The Comprehensive Study of the Thermal Etching Conditions for Partially and Fully Dense Ceramic Samples

Tomáš Spusta¹,²*, Marek Jemelka¹,², Karel Maca¹,²
¹CEITEC BUT, Brno University of Technology, Purkyňova 123, 612 00, Brno, Czech Republic
²Faculty of Mechanical Engineering, Brno University of Technology, 616 69, Brno, Czech Republic

Abstract:
An alternative approach to the thermal etching of oxide ceramic materials (α-alumina, t-zirconia, and c-zirconia) is presented and compared with the standardly used regime for thermal etching. The given approach was tested on partially (93.8 - 96.3 % t.d.) and fully (99 – 100 % t.d.) dense samples with the criterion of minimizing the density difference after and before etching and with the criterion of clear visibility of grain boundaries. The presented results show, that 900 °C/1 h etching regime is sufficient to reveal the studied microstructure for analysis of the surface of the samples sintered above 1355 °C without affecting the density and without thermal effect on the measured average grain size. The modern approaches as digital analysis of the images can help to reveal the thin grain boundaries after thermal etching at low temperatures.

Keywords: Thermal etching; Oxide materials; Alternative approach; Low temperature.

1. Introduction

A detailed investigation of a polished specimen’s microstructure by a scanning electron microscopy (SEM) usually requires the sufficient revelation and delineation of structures on the surface (e.g. grain boundaries, pores, secondary phases, etc.). As the standard procedure after polishing for the purpose of increasing recognition between singular phases and microstructural entities, etching is used. In general, the etching usually implies some sort of selective chemical interaction between phases for the revelation of the microstructure (e.g. for metals). In the case of the advanced ceramics, which are highly chemically inert, etching includes several noncorrosive techniques such as a thermal, plasma or ion etching [1].

The easiest and widely used etching technique for ceramic materials is the thermal etching consisting of heating the polished sample at a temperature lower than the sintering temperature. There are several publications presenting recommended conditions for various dense materials. The general recommendation is that the thermal etching should be performed at 50-200 °C below the sintering temperature for a certain amount of time [1-7]. In addition, there are recommendations which advice to utilize absolute etching temperatures – for an example the thermal etching of alumina: 1500 °C for 20-30 min [1], 1100-1300 °C for 120 min [1], 1300-1400 °C for 15-20 min [6], 1500 °C for 120 min [7]. Such etching regimes
have to be used with caution and should not be used without considering the used powder, sintering regime, sintering temperature, density of sample, etc.

In the case of the thermal etching, several risks of affecting the observed microstructure are possible. The first one is obviously altering the microstructure by additional annealing at excessive etching temperature. Therefore the microstructure will coarse (coarsening will be more effective in samples with fine/nano-sized grains), which means that the average grain size can increase during thermal etching and the analysis will not be accurate. Another issue of excessive etching temperature arises in the case of specimens with a considerable amount of porosity, where additional densification can occur.

The microstructure analysis is often used as a tool to predict and control the properties connected with grain size. For example hardness [8], fracture toughness [9], optical properties [10] are directly influenced by grain size, which tends to be kept at the lowest possible level. Moreover, ceramics materials for specialized applications required a certain amount of porosity [11-14] – presenting for hot isostatic pressing [15], membranes and filters [16, 17], bone replacements [18], etc. are often examined at a microstructure level to be sure about their expected properties.

The main goal of this paper is to present an alternative approach to thermal etching based on low etching temperature and a relatively long time. The second goal is to compare this approach to the widely used method of etching 50-200 °C below the sintering temperature for a short time. Those two approaches are tested on partially dense (92-96 % t.d.) and fully densified samples (99-100 % t.d.) of the selected oxide ceramic materials.

2. Materials and Experimental Procedures

2.1. Materials

Three types of commercially available oxide ceramic powders were used (Tab. I).

| Material | Powder type | Producer | Particle size [nm] | t.d.* [g/cm³] |
|----------|-------------|----------|--------------------|---------------|
| Al₂O₃    | TM DAR      | Taimei Chemicals | 100                | 3.99 [19,20]  |
| ZrO₂     | TZ3Y        | Tosoh    | 80                 | 6.08 [21,22]  |
| ZrO₂     | TZ8YSB      | Tosoh    | 140                | 5.99 [23,24]  |

*t.d. means the theoretical density of the material.

