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Properties of alumina ceramics obtained by conventional and non-conventional methods for sintering ceramics

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Properties

ABSTRACT

Purpose: The aim of this study was to obtain ceramic alumina materials by using the conventional free sintering process, 2.45 GHz microwave sintering (MW) and spark plasma sintering (SPS). Technical and ultra-pure alumina was used to obtain specimens. The effect of temperature and time of sintering on the density, porosity, Young's modulus and Vickers hardness of Al_2O_3 ceramics was determined. Mechanical and physical properties of the obtained materials were compared between the methods of sintering.
Design/methodology/approach: Al_2O_3 ceramics materials were sintered by the conventional free-sintering process and the non-conventional methods comprise microwave sintering and spark plasma sintering. Density, porosity, elastic modulus and Vickers hardness were determined for the obtained materials from technical and ultra-pure alumina.
Findings: The use of advanced sintering processes allowed the authors to receive alumina ceramic materials with good mechanical and physical properties at the time of one minute for microwave sintering to ten minutes for spark plasma sintering. According to the theory sintering temperature increases with increasing of alumina purity, which was confirmed in the carried out works on the basis of Young's modulus values and density values.
Practical implications: Alumina ceramics made by the microwave sintering process and spark plasma sintering can be applied as the ceramics for cutting tools and also elements of the pharmaceutical equipment because microwave sintering ensures purity of the sintered materials.
Originality/value: The non-conventional methods for sintering ceramics primarily comprises (SPS) and (MW). SPS simultaneously applies pulsed electrical current and pressure directly on the sample leading to densification at relatively lower temperatures and short retention times. In the recent years, MW occurred as an advanced sintering technique in the world. Among many works on sintering alumina and alumina-composites until now there have been no reports of microwave sintering of alumina in Poland. Microwave sintering offers increased density and requires lower sintering temperature and time. Shorter sintering prevents the grain growth process, which provides better microstructure and, thanks to these, better mechanical and physical properties.
Keywords: Ultra-pure alumina; Microwave sintering; Spark plasma sintering; Free sintering; Mechanical properties

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1. Introduction

In the recent years a continuous development can be observed in technologies of production of high density sintered materials. A clear tendency in the research consist in the search of methods, which use high purity powders and require lower sintering temperatures and shorter process times [1]. The microwave technique for sintering of various ceramic materials is one of advanced methods of sintering. There are many obvious advantages of volumetric heating and efficient transfer of energy in microwave processing. In conventional sintering methods thermal radiation received on the surface of the ceramic component reaches the core by thermal conduction producing high temperature gradients and stresses. The use of microwaves allows transfer of energy directly into the materials to take place, where it is convertered into heat through absorption mechanisms, such as ionic conduction, dipole relaxation, and photon-phonon interactions. In this context of microwave heating each constituent unit of the crystal lattice raises a certain constant amplitude vibration, which results in a highly uniform distribution of heat in the ceramic body [2-6]. Many materials including, ceramics, ceramic composites, ceramic-metal composites, even pure powdered metals, have been microwave sintered on the laboratory scale. At the same time some researches worked on the fundamentals of microwave-materials interactions and modelling of microwave heating [2]. Most research on ceramic processing by microwaves to date is based on the use of conventional low-frequency 2.45 GHz (which corresponds to wavelength equal 0.122 m) microwave magnetrons. In the case of sintering, the materials with low absorption microwave radiation (high coefficient reflectance) should be heated using materials absorbing microwave radiation, i.e. susceptors. Otherwise magnetrons, which are the source of microwaves, may be damaged during the process. During heating, the interior of the sample is heated directly by the microwave. Microwave energy absorption is proportional to the surface area of the sample, and heat loss is proportional to the surface area of the sample, the temperature gradient in the sample should depend on the volume to surface ratio. Local heating generally leads to thermal stress and cracks in the ceramics. Therefore, the size of sintering ceramics by 2.45 GHz microwave was limited to several centimetres [7]. In order to improve heat transfer to the sintered sample the authors developed microwave hybrid heating (MHH) techniques, which combine direct microwave heating with infrared heat sources. The hybrid heating system will heat the sample more readily at low temperatures and, at high temperatures, will flatten the temperature profile inside the ceramic body [5, 6].

