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Hybrid microwave sintering of alumina ceramics which contain waste alumina

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ABSTRACT

The use of microwave energy to sinter ceramic materials offers benefits compared to conventional sintering methods. Some of the benefits regarding less time consumption, achieving high heating rates and saving energy. The hybrid microwave sintering because of its advantages is a method of wide interest for improving the microstructure of sintered materials. In this study, the goal was to investigate the influence of the hybrid microwave sintering on the properties of alumina ceramics, which contain a considerable amount of waste alumina powder. The study was limited to hybrid microwave sintering of alumina green bodies in which the grain growth and densification were characterized. The waste alumina powder, which is generated during machining of alumina green compacts and high-purity (99.9 %) alumina powder, were used as starting materials. The alumina green bodies were obtained by the slip casting process. The dried green samples were then sintered by using a hybrid microwave furnace. The used hybrid microwave sintering atmospheric furnace consists of a 2.45 GHz microwave generator with a continuously adjustable power output from 0 to 3 kW and external heating elements. The sintered samples with the addition of waste alumina powder were showing higher density values, slightly smaller grain size, and higher linear shrinkage in comparison with the samples made of pure alumina powder. The observed microstructure for both samples was uniform with the average grain sizes smaller than 2 microns as a consequence of a hybrid microwave sintering.

1. INTRODUCTION

Sustainable development strategies of developed countries include the implementation of environmentally-friendly measures in terms of affecting production processes and efficient uses of the resource, as well as the generation and management of waste. The transformation of this waste into valuable materials is emerging as a possible solution to reduce environmental pollution. The reuse of recovered waste generated from the manufacturing processes involves the need for recycling as secondary raw materials [1-3]. This strategy is promoted by the recent Directive of the European Parliament and the Council on Waste (European Directive 2018/851) [4]. During the machining of the ceramic green body, a certain amount of waste ceramic powder is generated, which remains unused. Besides, the waste ceramic powder should be disposed of as non-hazardous waste in a legally prescribed manner.

Alumina ceramics are interesting materials for researchers due to their excellent properties like high hardness, thermal, and chemical stability [5]. In recent years, continuous development can be observed in technologies of production of high-density sintered materials. A clear tendency exists in the research of methods, which use various dopants or sintering additives and require lower sintering temperatures and shorter process times [6]. In particular, magnesium oxide (MgO) is the most studied additive [7-9]. Various alternative additives have also been investigated to refine alumina ceramics microstructure by changing their composition, such as the addition of manganese oxide [10, 11], titan oxide [12, 13], graphene oxide [14-16], and many others.

Microwave sintering (MWS) has been studied as an alternative to conventional sintering to rapidly sinter and improve ceramic properties. During microwave heating, the energy is directly transferred to the material which couples with the electric field. Consequently, the material is self-heating from the interior, which allows rapid heating with suppressed grain growth. The microwave sintering has disadvantages such as the formation of a temperature gradient between the surface and core of heated materials with the low microwave dielectric loss. The poor microwave absorption occurs in some ceramic materials, including alumina ceramics (Al_2O_3). During microwave sintering of such ceramic materials, the thermal instabilities resulting in catastrophic overheating of the sintered sample were noticed [17-19].

However, these disadvantages can be overwhelmed by using hybrid microwave sintering, where direct microwave heating is combined with radiant (infrared) heating. In this way, the sample with low dielectric loss can be heated up to a temperature where it will begin to sufficiently absorb the microwaves. Also, uniform heating is achieved throughout the core and surface of the sample because the thermal gradients are significantly reduced. Based on these reasons, microwave hybrid sintering technique was proposed as a possible solution for microwave sintering of alumina ceramics [20-22].

In this study, the results of hybrid microwave sintering of alumina ceramic material which contains a considerable amount of waste alumina powder are presented. The optimal sintering conditions were determined by applying the Box-Behnken design. For the optimal conditions the final linear shrinkage, density, and microstructure characteristics were determined. Furthermore, the final densities, linear shrinkage, and microstructures of alumina samples prepared from commercial alumina powder were compared to the samples with the addition of waste alumina powder. The goal of this study was to investigate the possibility of recovering a non-hazardous waste alumina powder as secondary raw material in ceramic manufacturing processes, as an attempt to contribute to the sustainable development in terms of safe reuse of industrial waste.