2.2. Green Body Preparation, Sintering, Polishing

Green bodies were prepared by initial uniaxial pressing (BROIO Hranice Ltd., Czech Republic) at 20 MPa in 30 mm diameter steel die and subsequently cold isostatically pressed (Autoclave Eng., USA) at 300 MPa. After the pressing, the green bodies were annealed at 800 °C/1h and then cut into smaller samples (ca. 3 x 3 x 6 mm).

The pressure-less sintering was performed in air superkanthal furnace (CLASIC CZ Ltd., Czech Republic) by regimes summarized in Tab. II. Fully dense samples were sintered with the heating rate of 10 °C/min up to 800 °C followed by 5 °C/min up to the sintering temperature and cooling rate of 25 °C/min with intention to reach maximum density (99 + % t.d.). Partially dense materials were sintered with the heating rate 10 °C/min up to the sintering temperature and cooling rate 25 °C/min with intention to reach maximum density (99 + % t.d.).
temperature and cooling rate 25 °C/min with intention to sinter the samples to close porosity stage (92-96 % t. d. according to material).

The density of sintered samples, as well as the ratio of open and closed porosity, were measured by Archimedes method [25] in distilled water. Three measurements of each sample were performed to obtain the relevant standard error of the density measurements.

The surface of sintered samples was ground and polished down to 1 µm using TegraPol-25 (Struers Inc., USA).

2.3. Etching and Microstructure Observation

The thermal etching of samples was performed in the superkanthal furnace (CLASIC CZ Ltd., Czech Republic). The microstructure of samples was studied using scanning electron microscopy (TESCAN LYRA3/ HRSEM VERIOS FEI). The average grain size (AGS) was estimated by linear intersection method [7].

In this paper two different approaches for the determination the desired etching temperature of selected materials were studied. The first one (long method – marked with blue squares in Figure 1-6) is focused on idea to find the lowest absolute temperature when the etching is still active with the dwell time of 1 hour. The first temperature was set to 1100 °C for all studied materials as a starting point with an idea to progressively decrease the temperature as low as possible until the observed microstructure will not meet the conditions mentioned below.

The second approach (short method – marked with red circles in Figure 1-6) is based on the standard idea of etching temperature relative to the sintering one. This approach starts at temperature 50 °C below sintering temperature (T_s) for partially sintered and at 100 °C below T_s for fully sintered and they were gradually decreasing down to T_s-350, i.e. that etching temperature was 350 °C below T_s.

We applied the following criteria for the determination of the etching parameters optimization:
- The difference between relative density before and after etching has to be minimized. This criterion is mainly applied for the partially sintered samples, where the thermal etching has the highest probability to influence the studied microstructure.
- Grain boundaries have to be clearly visible and match criterions stated in EN ISO 13383-1 [7]. For this particular study it means that minimum of 300 interceptions (total) were counted on 5 images and for one image there were 5 drawn lines.

3. Results
3.1. Densities of Used Samples

Tab. II summarizes sintering temperatures and relative densities for partially sintered and for fully dense samples before etching.

| Powder type | Sintering temperatures | Density |
|-------------|------------------------|---------|
|             | Partially dense [°C/min] | Fully dense [°C/min] | Partially dense [% t.d.] | Fully dense [% t.d.] |
| TM DAR      | 1365/1               | 1520/30  | 96.3  | 0.3       | 99.6  | 0.1       |
| TZ3Y        | 1355/1               | 1475/30  | 94.9  | 0.5       | 100.0 | 0.1       |
| TZ8YSB      | 1455/1               | 1560/30  | 93.8  | 0.4       | 99.0  | 0.2       |

*ρ is relative density, s is standard deviation from 21 measurements (7 samples)
3.2. Partially Dense Samples

In the case of the partially dense samples it can be seen that with etching temperature chosen unwisely high (50 - 100 °C below the sintering temperature) the density change before and after etching is significant as can be seen in Figure 1-3. In case of grain size, the expected results were obtained - with decreasing the etching temperature the measured average grain size also decreases.

**Fig. 1.** Dependence of relative density change (after and before etching) and grain size of the partially dense alumina (TM DAR) on etching temperature and time.

**Fig. 2.** Dependence of relative density change (after and before etching) and grain size of the partially dense tetragonal zirconia (TZ3Y) on etching temperature.