During the process of microwave sintering there are difficulties in temperature measurement. Measurements using a thermocouple may cause changes in the predicted field pattern, which instead of being uniform, is distorted and changes abruptly near the thermocouple tip. Such local variations in the electric-field intensity cause even larger variations in the locally absorbed power density, which is proportional to the square of electric-field intensity. Power deposition increases sharply near the thermocouple tip, causing increased localized heating results and possibly leading to thermal runaway and enhanced thermal gradients. E. Pert and others showed that when microwaves are present during heating, the theromocouple can reach >150° C higher than the pyrometer, which is mainly due to a field enhancement effect [8]. This indicated that the presence of the thermocouple within or near the sample had a strong effect on the evolution of the temperature in the sample during microwave processing. The use of optical pyrometry or optical-fibre thermometry gives good measurements results of temperature. However, the range of typical pyrometers is above 700°C. Spark plasma sintering (SPS) is a newly developed process a synthesis and processing technique – which enables sintering and sinter bonding at low temperatures and short periods by charging the intervals between powder particles with electrical energy and effectively applying high temperature spark plasma generated momentarily. It is regarded as a rapid sintering method, using the self-heating action from inside the powder, similar to self-propagating high temperature synthesis (SHS) and microwave sintering. SPS systems offer many advantages in relation to conventional systems, using hot press (HP), hot isostatic pressing (HIP) or atmospheric furnaces, including ease of operation and accurate control of sintering energy as well as high sintering speed, high reproducibility, safety and reliability. Pulsed electric current sintering (PECS) of the so-called SPS is a relatively new technology that enables us to carry out the sintering process for materials at lower temperature and in a shorter time than of the conventional sintering processes [9].

At this time about ninety percent of the advanced ceramics today are used for electronic or related applications. The rest constitutes the structural ceramics in which the mechanical properties, such as strength, fracture toughness, wear resistance, hardness etc., are of primary interest. Alumina is one of the important engineering ceramic materials due to its high elastic modulus, high wear resistance and chemical corrosion resistance, high temperature stability, retention of strength at high temperatures and low cost of the starting powder. In spite of many attractive properties of alumina ceramics one of the primary drawbacks is their brittle nature, characterized by low fracture toughness. A vast number of experimental methods with specimen geometry are presented and adopted to determine the fracture toughness of alumina ceramics. These methods base on the three-point (3PB) or four-point bending (4PB) of the beam with a notch, such as: single edge notched beam SENB, single edge precracked beam SEPB, double torsion DT, double notched beam DCB and chevron notched beam CVNB. More popular methods deal with the extension of small Vickers indention cracks under externally applied load in combination with the residual stress intensity factor [10].

The sintering temperature for alumina densification usually increases with the increase in its purity. If high purity alumina powders are prepared by the traditional sintering method, the sintering temperature should be over 1700 ° C to get a dense alumina sintered body. During the sintering of a powder compact, both densification and grain growth occur simultaneously. Grain growth is the process by which the mean grain size increases continuously during sintering without the change in grain-size distribution. As the mean grain size increases, it is obvious that some grains must shrink and disappear. Because grain growth of alumina is sensitive to the sintering temperature, abnormal grain growth in alumina would occur final stage of densification if the sintering temperature was too high, which would have a great influence on the flexural strength and wear resistance of alumina.

It is well known that the flexural strength and wear resistance of pure alumina increases with decreasing the grain size [11, 12]. To overcome the problem of grain growth, densification techniques and unconventional sintering have been used. These include the use of grain growth inhibitors in a solid solution for example magnesium oxide, which inhibits abnormal grain growth of alumina. The unconventional sintering methods of alumina include high-pressure densification, spark-plasma sintering and related techniques, shock densification, high-frequency induction heating and magnetic pulse compaction. However, these fabrication routes can be uneconomical for many applications or can be difficult to apply successfully. One of the advanced methods of sintering which allows for a shorter time of the process is the described above microwave sintering method.

