

# The effect of thermal processing parameters on the microstructure of extruded and sintered TiO<sub>2</sub> ceramics

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**Abstract.** There are no investigations concerning the microstructural homogeneity in cross section of extruded and sintered samples found in literature. In this work TiO<sub>2</sub> ceramics obtained by extrusion technology is investigated. Samples were sintered under three different sintering conditions: A) 1100→850 °C, B) 1100 °C and C) 1100→1450 °C. Two step sintering at 1100 – 850 °C leads to the formation of denser microstructure (77.2 % of TD) compared to single step sintering at 1100 °C (75.4 % of TD). After thermal treatment there are differences between microstructure in middle and edge part of all samples. Microstructure of samples after each sintering condition is different. Needle-shaped and irregularly shaped grains and bimodal porosity can be found in SEM investigations.

## 1. Introduction

Influence of rheological parameters on extrusion process of ceramic paste has been investigated in literature before [1-4]. Also the influence of sintering temperature on the microstructure and porosity of samples has been investigated [5, 6]. It has been observed that the grain orientation of extruded and sintered ceramic samples is in direction of extrusion (longitudinal) [7, 8]. However there are no investigations concerning the microstructural homogeneity in cross section of extruded and sintered samples.

In this work TiO<sub>2</sub> ceramics obtained by extrusion technology is investigated. Significant advantages of TiO<sub>2</sub> ceramics are: chemical stability, non-toxicity, ease of availability and relatively low price. TiO<sub>2</sub> ceramics can be used as electrodes for water treatment technology based on electrolysis [9]. In comparison with currently widely used electrodes (Pt, PbO<sub>2</sub>, IrO<sub>2</sub>, Pt- Ir, RuO<sub>2</sub>, MnO<sub>2</sub>, graphite etc.), titanium dioxide has good chemical stability, high resistance to corrosion and much lower production cost [10].

The most common ceramic powder forming methods are mechanical or hydraulic powder pressing, injection molding, gel casting and extrusion [11]. Extrusion is widely used in the traditional ceramics sector (manufacture of bricks, tiles, pipes or rods), where simple die form is used.

The most important factor for successful extrusion process is optimal plasticity of extruded mass. Extrusion mass has to be plastic enough to be extruded, but extruded products must also maintain form during further processing [12, 13]. The above requirements can be ensured due to developing of optimal composition of extrusion mass [14].

The aim of the work is to study the influence of thermal treatment conditions on microstructure of extruded and sintered samples. Not only density and porosity of material, but also the grain size, shape

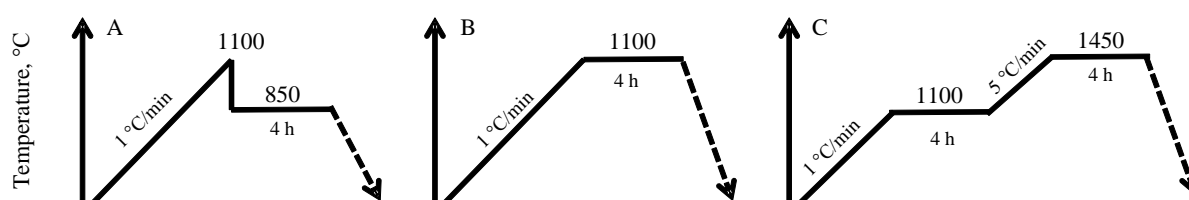


and other characteristics can be controlled by changing thermal treatment conditions [15-17]. Changes in microstructure affect the physical and mechanical properties of ceramic materials.

## 2. Experimental

Extrusion mass consists of TiO<sub>2</sub> anatase powder 74-78 wt. % (Hombitan, Sachtleben Chemie GmbH) with the particle size 200 – 300 nm, water 20-23 wt.%, lubricant 1.6 wt.% (Produkt KP 5144) and binder 02.-1.4 wt.% (Zusoplast C 93, Zschimmer & Schwarz GmbH & Co KG) [18, 19].

Cylindrical samples (Ø 13 mm) were obtained using ceramic mass extruder *DORST V 10 SpHV*. Extruded samples were dried for 48 h at room temperature (relative air humidity ~ 50 %). Dried samples were sintered under three different sintering conditions: A) 1100→850 °C, B) 1100 °C and C) 1100→1450 °C (figure 1.). To prevent crack formation in the samples, the temperature was raised slowly.



