mbar) at 1075 °C for 3 h with heating and cooling rate of 5 °C/min.

Density, open and closed porosity of the sintered and vacuum annealed samples were determined using a method based on Archimedes' principle [20]. The density values obtained from measurements were related to the theoretical density of anatase or rutile TiO₂.

Crystal phases of thermally treated samples were revealed by X-ray powder diffraction using *PANalitical X'pert PRO* model X-ray diffractometer (XRD) with Cu K_α radiation. For microstructural characterization, the samples after thermal treatment were fractured and then studied using the scanning electronic microscope (SEM) *Tescan Mira/LMU*.

In order to measure thermoelectric properties of the samples, after thermal treatment they were cut in 20 mm long cylinders. The Seebeck coefficient and the electrical resistivity of the samples were measured under a vacuum in the temperature range from room temperature to 300 °C in a self-made apparatus. To ensure good electrical contact between the samples and the measurement device, copper was deposited on both ends of the samples in a thermal vacuum evaporator.

III. RESULTS AND DISCUSSION

Fig. 1. shows XRD patterns of the air sintered (1100, 1250 and 1350 °C) and vacuum annealed samples. During a thermal treatment phase, transition from anatase to rutile occurred and only a single rutile TiO₂ phase was present in all of the samples. Oxygen deficient TiO_{2-n} phases after vacuum annealing were not observed.

Density and porosity of the samples as a function of air sintering temperature are shown in Fig. 2 and Fig. 3. As seen in Fig. 2, the density of the samples increases with an increase in the sintering temperature and reaches approximately 83% of the theoretical density at 1350 °C. The open porosity of the

samples (Fig. 3) decreases with an increase in heat treatment temperatures, while closed porosity remains essentially the same for all sintering temperatures. Since vacuum annealing temperature (1075 °C) is lower than air sintering temperature, it does not affect the density and porosity of the samples.