Microwave sintering of alumina was developed by many researchers [2-7]. However, among many works referring to sintering alumina and alumina-composites until now there have been no reports of too microwave sintering of alumina in Poland. Earlier studies, which were made in The Institute of Advanced manufacturing Technology (IOS), concerned ceramic cutting tools on base alumina. Those works determined the effect of TiB_2 and solid lubricant substances addition on the selected properties of Al_2O_3 ceramic tool material [13, 14]. Other works presented the method of manufacturing of composite materials based on porous Al_2O_3 ceramic, infiltrated by the liquid aluminium alloy [15-17].

The aim of this study is to obtain ceramic alumina materials by the microwave, spark plasma sintering and conventional free-sintered methods. Mechanical and physical properties of the obtained materials will be compared between the methods of sintering.

2. Experimental procedure

To prepare of the mixtures the following submicrometer alumina powders were used as base powders:

- technical CT3000-SG, produced by Alcoa, USA – measured average grain size: 0.48 μm;
- ultra-pure Al-600, produced by AEE Atlantic Equipment Engineers, USA (99.99% purity) – measured the average grain size: 1.68 μm;

* particle size distribution for alumina powders was measured by the Shimadzu apparatus.

Each mixture was prepared with the addition of 0.5% mass magnesium oxide as a stabilizing phase and inhibitor of abnormal grain growth.

The following mixtures were prepared by mixing the appropriate powders in isopropanol with the addition 5% mass polyethylene glycol as a dispersive agent using the colloid mill. After milling, the powder mixtures were dried and granulated. For conventional free-sintering samples of the size 16.5x16.5x6 mm were formed by pressing in the steel matrix at pressure of 130 MPa. For microwave sintering the samples of 20 mm diameter and a thickness of 16 mm were formed.

Next all compacts were cold isostatic pressed in the hydraulic press at pressure of 250 MPa. To burn of the dispersive agent the compacts were dried at 225°C for 48 hours.

The next essential step in the process consisted in microwave and free sintering received samples. Compacts were free sintered with programmed temperature increases from 1615 to 1665°C in the HT16/18 Nabertherm electric furnace in air atmosphere. In subsequent works compacts were microwave sintered in a microwave furnace at 2.45 GHz (MKH-4.8 Linn High Therm GmbH). The manual system control of sintering parameters was used during process. Four magnetrons were used operating at 50-60% at their full power. The sintered sample was placed in the retort of porous alumina and surrounded by SiC susceptors to initiate heating. The retort with susceptors and the sintered sample is presented in Fig. 1. The microwave furnace MKH-4.8 Linn High Therm located on the equipment of The Institute of Advanced manufacturing Technology (IOS) is shown in Fig. 2.

Fig. 1. The retort with the alumina sintered sample (cylindrical) surrounded sintered by SiC susceptors (dark colour)

Fig. 2. Microwave furnace MKH-4,8 Linn High Therm

This was found to be essential in minimizing the thermal gradients within the sample. Using the optical pyrometer able to work above 800°C was used as temperature control. To the point when the pyrometer is capable of measuring temperature, the increase of power magnetrons was carried out very carefully to prevent excessive overheating of susceptors and the sintered sample. The samples were sintered at maximum temperature (similar as free sintering) and in very short time of process.

To perform SPS sintering of starting powder mixtures of technical and ultra-pure alumina powders without the addition of a temporarily binding agent placed in a graphite matrix with a diameter of 25 mm and pressing at a pressure of 35 MPa in vacuum. Then the SPS furnace chamber introduced argon,

which acted as a protective gas and the sintering process was carried out. The SPS process was carried out in HPD 5 FCT System GmbH furnace. View of SPD 5 SPS furnace and graphite dies is shown in Fig. 3. The open chamber of furnace with graphite die containing sintered sample is shown in Fig. 4.

Fig. 3. SPS apparatus with graphite dies

Fig. 4. Open chamber SPS apparatus with graphite die containing alumina powder before the sintering process

The parameters of sintering and schedule of obtained samples are shown in Table 1.

