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Fabrication of mullite–zirconia composites by microwave sintering of corundum/amorphous silica particles and sol–gel substrates

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Abstract

Mullite–ZrO_2 composites were prepared using as starting materials corundum/amorphous silica particles or substrates formed by the sol–gel method. The sintering process has been carried out in a high temperature microscope and in a microwave oven. It was observed that the mechanism of mullite–ZrO_2 composite formation from composite particles (so called transient viscous sintering) was different from the process typical for substrates prepared by the sol–gel method.

Keywords: Mullite–zirconia composites; Microwave sintering; Sol–gel substrates

Introduction

Some difficulties that have occurred during sintering of mullite in a range of temperatures lower than 1600°C, have prohibited its use as a product of high density. One of the methods of synthesis and sintering of mullite in a lower temperature range was based on the use of mineralizer; however, it affected the purity of the final product. An introduction in the latter method of mullite synthesis from organic precursors did not improve this phenomenon because it has only lowered the temperature of mullite synthesis, but the sintering has still taken place in the solid state and at high temperatures. However in many applications it is important to obtain mullite with a density close to the theoretical. Therefore mullite synthesis and sintering has been continuously developed for many years. In 1991, Sacks suggested the so-called transient viscous sintering (TVS) method as a way to solve mullite sintering problems [1]. According to this idea, the specially prepared composite grains of corundum/amorphous silica were obtained by coating each grain of α-Al_2O_3 with a layer of amorphous silica following by sintering process. The process proceeds in two stages: in the first stage the transient viscous sintering (TVS) occurs, and in the second, the synthesis of mullite goes ahead forming the composite structure consisting of the dense matrix of SiO_2 containing randomly distributed corundum grains.

Comparative tests of synthesis and sintering of mullite from a mixture of corundum/amorphous silica particles or the substrates received from the sol–gel method have been performed. The sintering process has been done in a high temperature microscope and in a microwave oven of the author's design.

Experimental

The following starting materials have been used for the mullite synthesis from composite powder or powder prepared by the sol–gel method:

- tetraethylorthosilicate (TEOS) containing 98 wt.% SiO_2 (Aldrich, Germany),
- ZrO_2 powder with grain size $d < 0.48$ μm (United Ceramics, UK),
- α-Al_2O_3 powder with grain size $d < 0.49$ μm containing 99 wt.% of the alpha form,
- demineralized water,
- NaOH and HCl, "for analysis' grade (POCh, Poland).

The aforementioned composite particles were obtained according to the Wang et al. method [2], while the mullite sol–gel powders were obtained according to

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the Szewczenko et al. method [3]. Both powders were additionally mixed with ZrO_2 in a quantity of 5, 10 or 20 wt.%. The dimensions of samples were 3 mm in diameter and 3 mm high for sintering in the high temperature microscope, while those for the microwave oven sintering experiments were 20 mm in diameter and 3 mm high. The forming pressure and sintering conditions were as follows:

- Pressure 50 MPa,
- Temperatures up to 1800°C in the high temperature microscope (Leitz Wetzlar),
- Microwave oven power 1.8 kW at a frequency of 2.45 GHz.

The electrical scheme of the microwave oven is shown in Fig. 1. The dimensions of the heating chamber were: 60 mm in diameter and height of 45 mm. The chamber was made from insulating alumina cloth and was equipped with six microwave absorbing plates of dimensions $25\times25\times7$ mm^3. For the first experiments the absorbing plates were manufactured from a BN–Si_3N_4–C composite and for the final experiments from a mixture of AlN-40 vol.%, SiC-30 vol.% (grain size 28 μm) and 30 vol.% mixture of silicon and soot. In the last mixture, silicon and soot were used in a ratio adequate for forming of the secondary SiC.