**Fig. 3.** Dependence of relative density change (after and before etching) and grain size of the partially dense cubic zirconia (TZ8YSB) on etching temperature.
3.3. Fully Dense Samples

In the case of the fully dense samples (Figure 4-6) it can be seen that the temperature chosen for thermal etching had only a little effect on final grain size after etching in the case of “short” approach. On the other hand, in case of “long” approach, the temperature has significant effect on the final grain size. The effect of thermal etching conditions on the samples’ relative densities was negligible.

Fig. 4. Dependence of grain size of fully dense alumina (TM DAR) on etching temperature.

Fig. 5. Dependence of grain size of fully dense tetragonal zirconia (TZ3Y) on etching temperature.

Fig. 6. Dependence of grain size of fully dense cubic zirconia (TZ8YSB) on etching temperature.
4. Discussion

4.1. Using the Digital Images Instead of Printed Ones

The standard for linear intercept method analysis of ceramics [7] is designed with the intention to print micrographs on the paper, calibrate the image, draw the interception lines and count the interceptions between lines and visible grain boundaries. However, in the era of digital technology there are several valuable advantages of the linear intercept method analysis in digital space. The first one is possibility of automatic calibration of the image. The second is possibility of utilization of the full resolution of the acquired SEM image – digital zooming. The third one is that some programs are capable to automatize the whole analysis.

In this study we wanted to keep the analysis on semi-automatic level because of the ability to have maximal control of the analysis outputs, visibility of grain boundaries, etc. Therefore we only accompanied the automatic calibration of the images and digital zooming for the manual counting of the intersections, which was done in free graphic software Inkscape [26]. The automatic calibration of the images comes really useful time saving process when dealing with large batches of images and the ability to zoom the image is crucial for the analysis of the samples which were etched at low temperatures. As it was mentioned before, the low temperature etching is capable to reveal the grain boundary network, but the width of the grain boundary is relatively thin and in the case of samples with large grains, the ability of zoom in and see grain boundaries clearly is essential.

4.2. The Choice of Optimal Etching Approach for Partially and Fully dense samples

The analysis of the partially dense (93.8 - 96.3 % t.d.) samples provides quite similar observations. All studied materials were successfully etched at 900 °C/1 h and in the most cases (except the TM DAR) it is the best etching option in terms of previously mentioned conditions of this study. There is not density change present and the measured average grain size is the lowest. However, the main issue with such a low temperature is that the “healing effect” (removing light scratches and indentations from polishing during etching) is limited and the mentioned artefacts are visible on micrographs (see e.g. Figure 4A, Figure 5A), but they do not interfere with intersections counting.

In the second approach, which uses etching temperature relative to sintering one (T_s-x) for 5 minutes, the temperature T_s-50 evidently over-etched the samples, creating pillow-like grains with significant increase in density measured after etching. Even at T_s-150, there is a visible increase in the density after etching in TM DAR and TZ3Y samples (Figure 1-2). Therefore, the ideal etching temperature in case of the “short” approach would be below T_s-150. Similarly, thermal etching conditions of 1100 °C/1 h in “long” approach is already showing increase in the density after etching.

The analysis of fully dense (99 - 100 % t.d.) samples also confirms, that etching regime 900 °C/1 h is capable to clearly reveal microstructure of analyzed samples, although the digital zooming had to be used as it was mentioned before. The zooming comes extremely useful in the case of observation sample with large grains (e.g. Figure 6). The magnification required to capture enough grains in the micrograph was relatively low (large view field) and with combination of the thin width of grain boundary it would make analysis almost impossible from printed micrographs. The “short” approach provides expected results – the microstructure was clearly visible for the analysis even after etching at T_s-350.
4. Conclusion

Two possibilities of the thermal etching of three kinds of fine-grained advanced ceramic materials (α-alumina, t-zirconia and c-zirconia) were presented in this article. The “short” approach is viewed as the conventional one and it is widely used. However, when the microstructure analysis of various different materials with incomparable sintering temperatures is required, this standard approach struggles. The main disadvantage is the necessity to utilize several etching cycles with temperatures corresponding to different sintering regimes, which could be time/equipment consuming. In this article we present alternative approach with the main positive aspect of fixed etching regime for all studied materials. According to the presented results the etching procedure 900 °C/1 h is sufficient for revealing the microstructure of studied oxide ceramic materials sintered above 1355 °C. This approach provides the possibility to etch various ceramic samples in one furnace without the risk of thermally altering the studied microstructure at low temperature during one etching cycle. In addition, it was also demonstrated that digital zooming can significantly improve the recognition of thin grain boundaries revealed at so low etching temperatures.

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