New materials through a variety of sintering methods

L. Jaworska¹, J. Cyboroń¹, S. Cygan¹, J. Laszkiewicz-Łukasik¹, M. Podsiadło¹, P. Novak² and Y. Holovenko³

¹ The Institute of Advanced Manufacturing Technology, Wroclawska 37A, 30-011 Krakow, Poland;
² Department of Metals and Corrosion Engineering, University of Chemistry and Technology Prague, Technická 5, 16628 Prague, Czech Republic;
³ Department of Mechanical Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia.

E-mail: lucyna.jaworska@ios.krakow.pl

Abstract: New sintering techniques make it possible to obtain materials with special properties that are impossible to obtain by conventional sintering techniques. This issue is especially important for ceramic materials for application under extreme conditions. Following the tendency to limit critical materials in manufacturing processes, the use of W, Si, B, Co, Cr should be limited, also. One of the cheapest and widely available materials is aluminum oxide, which shows differences in phase composition, grain size, hardness, strain and fracture toughness of the same type of powder, sintered via various methods. In this paper the alumina was sintered using the conventional free sintering process, microwave sintering, Spark Plasma Sintering (SPS), high pressure-high temperature method (HP-HT) and High Pressure Spark Plasma Sintering (HP SPS). Phase composition analysis, by X-ray diffraction of the alumina materials sintered using various methods, was carried out. For the conventional sintering method, compacts are composed of $\alpha$-Al$_2$O$_3$ and $\theta$-Al$_2$O$_3$. For compacts sintered using SPS, microwave and HP-HT methods, $\chi$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ phases were additionally present. Mechanical and physical properties of the obtained materials were compared between the methods of sintering. On the basis of images from scanning electron microscope quantitative analysis was performed to determine the degree of grain growth of alumina after sintering.

Keywords: Sintering, SPS, HP SPS, alumina, phases composition, size of grains.

1. Introduction

Research regarding ceramic materials are mainly focused on improving fracture toughness $K_{IC}$, by limiting grain size in compacts, improving properties at high temperatures, improving resistance to thermal shock. One of the main goals of modern ceramic technologies is still the manufacture of dense ceramic parts with submicrometric or nanostructured grains. The most important factors which have influence on ceramics properties are:

• powders – their method of obtaining and characteristics (particle size, shape and structure),
• green bodies forming – compression ratio, dimensional changes during compaction,
sintering – temperature, time and the furnace atmosphere.

There are a lot of material synthesis methods which are helpful in developing new kinds of materials and in powders compaction. The main problem of this, is difficulty with nanopowders compaction, because of large surface area of these powders and huge amount of gases absorbed on the powders surface. There are known techniques of the green bodies ceramic forming, such as: cold pressing, uniaxial pressing, cold isostatic pressing, aqueous injection moulding, direct coagulation casting, electrophoretic forming, gelcasting, hydrolysis assisted solidification, pressure filtration, explosive compaction, lithography [1,2]. The last step for ceramic materials preparation is the sintering process. Sintering of ceramic or metallic powders is a phenomenon that occurs spontaneously at elevated temperatures (below melting point), as a result of the system's desire to lower its surface energy, which decreases as the grains are joined [3]. The goal of the sintering process is to convert highly porous compacted powder into high strength bodies. The process is often accompanied by shrinkage.

The processing of materials is another key parameter that will have implications on the final properties of the ceramic material. Many researchers have observed that the mechanical strength and fracture toughness of ceramics can be improved by the use of different sintering techniques [2]. Variety of sintering methods are available for sintering the ceramic compacts i.e., conventional (free) sintering, reaction-sintering, hot pressing (HP), post-reaction sintering, recrystallization sintering, ultra-high-pressure sintering and isostatic hot pressing (HIP). Generally, the pressure value has strong influence on the sintering. Fig. 1 presents various methods of sintering depending on the type of furnace.

![Fig. 1. Different type of furnace using in sintering ceramic composites.](image)

The different physical phenomena used in sintering technologies change thermodynamic conditions of the process, which may affect the crystalline form of the sintered phase and thereby change the properties of the sintered material.
The most characteristic methods of sintering because of physical phenomena are microwave, SPS, HP-HT and SLS methods.