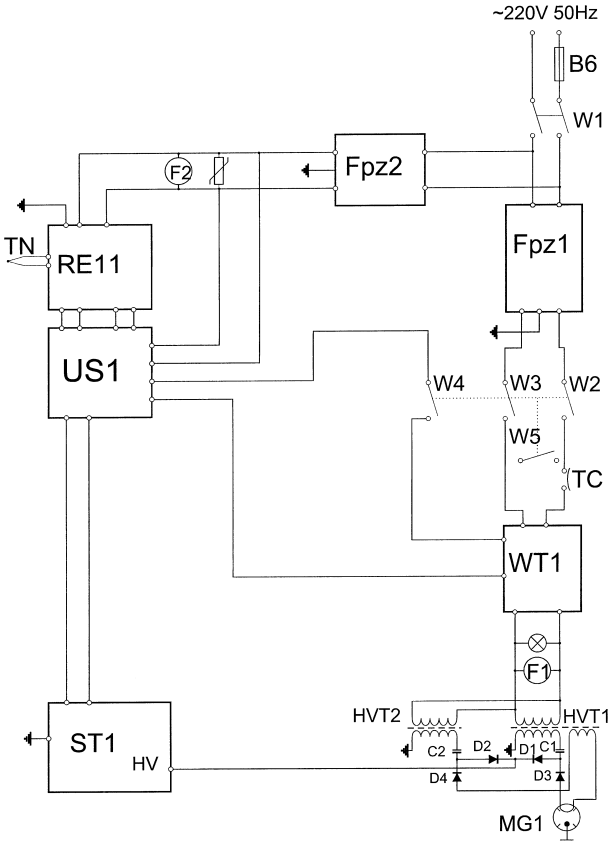

Fig. 1. Electrical scheme of the microwave oven.

AlN-SiC absorbing plates were sintered at temperatures up to 1650°C in a protective nitrogen atmosphere in the powder bed composed of BN and MgO. The final porosity of the absorbing plates was approximately 40 vol.% (by adding a pore former to the mass composition) [4].

The heating chamber has been covered with microwave absorbing plates to obtain an additional hybrid heating effect. The scheme of the microwave oven, with the heating chamber covered with absorbing plates, is presented in Fig. 2.

The temperature inside the heating chamber was measured initially by means of a jacket thermocouple Pt87%Rh13%–Pt connected to the programmer of the microwave oven, and simultaneously with the pyrometric cones placed inside the heating chamber. The method of measuring the temperature by means of a PtRh–Pt thermocouple in the microwave oven was applied earlier by Piluso et al. [5]. However during our experiments, the thermocouple melted due to the formation of an electric arc. A new system for the temperature measurement in the microwave oven was prepared using a pyrometer measurement and temperature sensors.

Results and discussion

The sintering process of the composite mullite powders (α–Al_2O_3/amorphous SiO_2) and powders prepared by the sol-gel method in the high temperature microscope is presented in Fig. 3. The data indicating the beginning of the sintering process for these powders are summarised in Table 1.

The results of the experiments indicate clearly that the sintering process of the composite powders begins at lower temperatures than for the powders prepared by the sol–gel method (Table 1). This phenomenon is explained by the occurrence of the transient viscous sintering (TVS) in the former case.

Three periods can be observed in the sintering process of the composite powder:

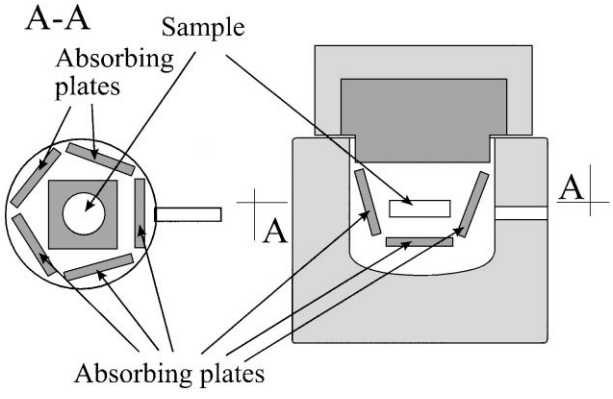

Fig. 2. Heating chamber with the composite AlN–SiC absorbing plates located inside the chamber.