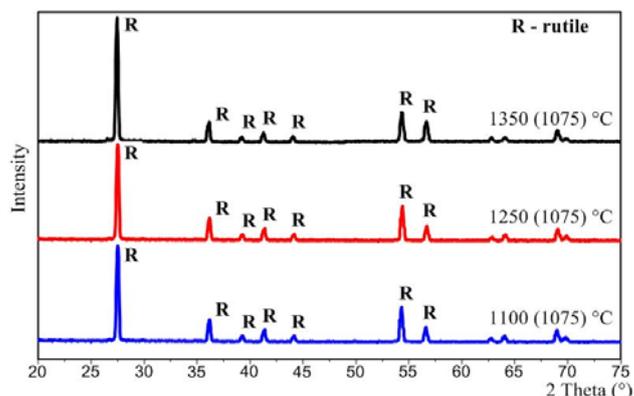


Fig. 1. XRD patterns of the samples after thermal treatment

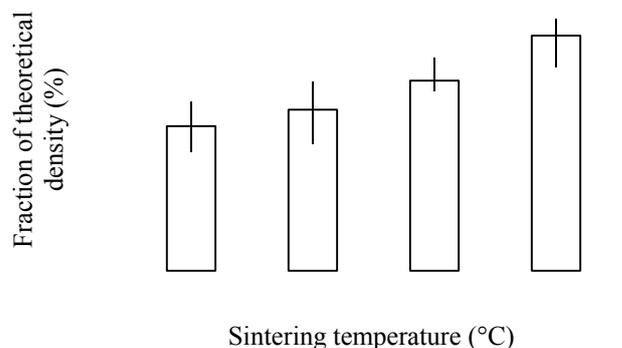


Fig. 2. Density of the samples as a function of sintering temperature

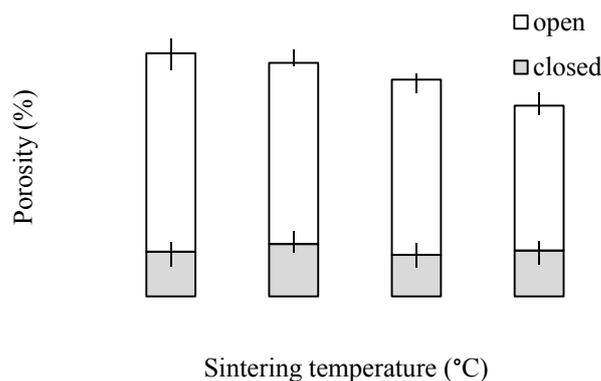


Fig. 3. Porosity of the samples as a function of sintering temperature

SEM micrographs of fracture surfaces of the samples after sintering in air at 1100, 1250 and 1350 °C and subsequent vacuum annealing at 1075 °C are shown in Fig. 4. As seen, the grain size of the samples increases with an increase in the sintering temperature. For the samples sintered at 1100 °C, the grains are mostly elongated in shape. For sintering temperatures from 1250 °C, the grains become more equiaxed.

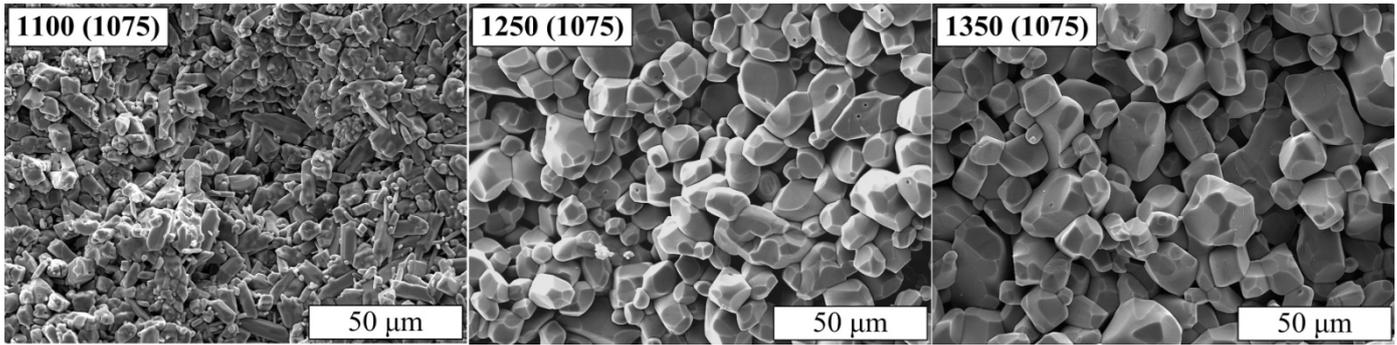


Fig. 4. SEM micrographs of fracture surfaces of the air sintered and vacuum annealed samples

The temperature dependence of the electrical conductivity of the air sintered and vacuum annealed samples are demonstrated in Fig. 5. The behaviour of electrical conductivity for the samples is semiconducting as their conductivity increases with increasing temperature. As can be seen, conductivity of the samples is related to their microstructures formed during air sintering. Electrical conductivity increases as the grain size of the samples increases and porosity decreases. This effect can be caused by the grain boundary area, which is much smaller with coarse grains. In the samples with a reduced grain boundary area there is less electrical barrier present. Also effective conducting volume is smaller for the samples with higher porosity, which can be another reason for the differences in conductivities of the samples [18].

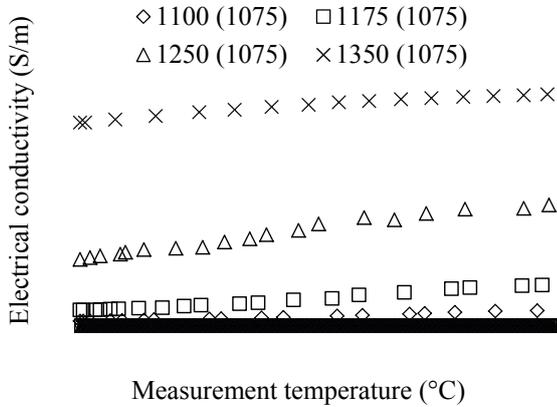


Fig. 5. The electrical conductivity of the air sintered and vacuum annealed samples as a function of temperature