Microwave method has been known since the 1950s [4]. More recent developments in ceramic composites resulted in a new set of challenges for the theory of sintering, particularly when different parts of a structure densify at different rates and temperatures [4]. Many ceramic materials that are difficult to heat at room temperature, possess electrical conductivity or dielectric loss factors that rapidly increase in magnitude as the temperature rises. Thus, these materials will absorb microwave energy if they can be preheated to a suitable temperature using another heat source [4,5]. Microwave sintering process depends on:

- microwave absorption characteristics (dielectric loss factor - low-loss, electrical conductivity),
- size and shape of green bodies,
- sintered materials distribution in the furnace.

Ceramic materials will absorb microwave energy when they can be preheated to suitable temperature using another heat source for example gas or electric furnace or external susceptor material (as SiC) [6]. This kind microwave hybrid heating (MHH) could result in samples with no significant density gradient throughout the cross-section [5].

In the SPS process, a pulsed DC is applied repeatedly from the beginning to the end of the sintering cycle [7]. In the presence of pressure and electric current, localized necking occurs faster, which speeds the sintering process due to joule heating. The temperature rises very fast and the densification is completed within few minutes. The grain boundary area for this method of sintering shows direct grain-to-grain contact, which is attributed to the physical activation of powder particle surface during pulsed current application what has influence on enhanced grain boundary diffusion process [8–10]. Three mechanisms may contribute to Spark Plasma Sintering:

- activation of powder particles by pulsed current,
- resistance sintering,
- pressure application [8].

Benefits for the SPS sintering are: reduced sintering duration, good grain to grain bonding, clean grain boundaries, lower temperature of sintering and possibility of sintering materials with significant difference of melting point.

In high pressure high temperature (HP-HT) sintering, special apparatuses is used. The pressure depends on the anvils construction and on the size of the samples. Pressure during the sintering process depends on the apparatus being used. For piston units, it is possible to receive pressure up to 4 GPa, for the Belt type anvils 6-10 GPa, for the Bridgman, the Toroid and the Paris-Edinburg type anvils up to 20GPa. In the multianvils chamber it is possible to generate the pressure in the range 30-100 GPa. Sintered materials should be placed in special gaskets. Limitation for this method is the size of the sintered samples and the high cost of the apparatus assembly parts.

Research concerning the influence of pulsed current employed for heating during high pressure sintering yields very interesting results. For example the results shown in [11] indicate that for HP SPS (High Pressure Spark Plasma Sintering) in comparison to HP-HT technique are characterized lesser amount of phases within the material after sintering. Additionally for HP SPS during the sintering of diamond with Ti and B it was shown that the kinetics of the process results in lower graphite formation, which is very beneficial for this type of materials.
Direct Selective Laser Sintering still does not guarantee high density of most of sintered ceramics powders. The main consolidation mechanism of this process seemed to be partial melting. However, since several mechanisms (partial melting, full melting and solid-state sintering) might act together, it is sometimes not clear which consolidation/binding mechanism is active. The relative density of the alumina compacts prepared using this method was about 85% [11].

Advanced ceramics based on Al₂O₃ exhibit excellent properties such as high thermal resistance, good chemical stability and moderate to high mechanical strength. However, the fracture toughness of the materials is low. The brittleness and poor damage tolerance have so far limited the application of these composites. In relation with that, many authors studied the influenced of additives such as: TiB₂, cBN, Mo or graphene on main properties of the composites [12–15].

The aim of presented work was to investigate the influence of various sintering techniques on microstructure and selected properties of alumina compacts. The alumina was sintered using the conventional free sintering process, microwave sintering, SPS, High Pressure-High Temperature method (HP-HT) and High Pressure Spark Plasma Sintering (HP SPS).

2. Materials and methods

Al₂O₃ (ALCOA, CT300-SG), with an average particle size of 0.7 µm, and 0.3 % MgO (FLUKA), with a particle size in the range of 0.5–1 µm, powders were used. Mixture of powders was prepared in colloidal ball mill through 30 hours with presence of isopropyl alcohol.