**Figure 1.** Thermal treatment conditions in air.

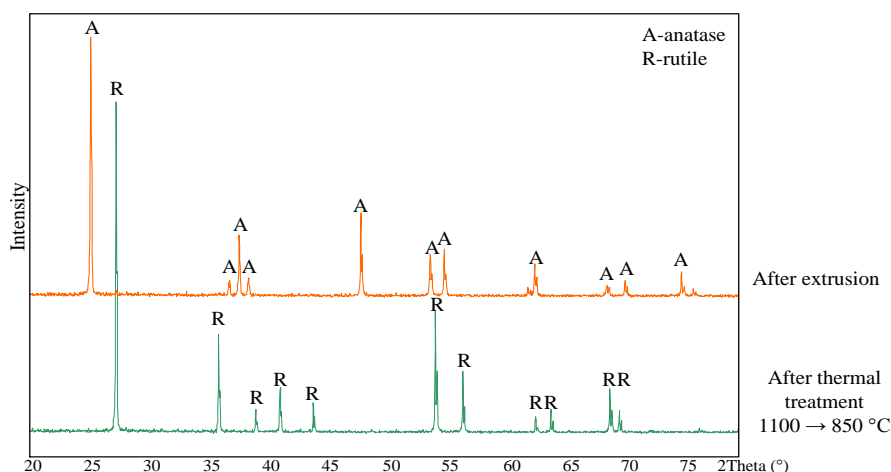
Crystalline phases in the samples were identified using X-ray diffraction (XRD) (PANalytical X'Pert Pro). Cu K $\alpha$  filtered radiation in 2 $\theta$  range from 20° to 80° was used.

Relative density was calculated using geometric dimension and weight of the dried samples and indicated as a percentage from theoretical density of TiO<sub>2</sub> anatase (3.89 g/cm<sup>3</sup>) or rutile (4.23 g/cm<sup>3</sup>). Density and porosity of samples after thermal treatment was determined using Archimedes method [20].

Microstructure of the sample fracture surface was investigated using field emission scanning electron microscopy (FE-SEM, Tescan Mira/LMU).

## 3. Results and Discussion

Crystalline phases identified in XRD patterns of the samples are shown in figure 2. After sintering in the air atmosphere, only TiO<sub>2</sub> rutile crystalline phase have been found.



**Figure 2.** XRD patterns of samples after extrusion and thermal treatment in air.

After extrusion samples were sufficiently mechanically tough for handling without observable cracks and deformations.

Relative density of the obtained green body was on average 53 % of TD. The relative density values of thermally treated samples are summarized in table 1.

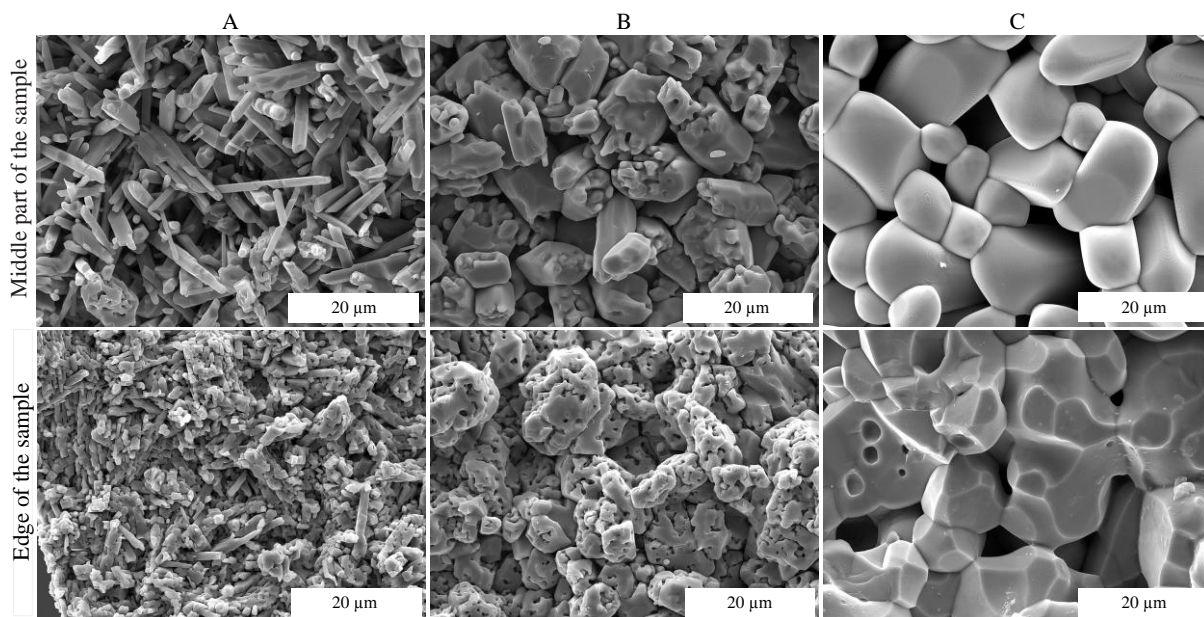
Relative density of samples after sintering in conditions A is about 2 % higher than after sintering in conditions B, but about 8 % lower than after sintering in conditions C. The values of sample relative density correlate with values of total porosity. It was observed that after sintering in conditions C, the open porosity did not decrease significantly compared to ceramics sintered in conditions A and B. It was observed that with increase of sintering temperature closed porosity decreases.