Fig. 6 shows the temperature dependence of the Seebeck coefficient for the samples. Increase in electrical conductivity (Fig. 5) for most of the samples decreases their Seebeck coefficient. It is well known that the absolute values of Seebeck coefficient decrease with an increase in carrier concentration. However, the highest Seebeck coefficient values are shown by the sample sintered in air at 1175 °C, with maximum value (~410 $\mu\text{V/K}$) around 280 °C, while its electrical conductivity is higher than that of the sample sintered at 1100 °C. It is possible that the samples sintered at 1175 °C have lower carrier concentration but higher carrier mobility than the samples sintered at 1100 °C. For the samples sintered at 1100 and 1175 °C, the Seebeck coefficient

increases with increasing temperature, while for the samples sintered at 1250 and 1350 °C it decreases or remains the same.

Values of thermoelectric power factor ($S^2\sigma$) for the samples as a function of temperature can be seen in Fig. 7. Power factor is mainly influenced by the electrical conductivity of the samples. It increases monotonically with temperature. The highest value of thermoelectric power factor is obtained at 300 °C ($3.25 \times 10^{-6} \text{ W/m}^1\text{K}^{-2}$) for the samples sintered at 1175 °C.

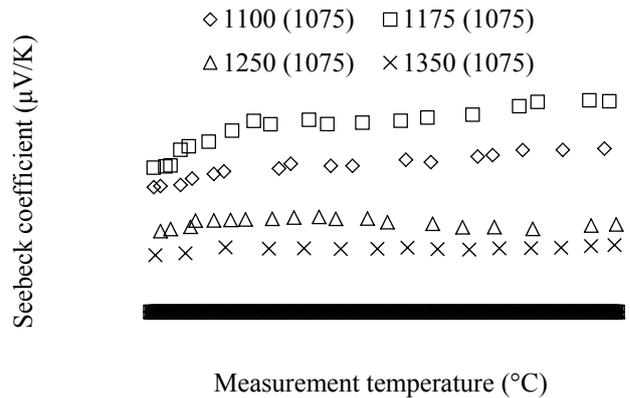


Fig. 6. The Seebeck coefficient of the air sintered and vacuum annealed samples as a function of temperature

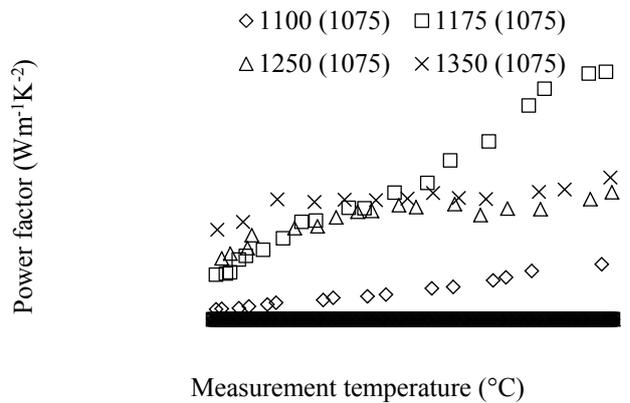


Fig. 7. The power factor of the air sintered and vacuum annealed samples as a function of temperature

IV. CONCLUSIONS

The thermoelectric properties of air sintered and vacuum annealed TiO₂ samples formed by the extrusion method have been investigated. The samples were sintered in air at 1100, 1175, 1250 and 1350 °C and subsequently annealed under vacuum at 1075 °C. The electrical conductivity of the samples increases with an increase in air sintering temperature. The highest Seebeck coefficient (~410 μV/K) and thermoelectric power factor (3.25×10^{-6} W/m⁻¹K⁻²) at 280 °C were obtained for the samples sintered at 1175 °C.