2. MATERIALS AND METHODS

The components used in the study were commercially available Al_2O_3 (Alcan Chemicals, USA) with a chemical purity of 99.9% and the average particle size of 300-400 nm, waste (secondary) alumina powder which is obtained after green machining in factory production of ceramics. A commercial dispersant Tiron (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate) manufactured by Sigma-Aldrich Chemie GmbH, Germany was used to stabilize

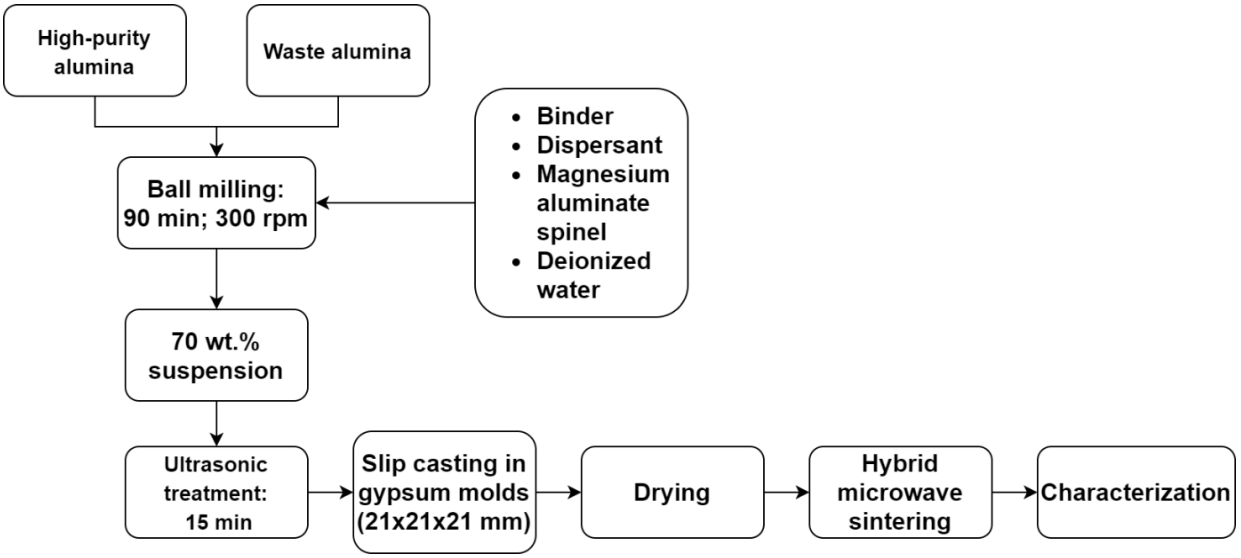


Figure 1. Process flow chart for sample preparation.