For free-sintering and microwave sintering samples were formed by uniaxial pressing in the steel matrix at pressure of 130 MPa and next in the hydraulic press at pressure of 250 MPa. Green bodies were free sintered during 60 min in the HT 16/18 Nabertherm electric furnace. For microwave sintering 2.45 GHz in MKH-4.8 Linn High Therm GmbH microwave furnace was applied. Four magnetrons were used which were operating at 50-60% of their full power. The sintered sample was placed in the chamber which were made of porous alumina, and additionally surrounded by SiC susceptors to improve heating.

SPS sintering of starting powder mixtures of alumina powder, without the addition of a temporary binding agent, were placed in a graphite matrix with a diameter 25 mm and pressed at 35 MPa in vacuum. SPS sintering processes were conducted in protective, argon atmosphere during 15 min. Additionally second batch of samples was sintered using SPS method, where the only difference was that, the samples were insulated from the graphite using hBN layer.

HP-HT and HP SPS processes were realized at 4 GPa during 60s, where for HP SPS direct pulsed current was used with 40 ms impulse lenght and 20 ms impulse interval. Difference between duration of alumina sintering processes are presented in Fig.2.
Fig. 2. Comparison of heating, sintering, cooling durations for different type of sintering.

The microstructure investigations were performed using a Jeol JSM-6460LV scanning electron microscope. Density was measured using the hydrostatic method. The hardness was determined by the Vickers method under the load of 9.81N, using a Future Tech FLC-50VX Vickers hardness tester. For each sample, 5 indentations were realized. Young's modulus of the composites was measured with using a Panametrics Epoch III ultrasonic flaw detector; the measurements were based on the transition velocity of the ultrasonic waves through the sample. The velocities of transversal and longitudinal waves were determined as the ratio of the sample thickness and the relevant transition time. Considering that the error in the thickness measurements was ±0.01 mm and in the time-of-flight measurements (±1 ns), the resulting error in the ultrasonic velocity was about 1%. Consequently, the error of Young's modulus could be estimated to be 2%. The X-ray diffraction patterns were obtained by using a PANalitical Empyrean diffractometer with copper radiation (λCu Kα = 1.5406 Å). The phase analysis was conducted using ICDD (PDF-4+ 2016) files.

The grains size were calculated using the intercept method. According to this method, the average length of grains in the pictures scale of the microstructure was converted to the real given in the μm [16].

3. Results and discussion

Each of sintering method was optimized within the temperature range from 1500°C up to 1650 °C to obtain material with possibly highest values of density and Young’s modulus. Table 1 shows the optimized sintering temperatures for microwave, free, SPS, HP-HT and HP SPS sintering processes.
Table 1. Optimized sintering temperature for each of method

| Sintering method                  | Optimized sintering temperature [°C] |
|-----------------------------------|--------------------------------------|
| Free sintering                   | 1620                                 |
| Microwave sintering               | 1620                                 |
| SPS and SPS with hBN insulation   | 1550                                 |
| HP-HT and HP-SPS                  | 1600                                 |

The alumina has got many polymorphic varieties. Some of their crystalline structures and physical properties are presented in the Table 2.

Table 2. Main crystallographic structures of Al₂O₃ [17]

| Type of Al₂O₃ | Crystal system | Unit cell parameters | Density [g/cm³] | Temperature of melting point [°C] |
|---------------|----------------|----------------------|-----------------|----------------------------------|
| α-Al₂O₃       | Rhombohedral   | a 0.476  b 0.476  c 1.299 | 3.99           |                                  |
| γ-Al₂O₃       | Cubic          | a 0.794  b 0.794  c 0.794 | 3.47           |                                  |
| δ-Al₂O₃       | Tetragonal     | a 0.796  b 0.796  c 1.170 | 3.20           | 2072                            |
| θ-Al₂O₃       | Monoclinic     | a 1.174  b 0.572  c 1.124 | 3.56           |                                  |
| χ-Al₂O₃       | Hexagonal      | a 0.563  b 0.563  c 2.260 | 3.35           |                                  |

The comparison of the alumina phase composition for different sintering method are presented in Fig.3. The diffractogram for the free sintering and SPS sintering with hBN insulation were similar as HP SPS. They are not included in the Fig. 3. Evaluation of the quantitative phase composition of these materials are difficult. Based on the height and width of the peaks coming from θ and χ- Al₂O₃ phase, it can be stated that their total content in the material is about 1.5 - 2% wt. Quantity of the others phases (γ- Al₂O₃ and Al₂O₃- Ref. Nr.-00-012-0539) are at the trace level.
Fig. 3. Phase composition of alumina compacts obtained after different method of sintering.