**Table 1.** Relative density and porosity of TiO<sub>2</sub> samples after extrusion and thermal treatment.

Sintering condition	Relative density of TD, %	Porosity, %	
		Total	Open
<b>A) 1100→850 °C</b>	77.2	22.8	10.2
<b>B) 1100 °C</b>	75.4	24.6	12.4
<b>C) 1100→1450 °C</b>	85.6	14.4	10.3

After thermal treatment there are differences between microstructure in middle and edge part of all samples (figure 3). Microstructure of samples after sintering in conditions A is composed of needle-shaped grains, especially in the middle part of the sample. Sintering in conditions B leads to the formation of irregularly shaped grains in all parts of sample. Additionally formation of bimodal porosity in edge part is observed. After sintering in conditions C, larger grains are formed in the middle part of the sample. Increase of treatment temperature induces structure densification and grain growth.

It was also observed that the edge of all samples was 2-3 % denser than the middle. It is supposed that such microstructural differences occurred due to the pressure differences across the sample cross section during the extrusion.



**Figure 3.** SEM micrographs of sample fracture surfaces after sintering in air atmosphere.

#### 4. Conclusions

Not only density and porosity of material, but also the grain size and shape can be controlled by changing thermal treatment conditions. Two step sintering at 1100 – 850 °C leads to the formation of denser microstructure compared to single step sintering at 1100 °C. Microstructural and density differences in the middle and edge part of the samples occur during the sintering in air atmosphere.

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#### References

- [1] Benbow J J, Blackburn S and Mills H 1998 *J Mater Sci* **33** 5827–5833
- [2] Nath Dasa R, Madhusoodana C D, Okada K 2002 *J. Eur. Ceram. Soc.* **22** 2893–2900
- [3] Chevalier L, Hammond E and Poitou A 1997 *J. Mater. Process. Technol.* **72** 243–248
- [4] Engländer A, Burbidge A and Blackburn S 2000 *Chem. Eng. Res. Des.* **78** 790–794
- [5] Xiao-Ming G, Yong-Jie Y, Jian C, Zheng-Ren H and Xue-Jian L 2009 *Journal of Inorganic Material* **24** No.6
- [6] Habelitz S, Gunter Carl G and Russel C 2001 *Mater. Sci. Eng., A* **3** 1–14
- [7] Kaya C and Butler E G 2002 *J. Eur. Ceram. Soc.* **22** 1917–1926
- [8] Blackburn S D and Wilson D I 2008 *J. Eur. Ceram. Soc.* **28** 1341–1351
- [9] Reimanis M, Ozolins J, Malers J, Locs J, Juhna T 2011 *IPCBE Proceedings of 2nd Int. Conf. on Environmental Engineering and Applications* vol 17 (IACSIT Press, Singapore) 264-270
- [10] Chen X, Gao F and Chen G 2005 *J. Appl. Electrochem.* **35** 185–191
- [11] Evans J R G 2008 *J. Eur. Ceram. Soc.* **28** 1421–1432
- [12] Rahaman M N 2003 *Ceramic processing and sintering. Second edition* (New York: Marcel Dekker) 875 pp
- [13] Handle F 2007 *Extrusion in Ceramics* (Berlin: Springer) 413 pp
- [14] Pavlova A, Berzina-Cimdina L, Locs J, Loca D, Bossert J 2008 *Advances in Science and Technology* **54** 261-264.
- [15] Song S H, Wang X and Xiao P 2002 *Mater. Sci. Eng. B* **94** 40-47,
- [16] Meng F 2005 *Mater. Sci. Eng. B* **117** 77-80
- [17] Rubenis K, Kundzins K, Locs J and Ozolins J 2013 *Key Eng. Mater.* **527** 154-158
- [18] Pura A, Rubenis K, Stepanovs D and Berzina-Cimdina L 2012 *Processing and Application of Ceramics* **6** 91-95
- [19] Pavlova A, Reinis A, Berzina-Cimdina L and Kroica J 2011 *Advanced Materials Research* **222** 301-304
- [20] Kwan Y B P, Alcock J R 2002 *Journal of Materials Science* **37** 2557 – 2561