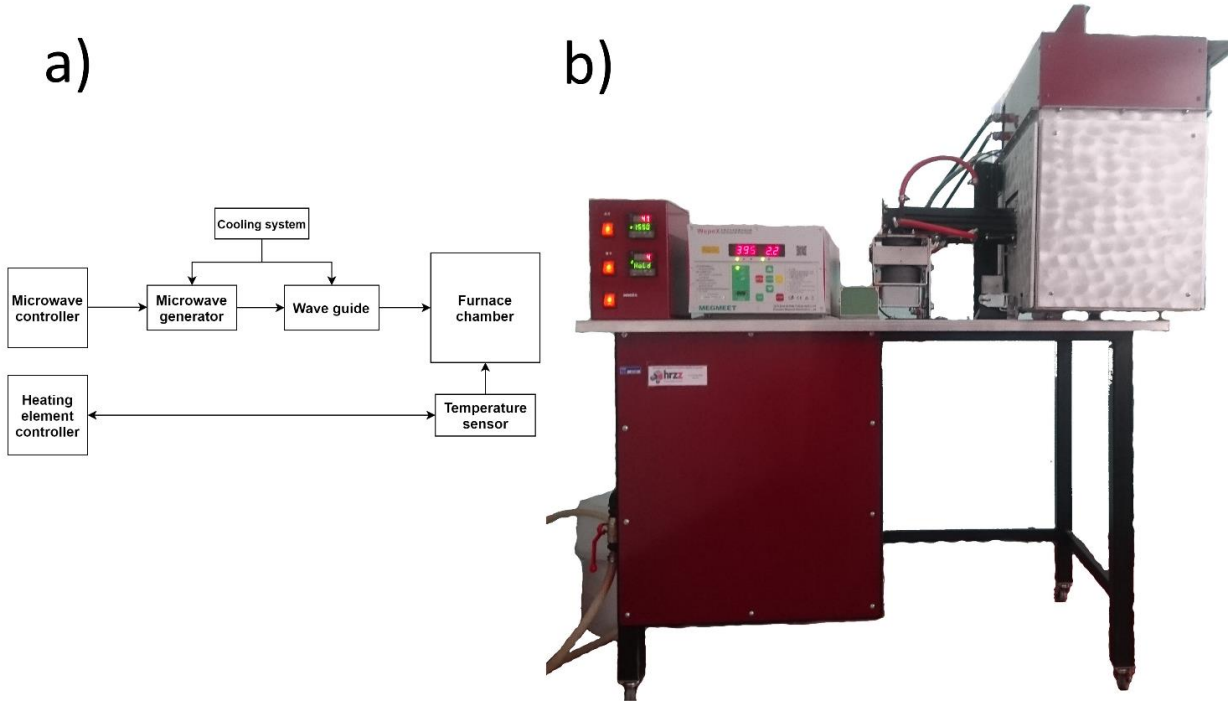


Figure 2. The schematic diagram (a) and photograph of the hybrid microwave furnace (b).

highly concentrated alumina suspensions [23]. The binder PVA manufactured by Sigma-Aldrich Chemie GmbH, Germany [24] was added to the ceramic suspension in order to improve the strength of the green bodies. Magnesium spinel (magnesium aluminate oxide) manufactured by Alfa Aesar, USA was used to inhibit the abnormal alumina grain growth during the sintering process of alumina green bodies [25].

The alumina samples were prepared through the procedure shown in Fig. 1. The mixture of dry alumina powders was prepared by mixing 20 wt.% of waste alumina powder versus 80 wt.% of high-purity alumina powder expressed on a dry weight basis of alumina powders. The solution of PVA – poly (vinyl alcohol) was prepared by dissolving the 0.1 wt.% of PVA in deionized water heated up to 80 °C. Afterwards, 0.05 wt.% of dispersant Tiron and 0.2 wt.% of magnesium aluminate spinel were mixed with the prepared solution and added into the grinding jar of the planetary ball mill PM 100 (Retsch GmbH, USA). Next, the previously prepared mixture of dry alumina powders was placed into the grinding jar of the planetary ball mill with ten alumina balls used for the suspension homogenization. The homogenization lasted for 90 minutes at a speed of 300 rpm to make a suspension with a solids content of 70 wt.%. Alumina balls were separated from the suspension after the homogenization using a strainer (opening 2 mm). The suspension underwent an ultrasonic treatment for 15 min in an ultrasonic bath – BRANSONIC 220 (Branson Ultrasonics Corp., USA) to remove the air bubbles and achieve better homogeneity.

Finally, prepared suspensions were cast in gypsum molds (21x21x21 mm^3) to prepare green alumina samples. In terms of comparison, the same experimental procedure was used to obtain pure alumina green samples just without the addition of waste alumina powder.

After drying, the green alumina samples were additionally cut into smaller pieces and sintered via a hybrid microwave furnace. The schematic diagram and photograph of the hybrid microwave furnace are given in Fig. 2., which was designed and made by OVER industrijska elektronika d.o.o., Kerestinec, Croatia.