The comparison of the phase composition for alumina compacts after sintering by various method is presented in the Table 3.

Table 3. Phase composition of alumina compacts obtained after different method of sintering

| Sintering method              | α-Al₂O₃ R-3m | θ-Al₂O₃ C2m | γ-Al₂O₃ P63/mmc | γ-Al₂O₃ Fd-3m | Al₂O₃ 00-012-0539 |
|------------------------------|--------------|-------------|-----------------|--------------|------------------|
| Initial powder               | ✔            |             |                 |              |                  |
| Free sintering               | ✔            | ✔           |                 |              |                  |
| Microwave sintering          | ✔            | ✔           | ✔               |              |                  |
| SPS                          | ✔            | ✔           | ✔               | ✔            |                  |
| SPS with hBN insulation      | ✔            | ✔           |                 |              |                  |
| HPHT                         | ✔            | ✔           | ✔               | ✔            |                  |
| HP SPS                       | ✔            | ✔           |                 |              |                  |

Materials after sintering, polishing and etching were subjected to observation under a scanning electron microscope at a magnification 5000x. Microstructures are presented in Fig.4a - Fig.4d. The microstructures and properties of alumina compacts obtained by using High Pressure–High Temperature method were not presented because cracks in the materials. The pressure in the samples during sintering is higher than compressive strength of alumina, so in the compacts severe cracks were present.
The use of non-conventional sintering methods, such as Spark Plasma Sintering and microwave sintering, contributes to obtaining a well-densified material with good physical-mechanical properties at relatively short sintering times. Applied sintering methods allow to receive practically non-porous microstructures of obtained samples with mainly isometric grains of Al$_2$O$_3$ (Fig. 4a-d). The size of grains were calculated using the intercept method. In the Table 4 the size of grains for each methods are presented.

### Table 4. Grain size of alumina compacts obtained after different method of sintering

| Sintering method                  | Mean grain size, d [µm] |
|-----------------------------------|-------------------------|
| Free sintering                    | 2.57±0.12               |
| Microwave sintering               | 2.86±0.14               |
| SPS                               | 1.41±0.07               |
| SPS with hBN insulation           | 1.23±0.05               |

Microwave and free sintering methods did not prevent grains growth of Al$_2$O$_3$. Mean grain size of Al$_2$O$_3$ is (~2.86 µm) for microwave sintering and (~2.57 µm) for free sintering. The finest grain of alumina was obtained for the SPS sintering.

The results of density, elastic modulus hardness and $K_{IC}$ obtained for all alumina materials are summarized in Table 5.
Table 5. Selected physical and mechanical properties of alumina compacts obtained by various method of sintering

| Sintering method          | Density [g/cm³] | Young’s modulus [GPa] | Hardness HV1 | K IC [MPa*m¹/²] |
|---------------------------|-----------------|------------------------|--------------|-----------------|
| Free sintering            | 3.91 ± 0.01     | 383 ± 3                | 1868 ± 25    | 5.29 ± 0.31     |
| Microwave sintering       | 3.87 ±0.01      | 387 ± 6                | 1600 ± 106   | 5.32 ± 0.42     |
| SPS                       | 3.95 ± 0.01     | 389 ± 4                | 1806 ± 34    | 6.80 ± 0.32     |
| SPS with hBN insulation   | 3.95 ± 0.01     | 390 ± 5                | 1803 ± 37    | 7.17 ± 0.36     |

The density increases from 3.87 g/cm³ up to 3.95 g/cm³ for materials obtained after microwave and SPS sintering, respectively. It is increasing with alumina χ-Al₂O₃ content in the material is fallen. This is related to the theoretical density of χ-Al₂O₃ which is the smallest for each of forms of alumina. In the course of these studies, no significant differences were found in hardness values for Al₂O₃ materials after various methods of sintering, apart from the results for material sintered by microwave method. The smallest hardness for this material could be connected with additional form of alumina (χ-Al₂O₃). In the remaining materials, if there is χ-Al₂O₃ present, its properties are compensated by other forms which are characterized by higher density and different crystalline structure.