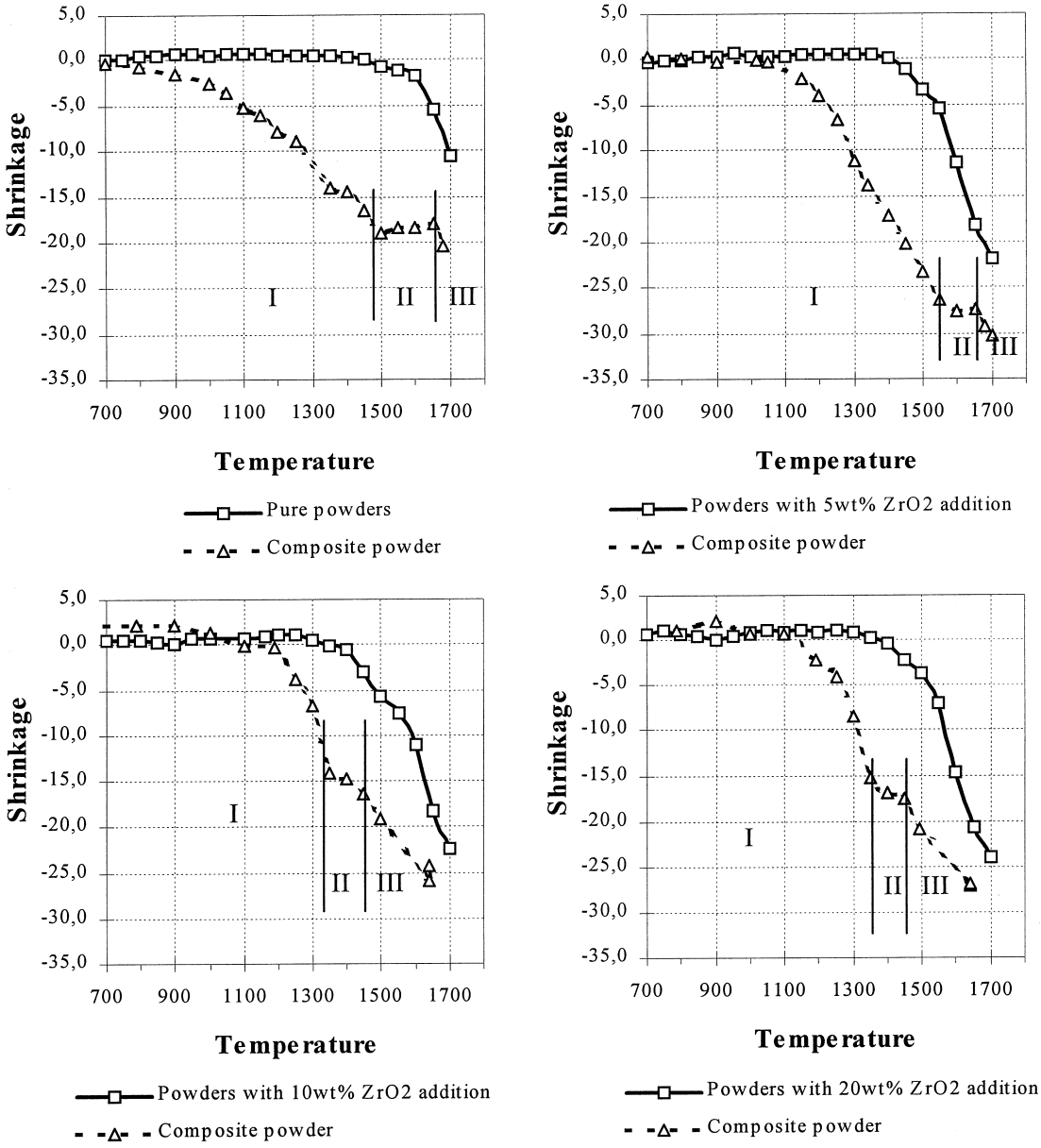

Fig. 3. Shrinkage of the sinters made from the composite (α-Al_2O_3/amorphous SiO_2) and from the sol–gel method obtained powders, with and without ZrO_2 addition (5, 10, 20 wt.%).

Table 1
Initial temperature of the composite and sol–gel method obtained powder sintering in the conventional oven

Addition wt.%	Beginning of the sintering process (°C)		ΔT (°C)
	Mullite powder from sol–gel method	Mullite composite powder (α-Al_2O_3/SiO_2)	
Pure mullite	1400	800	600
Mullite + 5%ZrO_2	1400	1000	400
Mullite + 10%ZrO_2	1400	1100	300
Mullite + 20%ZrO_2	1400	1100	300

1. the rapid sintering, from the beginning of sintering to 1300≡1500°C;
2. the flattened phase, when the sintering process is very slow or even stops;
3. the final sintering above 1400≡1650°C when the process is again accelerated.