The used hybrid sintering atmospheric furnace consists of a 2.45 GHz microwave generator with a

continuously adjustable power output from 0 to 3 kW and external (around the inner wall of the furnace) molybdenum disilicide heating elements. Temperature control is performed employing a thermocouple, which was positioned 1 cm from the sintered sample in order to avoid possible electric discharge at elevated temperatures. The furnace chamber was made of silicon carbide, which is commonly used as a susceptor material because of its excellent dielectric loss and oxidation resistance. By applying the Box-Behnken design the optimal sintering conditions were investigated. The input power of magnetron from 1 to 2 kW, sintering temperature from 1550°C-1650°C, and dwell time from 2-4 hours were monitored. The cooling rate of the samples in the furnace chamber was not controlled. After sintering and cooling, the microstructure analysis of the polished surface of sintered samples was conducted by a *Tescan Vega* scanning electron microscope (SEM). For determining the average grain size, the line intercept method was used. The bulk density of the samples was measured by using Archimedes principle by immersing in distilled water. The theoretical density of alumina for calculation of relative densities was taken as 3.98 g cm^{-3}.

3. RESULTS AND DISCUSSION

In order to determine the optimal sintering conditions for alumina samples by using the experimental hybrid microwave furnace, the Box-Behnken design was applied.

The value range of each sintering factor was determined according to preliminary tests. The investigated range of sintering temperature was set from 1550 to 1650°C; the range of input power 1-2 kW; the range of holding time 2-4 hours. By combining the 3 factors at 3 levels a total sum of 15 experiments in randomized order, as per *Design Expert*® software, Box-Behnken response surface design was developed. The corresponding response, the density of each sintered sample was measured (Table 1). Then the response surface method was used to find out the optimal value of each factor to obtain maximum density.

By studying the ANOVA data (Table 2) the higher model *F*-value (34.35) and the associated lower *p*-value (p=0.0002) demonstrated that the polynomial regression model was suitable to determine the optimum sintering conditions of alumina ceramic samples, which contain 20 dwb. % waste alumina powder (expressed on dry weight basis dwb. %). The *p*-values less than 0.0500 indicate model terms are significant. In this case sintering temperature (*A*), holding time (*B*), as their interactions (*AB*, *AC*, *BC*, B^2, C^2) were

Table 1. Box-Behnken design and experimental data.

Run	Factor *A*: Temperature, °C	Factor *B*: Holding time, h	Factor *C*: Input power, kW	Response: Density, g/cm^3	Predicted: Density, g/cm^3
1	1650	3	1	3.850	3.846
2	1600	3	1.5	3.857	3.859
3	1650	4	1.5	3.810	3.812
4	1600	2	1	3.841	3.843
5	1550	4	1.5	3.851	3.849
6	1550	3	1	3.845	3.844
7	1600	4	1	3.807	3.810
8	1600	2	2	3.827	3.824
9	1600	3	1.5	3.860	3.859
10	1550	3	2	3.846	3.851
11	1600	4	2	3.819	3.816
12	1650	3	2	3.825	3.826
13	1600	3	1.5	3.862	3.859
14	1650	2	1.5	3.856	3.858
15	1550	2	1.5	3.844	3.843

Table 2. ANOVA.

Source	*Sum of Squares*	*df*	*Mean Square*	*F Value*	*p-value Prob > F*
Model	0.0045	8	0.0006	34.35	0.0002
A-Temperature	0.0003	1	0.0003	15.61	0.0075
B-holding time	0.0008	1	0.0008	50.59	0.0004
C-Power	0.0001	1	0.0001	5.21	0.0625
AB	0.0007	1	0.0007	43.32	0.0006
AC	0.0002	1	0.0002	10.42	0.0179
BC	0.0002	1	0.0002	10.42	0.0179
B^2	0.0013	1	0.0013	79.72	0.0001
C^2	0.0011	1	0.0011	58.97	0.0006
Residual	0.0001	6	0.0000		
Lack of fit	0.0001	4	0.0000	3.34	0.2435
Pure Error	0.0000	2	6.333×10^{-6}		
Cor Total	0.0046	14		R^2	0.9786
Std. Dev.	0.0040			*Adjusted* R^2	0.9501
Mean	3.84			*Predicted* R^2	0.8001
C.V. %	0.1049			*Adeq. Precision*	15.8499

significant. The remaining variable, input power of magnetron (*C*) showed negligible effect on the achieved density values according to high p-value (p>0.05). High R^2 (0.979), *adjusted* R^2 (0.950), and smaller *predicted* R^2 (0.800) values indicate that the variation could be accounted for by the data satisfactorily fitting the model. Because of the higher difference between *predicted* R^2 and *adjusted* R^2 the model was tested by doing confirmation runs.