4. Conclusion

- The phase composition of the alumina compacts after SPS sintering, SPS with hBN insulation and HP SPS is similar, composed of α-Al₂O₃ and θ-Al₂O₃, for HP-HT, SPS (without insulation) and microwave sintering the χ-Al₂O₃ appears in the material.
- The χ-Al₂O₃ participation has influence on density and hardness of compacts.
- High pressure methods above 4 GPa generated severe cracks in the material.
- Materials obtained using the SPS methods are characterized by better compaction and higher mechanical properties, size of grains is lower than for materials obtained using microwave and free sintering methods.

Acknowledgments

This research was supported by COST Action CA15102 – “Solutions for Critical Raw Materials Under Extreme Conditions” (CRM-EXTREME) and by the statutory activity grant to the Institute of Advanced Manufacturing Technology, Cracow, Poland (DS-17.3.2).

References:

[1] Sigmund W M, Bell N S and Bergström L 2004 Novel Powder-Processing Methods for Advanced Ceramics Journal of the American Ceramic Society 83 1557–74
[2] Deckers J, Vleugels J and Kruth J P 2014 Additive manufacturing of ceramics: A review Journal of Ceramic Science and Technology 5 245–60
[3] A.Lakshmanan E by 2012 Sintering of Ceramics - New Emerging Techniques
[4] Von Hippel A R 1954 Dielectric Materials and Applications
[5] Menezes R R, Souto P M and Kiminami R H G A 2012 Microwave Fast sintering of ceramic materials Sintering of ceramics - New Emerging Techniques (InTech)
[6] Krage M 1981 Microwave sintering of ferrites American Ceramic Society Bulletin, 60 1232–4
[7] Suárez., Fernández J, L. Menéndez R, Torrecillas H, U. Kessel J, Hennicke R and Kessel K and T 2013 Challenges and Opportunities for Spark Plasma Sintering: A Key Technology for a New Generation of Materials Sintering Applications (InTech)
[8] Munir Z A, Anselmi-Tamburini U and Ohyanagi M 2006 The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method Journal of Materials Science 41 763–77
[9] Tokita M 2013 Spark Plasma Sintering (SPS) Method, Systems, and Applications Handbook of Advanced Ceramics: Materials, Applications, Processing, and Properties: Second Edition 1149–77
[10] Kessel H U 2009 Sintered Materials on the Way to Production by Means of Modern SPS Technologies Ceramic Forum International Berichte Der Deutschen Keramischen Gesellschaft 10 145–52
[11] Deckers J, Meyers M, Wijremblewski B, Vleugels J and Kruth J P 2014 Direct selective laser sintering/melting of fine grained alumina with a novel experimental setup Mater. Sci. Tech.: Special issue on 3D printing
[12] Putyra P, Jaworska L, Podsiadło M, Laszkiewicz-Łukasik J and Krzywda T 2016 The ceramic materials to forming by EDM method ISNNM-2016 The 14th International Symposium on Novel and Nano Materials
[13] Klimczyk P, Cura M E, Vlaicu A M, Mercioniu I, Wyzga P, Jaworska L and Hannula S P 2015 Al₂O₃-cBN composites sintered by SPS and HPHT methods Journal of the European Ceramic Society 36 1783–9
[14] Broniszewski K, Wozniak J, Kostecki M, Czechowski K, Jaworska L and Olszyna A 2015 Al₂O₃–Mo cutting tools for machining hardened stainless steel Wear 41 14190–6
[15] Morgiel J, Klimczyk P, Major Ł, Jaworska L, Maj Ł, Cygan T and Olszyna A 2017 TEM investigations of wear mechanism of Al₂O₃ and Si₃N₄ compacts with GLPs additions Ceramics International 43 8334–42
[16] Ryś J 1995 Stereologia materiałów (Kraków: FotoBit Design)
[17] Programme 2016 ICDD base PDF 4+2016