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Kristaps Rubenis, Valdis Teteris, Jānis Locs, Jānis Barloti, Līga Bērziņa-Cimdina. Ekstrudētas TiO₂ keramikas termoelektriskās īpašības pēc termiskās apstrādes gaisa vidē un sekojošas termiskās apstrādes vakuuma apstākļos

Darbā pētīta termiskās apstrādes (gaisa un vakuuma apstākļos) ietekme uz ekstrūzijas ceļā iegūtas TiO₂ keramikas termoelektriskajām īpašībām. No komerciāla TiO₂ pulvera, ūdens un piedevām izgatavota plastiska masa. No iegūtās masas ar ekstrūzijas paņēmieni formēti apaļa šķērsriezuma stienīši (paraugi). Pēc žāvēšanas tie saķepināti gaisa vidē 1100, 1175, 1250 vai 1350 °C temperatūrā. Pēc saķepināšanas stienīši

termiski apstrādāti vakuuma apstākļos 1075 °C temperatūrā, elektrovadītspējas uzlabošanai. Termiski apstrādātajiem paraugiem noteikts kristālisko fāžu sastāvs, blīvums un porainība, pētīta mikrostruktūra, mērīta elektrovadītspēja un Zēbeka koeficients temperatūru intervālā no 20 līdz 300 °C, aprēķināts termoelektriskais jaudas faktors. Pēc termiskās apstrādes visos paraugos novēroti tikai rutila kristāliskajai fāzei atbilstošie maksimumi, nestehiometriskie TiO_{2-n} savienojumi netika konstatēti. Palielinot paraugu termiskās apstrādes temperatūru gaisa vidē, pieaug paraugu blīvums un graudu izmērs, savukārt porainība samazinās. Konstatēts, ka paraugu elektriskās īpašības būtiski ietekmē mikrostruktūra, kāda tajos izveidojusies saķepināšanas laikā gaisa vidē. Pieaugot blīvumam un graudu izmēram (palielinoties saķepināšanas temperatūrai gaisa vidē), paraugu elektrovadītspēja pieaug, lai gan vakuuma termiskā apstrāde visiem paraugiem veikta identiskā (1075 °C) temperatūrā. Nosakot paraugu termoelektriskās īpašības, konstatēts, ka visu paraugu elektrovadītspēja pieaug, paaugstinoties to temperatūrai. Augstāko Zēbeka koeficientu ($\sim 410 \mu V/K$) un termoelektrisko jaudas faktoru ($3,25 \times 10^{-6} W/m^1K^{-2}$) 280 °C temperatūrā uzrāda paraugi, kuri pirms termiskās apstrādes vakuuma apstākļos gaisa vidē saķepināti 1175 °C temperatūrā.

Кристанс Рубенис, Валдис Тетерис, Янис Лочс, Янис Барлотс, Лига Берзиня-Цимдиня. Зависимость термоэлектрических свойств образцов из керамики TiO_2 , полученных путём экструзии, от термообработки в воздушной среде и последующей термообработки в условиях высокого вакуума.

Исследовано влияние термической обработки на воздухе и в условиях высокого вакуума на термоэлектрические свойства образцов керамики TiO_2 . Пластическая масса приготовлена из коммерческого порошка TiO_2 , воды и связывающих добавок. Из полученной массы путём экструзии изготовлены образцы круглого сечения. После сушки образцы спекались в воздушной среде при температурах 1100, 1175, 1250 и 1350 °C, потом подвергались термообработке в условиях высокого вакуума при температуре 1075 °C. Для образцов определены: состав кристаллографических фаз, плотность, пористость, микроструктура, электропроводность и коэффициент Зеебека в интервале температур от 20 до 300 °C, а также термоэлектрический фактор мощности. Во всех образцах после термообработки констатирована кристаллическая фаза - рутил. Нестехиометрические соединения типа TiO_{2-n} не обнаружены. При увеличении температуры термообработки в воздушной среде увеличивается плотность и размер зерен, а пористость уменьшается. Обнаружено, что на электрические свойства существенно влияет микроструктура, которая образовалась при спекании в воздушной среде при увеличении плотности и размера зерен (при возрастании температуры в воздушной среде) электропроводность образцов увеличивается несмотря на то, что температура термообработки в условиях высокого вакуума была одинакова – 1075 °C. После измерения термоэлектрических свойств образцов установлено, что при увеличении температуры нагрева образцов наблюдается возрастание электропроводности. Наибольшие значения коэффициента Зеебека ($\sim 410 \mu V/K$) и термоэлектрического фактора мощности ($3,25 \times 10^{-6} W/m^1K^{-2}$), определенных при 280 °C, обнаружены у образцов спечённых в воздушной среде при температуре 1175 °C.