By applying multiple regression analysis on the experimental data, the following reduced quadratic equation is obtained which describes the relationship between the dependent and the independent variables:

$$Y\left(density, \frac{g}{cm^3}\right) = +1.19734+0.001072*A +0.506298*B+0.579346*C-0.000265*A*B -0.000260*A*C+0.013000*B*C -0.018654*B^2-0.069615*C^2 \quad (1)$$

where *A* is sintering temperature (°C), *B* is holding time, and *C* is the input power of magnetron (kW).

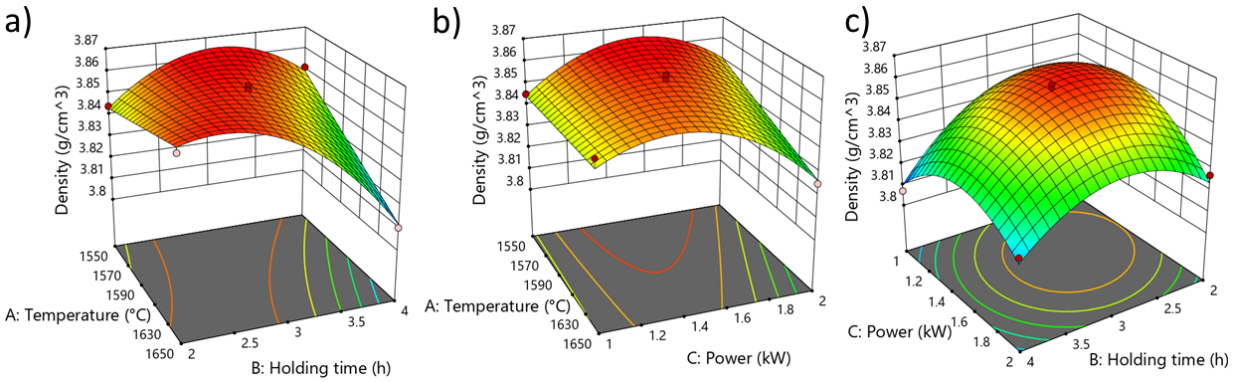


Figure 3. a-c) represents the response surface plots (3D) showing the effects of sintering parameters on the response density of sintered samples: a) fixed value of input power at 1.5 kW, b) fixed value of holding time at 3h, c) fixed value of sintering temperature at 1600 °C.

Table 3. The linear shrinkage of sintered samples.

	Total number	Dimensions	Shrinkage, %	Standard deviation
Pure alumina	30	a	7.59	2.83
	30	b	7.49	2.95
	30	c	8.03	4.08
20 dwb. % of waste alumina	30	a	9.24	1.93
	30	b	8.03	2.25
	30	c	8.53	2.56

Table 4. The obtained density values before and after sintering.

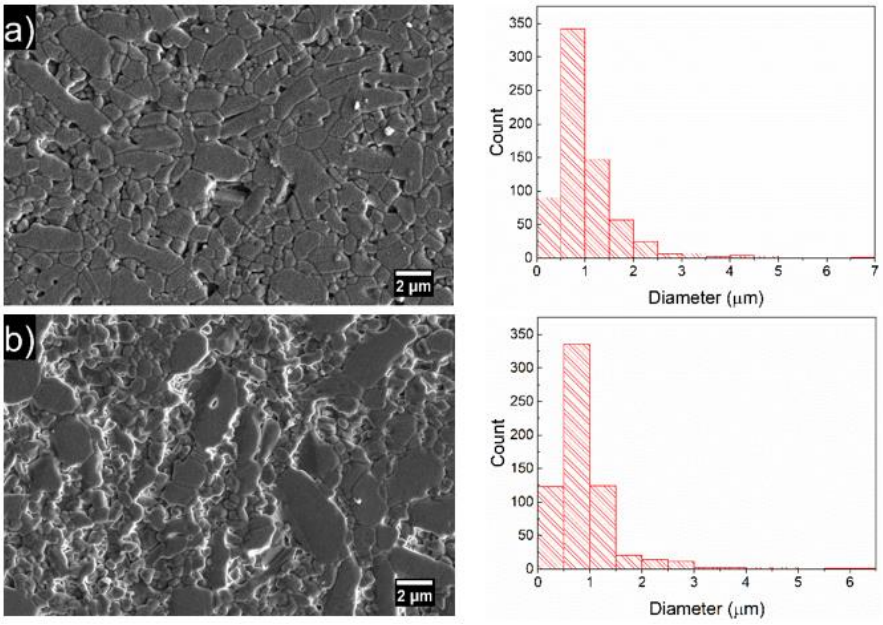
	Total number	Density, g/cm^3 (before sintering)	Standard Deviation	Density, g/cm^3 (after sintering)	Standard Deviation
Pure alumina	30	2.273	0.189	3.762	0.031
20 dwb. % of waste alumina	30	2.397	0.103	3.844	0.028