The high initial temperature of the sintering process of the powders from the sol–gel method can be explained by the fact that the powders were primarily calcined at the temperature of 1100°C. It means that the sintering process starts at a temperature higher than the temperature of the mullitization process of the sol–gel

Table 2
Properties of microwave and conventional sinters obtained at 1400°C

Properties	Mullite (green compact $d = 1.28$ g/cm^3)		Mullite + 20 wt.% ZrO_2 (green compact $d = 1.30$ g/cm^3)	
	Conventional sintering[a]	Microwave sintering[b]	Conventional sintering[a]	Microwave sintering[b]
Linear shrinkage (%)	8.9	17.3	9.9	16.8
Total pore area (m^2/g)	2.743	0.294	2.378	0.110
Median pore diameter (mm)	0.4518	1.4516	0.4206	2.6110
Apparent density (g/cm^3)	3.0662	2.7995	3.3818	3.0667
Bulk density (g/cm^3)	1.5725	2.1549	1.8324	2.5251
Relative density (%)	51.0	76.0	54.0	82.0

[a] Laboratory high temperature oven Carbolite with heating rate 4°C/min.
[b] Heating rate 400°C/min.

mixture, however lower than the typical mullitization process which takes place in the solid state.

According to Wang et al. [6] the synthesis of mullite from the composite powder takes place at the temperature of 1500°C which is in a good agreement with our results. For composite powder doped with ZrO_2, the temperature of mullite synthesis drops down even to the temperature of 1350°C which was proved by X-ray examination results. This can be accounted on the basis that the ZrO_2 addition plays a mineralizer's role. The XRD examinations indicate also the differences in behaviour of both kind of powders in the sintering process. In the composite (α-Al_2O_3/amorphous SiO_2) doped with ZrO_2 the formation of $ZrSiO_4$ at the temperature 1300°C was observed. This compound dissociated again to ZrO_2 and SiO_2 at higher temperatures. The latter reacts with the corundum and forms the mullite. In the sinters obtained from the sol-gel powder the formation of $ZrSiO_4$ has not been observed, however the mullitization reaction took place already at the temperature of 900°C.

Investigation of the sintering process in the microwave oven (hybrid heating method) showed a possibility to reach the temperature of 1800°C even in five minutes (400°C/min), which is of about 100 times higher than the rate of heating in the high temperature microscope with the heating rate of 4°C/min.

Comparison of some selected properties of ceramic samples sintered in microwave and conventional furnaces at 1400°C is presented in Table 2.

The results presented for the microwave and conventional sintering processes are still very preliminary, however they indicate essential differences between the two methods of heating. The characteristic features of the microwave sintering process are: 1.3 times increase in the bulk density of alumina/zirconia ceramics, very strong decrease in the total pore area (5 to 20 times) and also increase in the average diameter of pores. The clear gain in the densification degree of the samples sintered in the microwave oven was partly counteracted by the occurrence of the macroscopic cracking network in the sintered bodies (revealed from the microscopic observation). It is obvious that during the microwave heating process the safe heating rate was exceeded. Nevertheless, both the increase in the bulk density as well as the higher linear shrinkage of the tested systems proved that the application of the microwave heating system is very promising for speeding-up the sintering process of ceramic materials.

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References

[1] M.D. Sacks, G.W. Scheiffele, N. Bozkurt, R. Raghunathan, Ceram. Trans. 22 (1991) 437.
[2] J.G. Wang, C.B. Ponton, P.M. Marquis, J. Am. Ceram. Soc. 74 (1992) 3457.
[3] A. Szewczenko, J. Raabe, E. Dudnik, V. Petrovsky, Synthesis, Properties and Opportunities for Increasing of Fracture Toughness of Material in System Mullite–ZrO_2, in: Współczesna Ceramika. Wybrane technologie i metody badań, IPPT PAN, Warsaw, Poland, 1998, p. 393.
[4] J. Raabe, E. Bobryk, V. Petrovsky, Sintering of Ceramics in Microwave Processing and the Device for it of Realisation, in: Współczesna Ceramika. Wybrane technologie i metody badań, IPPT PAN, Warsaw, Poland, 1998, p. 35.
[5] A. Piluso, N. Lequeux, P. Bock, Third Euroceramic 1 (1993) 1017.
[6] K. Wang, M.D. Sacks, J. Am. Ceram. Soc. 79 (1996) 12.