The relationship of the free-sintering temperature versus time is presented in Fig. 5 and the dependence of the microwave sintering temperature time is presented in Fig. 6. The curve presenting the course of sintering by SPS technique is shown in Fig. 7. The presented curves show the distribution of the sintering temperature depending on sintering time. Time of warm-up of the furnace is presented by the growing section of the curves. The time of essential sintering process is presented by a steady progress of curves and time of furnace cooling is described by the decreasing section of curves.

Table 1.
Sintering parameters and obtained samples

Mixture	Sintering parameters		Sample
	temperature [°C]	time [min]	
Free sintering I			
CT3000-SG	1615	60	F-CT3000-SG.I
Al-600			F-Al-600.I
Free sintering II			
CT3000-SG	1640	60	F-CT3000-SG.II
Al-600			F-Al-600.II
Free sintering III			
CT3000-SG	1665	60	F-CT3000-SG.III
Al-600			F-Al-600.III
Microwave sintering I			
CT3000-SG	1620	1	M-CT3000-SG.I
Al-600			M-Al-600.I
Spark plasma sintering I			
CT3000-SG	1550	10	S-CT3000-SG.I
Al-600	1550	10	S-Al-600.I

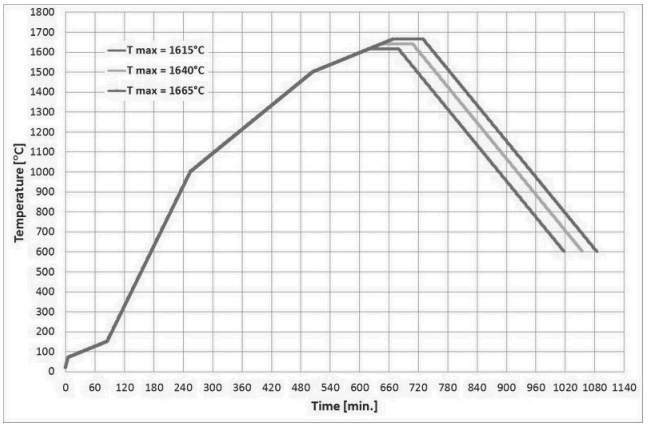

Fig. 5. Relationship of free-sintering temperature versus time of process for regime of temperature described in Table 1

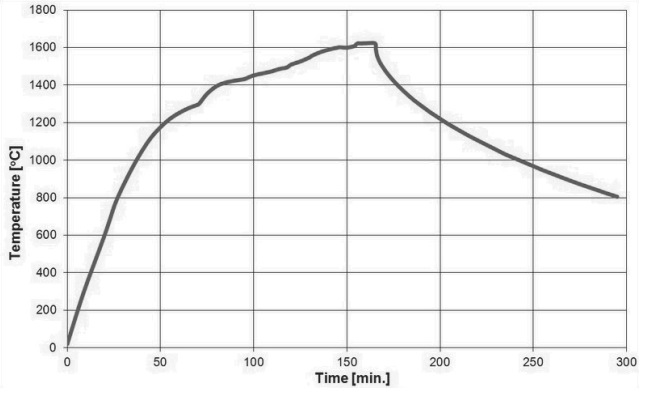

Fig. 6. Relationship of microwave sintering temperature versus time of process for regime of temperature described in Table 1

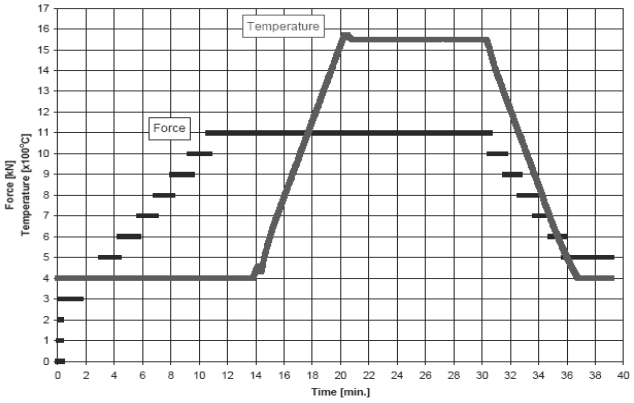

Fig. 7. Relationship of SPS sintering temperature versus time of process for regime of temperature described in Table 1