The criteria for optimization were set to maximize the density of sintered samples while keeping the independent variables in the investigated range. Based on Equation 1, multiple solutions were generated, where the ramp solution showed desirability of 1. Also, the obtained equation was used to calculate the predicted density values in Table 1. The determined optimum values were as follows, the sintering temperature of 1550°C, holding time in the duration of 2 hours, and the input power of 1.5 kW.

The determined optimal sintering conditions were tested by doing confirmation runs, which is usual practice for the empirical models. A total of 60 samples were sintered at optimal sintering conditions. More precisely, 30 samples with addition (20 dwb. %) of waste alumina powder and 30 samples without waste addition were sintered. After the sintering, linear shrinkage and density values were compared.

The determined linear shrinkage (Table 3), considering all three dimensions of sintered samples, is 7.69±3.31% for the pure alumina samples and 8.13±2.26% for waste alumina samples. The slight difference in the linear shrinkage can be explained by organic sintering additives, which are present in the waste alumina. The organic components are removed during sintering, which results in higher shrinkage of sintered samples containing waste alumina.

The obtained density values before and after sintering are shown in Table 4. The determined density for the green samples is considerably lower than the density after the sintering process. The higher density values after sintering are a consequence of consolidating alumina particles during the sintering process. The density of green samples that contain waste alumina is higher than the density of samples without the addition of waste alumina powder. This difference also can be explained by sintering additives already present in waste alumina powder. Specifically, binders because their presence enhance the density of the green ceramic samples. The density after sintering remained higher for samples that contain waste alumina. Also, the calculated relative density suggests the presence of pores. The obtained relative density was 96.58±0.71% for samples with the addition of waste alumina powder and 94.53±0.78 respectively for pure alumina samples. The examined microstructure of the polished surface showed small, irregularly shaped alumina



Total Number	Mean grain size	St. Dev.
684	1.022	0.679

Total Number	Mean grain size	St. Dev.
642	0.921	0.675

Figure 4. The micrographs of alumina samples a) pure alumina, b) with addition of waste alumina (20 dwb. %) and their corresponding grain size distribution from image analysis of SEM micrographs.

grains. The sample with the addition of waste alumina powder (Figure 4.b) showed a slightly smaller average grain size (0.92±0.68) in comparison with the pure alumina sample (1.02±0.68) as depicted in Figure 4.a). In general, the obtained average grain size for both compositions are smaller than 2 microns, which is a result of hybrid microwave sintering.

4. CONCLUSION

After the hybrid microwave sintering, the characterized samples with the addition of 20 dwb. % waste alumina powder exhibited slightly higher density values, smaller grain size, and higher linear shrinkage compared to samples prepared with pure alumina powder. The highest relative density was 96.58±0.71% for samples with the addition of waste alumina powder and 94.53±0.78 respectively for pure alumina samples, which can be explained by the fact that alumina is a very poor microwave absorber. The average grain size was smaller than 2 microns for both observed compositions. The smaller grain size can be explained by the fact that the rapid heating of the microwave prevented grain size growth. The linear shrinkage was 7.69±3.31% for the pure alumina samples and 8.13±2.26% for waste alumina samples. The slight difference in the linear shrinkage can be explained by organic sintering additives, which are present in the waste alumina powder. The burned organic components during sintering resulted in higher shrinkage of sintered samples containing waste alumina.

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