After sintering, the materials were subjected to a study of physical and mechanical properties. For this study, metallographic specimens were prepared using Struers machines and polishing agents. Apparent density ρ_p, and porosity was measured using the hydrostatic method. Young's modulus measurements of the sintered samples were also taken, using the ultrasonic method of measuring the transition speed of transverse and longitudinal waves, using the Panametrics Epoch III flaw detector. The elasticity modulus values are characteristic parameters for many technical materials. In the case of ceramics the elasticity modulus can be considered as the main parameter, which determines their properties as well as suitability for given applications. The calculations are carried out according to the following formula (1):

$$E = \rho \cdot V_T^2 \cdot \frac{3V_L^2 - 4V_T^2}{V_L^2 - V_T^2} \quad (1)$$

where: E – Young's modulus, ρ – density of the material, V_L – velocity of the longitudinal wave, V_T – velocity of the transversal wave.

Hardness was determined by the Vickers method at a load of 98.7 N using a digital hardness tester (future Tech. Corp. FM-7).

3. Results and discussion

The results of measurements of the relative density, porosity, Young's modulus and Vickers hardness of the samples obtained by free-sintering, SPS and microwave sintering are given in Table 2.

During free sintering all samples were sintered at constant time of 60 min and variable sintering temperature of every 25°C, from 1615°C to 1665°C. For the samples made from technical Al_2O_3 maximum density was reached at the level of 3.91 g/cm^3 and Young's modulus at the level of 380 GPa. In this case higher sintering temperature did not improve physico-mechanical properties of the obtained sinters and hardness decreased with the growth of sintering temperature. Increasing the temperature of free sintering of high purity Al_2O_3 samples led to the increase of density of the obtained material and Young's modulus. Hardness of the sample material grew simultaneously with the increase of sintering temperature.

In the case of applying advanced sintering techniques the authors obtained the results for density, Young's modulus and hardness for short sintering intervals of 10 min for the SPS process and at 1 min for microwave sintering.

Table 2.
The results of the density, porosity, Young's modulus and Vickers hardness for the obtained samples

Sample	Density [g/cm^3]	Porosity [%]	Young's modulus [GPa]	Hardness [HV1]
Free sintering I – 1615°C				
F-CT3000-SG.I	3.91	0.19	386	1870
F-Al-600.I	3.54	5.62	279	1200
Free sintering II – 1640°C				
F-CT3000-SG.II	3.92	0.00	387	1760
F-Al-600.II	3.68	0.04	312	1330
Free sintering III – 1665°C				
F-CT3000-SG.III	3.91	0.04	384	1600
F-Al-600.III	3.75	0.05	329	1460
Microwave sintering I – 1620°C				
M-CT3000-SG.I	3.87	0.00	376	1600
M-Al-600.I	3.83	0.00	379	1610
Spark plasma sintering I – 1550°C				
CT3000-SG	3.88	0.01	381	1600
Al-600	3.83	–	362	1700

4. Conclusions

In the paper was been presented the methods of powder sintering of technical Al_2O_3 and extra pure Al_2O_3 with 0.5 magnesium oxide as the agent preventing excessive grain growth. Sintering was carried out by three different techniques: conventional free sintering, spark plasma sintering and microwave sintering. Density and Young's modulus in particular was assumed to be a criterion of material agglomeration. Hardness measurements supplemented the measurements performed on sintered samples. In the case of free sintering for the samples of technical Al_2O_3, increasing the sintering temperature did not practically result in any change of material density and Young's modulus. In this case sintering can be carried out in lower temperature since too high temperature can lead to unfavourable grain growth. Increasing the sintering temperature resulted in the increase of material brittleness, which was proved by the decrease of material hardness. Respectively, for the samples made from high purity Al_2O_3, sample density, Young's modulus and hardness increased with the growth of sintering temperature. Sintering of extra pure Al_2O_3 usually grows with the increase of its purity which was confirmed during free sintering.

The use of non-conventional sintering methods, such as spark plasma sintering and microwave sintering, contributes to obtaining a well-densified material with good physico-mechanical properties at relatively short sintering times.

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