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ADDITIVES IN COARSE GRAIN ALUMINA CERAMICS FOR METALLIZATION

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The metal to ceramics seals are widely used as permanent seals in high vacuum technology. For these seals a coarse grain alumina ceramics is needed since a high temperature MoMn metallization is often applied because of several advantages, such as high mechanical strength, low dielectric losses at high frequencies and others. The coarse grain ceramics are produced by sintering alumina with different additives which have to promote densification and grain growth with the liquid phase during sintering. The CaO-SiO_2 and CaO-MgO-SiO_2 systems were used as additives in the present work. Different characteristics of the formed liquid phases have caused similar densification but different grain growth rates.

1. Introduction

The liquid phase sintering of alumina is a widely used process. It is more significant phenomenon than the solid state sintering of this material [1]. Many different additives are used to produce liquid phase with the aim to promote liquid phase sintering and perhaps also the desired microstructure development. The matter of our attention were additives from the CaO-MgO-SiO_2 and CaO-SiO_2 system, which should assure coarse grain ceramics with high dielectric strength [2].

The liquid phase sintering is often divided into three stages [3]:

- particle rearrangement: motion of solid particles due to capillary forces is responsible for the initial densification of the compact,
- solution–reprecipitation: different solubilities of the solid in the liquid are responsible for the transport of the material from the points of solid–solid contacts to the free surfaces of the particles,
- coalescence: permanent solid–solid contacts between particles form liquid phase sintering ends.

S. Pejovnik [4] has concluded that particle rearrangement is the primary mechanism of densification in the liquid phase sintered alumina. There are two types of rearrangement [4]:

- rearrangement of initial alumina particles,
- rearrangement of alumina grains after a liquid has dissolved the solid necks between these grains.

The second type of rearrangement can take place in different stages of the liquid phase sintering process and affects densification.

Viscosity of the liquid phase is a very important characteristic, which can influence densification in these stages. Viscosity depends on the temperature and also on the chemical composition of the liquid phase. E. Kostić showed that for a good densification, the most suitable were additives forming an equilibrium liquid phase at sintering temperature, but not entering in the chemical reactions [5]. She studied a wide range of different additives; the most suitable for our purposes (high dielectric strength) is the eutectic from CaO-MgO-SiO_2 system with melting point at 1320 °C. It forms an equilibrium liquid phase at sintering temperature, but does not react with Al_2O_3. The viscosity increase is caused by formation of the reaction products between Al_2O_3 and liquid phase. This can be avoided if CaO/SiO_2 ratio is kept within a fixed range (0.47-1.23) [6].

Our previous investigations indicated an influence of additive composition on microstructure development [7]. An effect of addition of small amounts of MgO on alumina microstructure is well known. A fine microstructure is caused by MgO precipitation on grain boundaries. A slower grain growth and also appearance of large spinel ($MgAl_2O_4$) grains is caused at larger MgO concentration (about 20 wt.%) in the additive composition.

2. *Experimental*

A coarse grain low soda alumina Alcoa CL 2500 was used in this study. Additives selected from the CaO-SiO_2 and CaO-MgO-SiO_2 systems, used in this work, are given in Table 1.

TABLE 1.
Compositions of additives in wt.%.

Sample	CaO	MgO	SiO_2
1	40	–	60
2	30	10	60

The additives were prepared from reagent grade $CaCO_2$, MgO and high purity SiO_2. The powders were dry mixed in a turbula mixer and pressed into briquettes. Glasses were prepared by melting briquettes at 1550 °C for 1 hour, followed by quenching in water.

The additives were prepared by a classic ceramic procedure: milling in a ball planetary mill for 6 hours and in an attrition mill for 20 hours. A homogenization of 2 wt.% of the additive and alumina was made by mixing and milling in the planetary mill in alcohol for 1 hour. Dried mixtures were pressed into pellets ϕ16 mm at 100 MPa.

Sintering was performed in an electric furnace at 1700 °C for 4 hours. The heating rate was 1 °C/min. The characterization of sintered samples involved density measurements and microstructural examinations.

3. *Results and discussion*

3.1. *Densities*

The main purpose of this study was to produce high density coarse grain alumina ceramics. Densities of sintered samples are given in Table 2.

TABLE 2.
Densities and grain sizes of samples, sintered for 4 hours at 1700 °C.

Sample	ρ [g/cm^3]	ρ_{th} [%]	d [μm]
1	3.78	95	17
2	3.79	95	9

The estimated theoretical density of 98% Al2O3 is 3.97 g/cm^3, due to density of used glass, which is supposed to be about 2.8–2.9 g/cm^3 [8]. The selected additives are suitable for liquid phase sintering of the coarse grain starting alumina. Both additives enable sintering of the alumina to 95% and higher of the theoretical densities. A starting alumina Alcoa CL 2500 has grain size about 2–2.5 μm and does not sinter without additives during sintering at 1700 and 1750 °C (density after sintering for 4 hours at 1750 °C is about 3.60 g/cm^3). The densities achieved by the two additives are almost the same and high enough for ceramics to be metallized using MoMn process.

3.2. Microstructure

The commercial starting alumina powder has bimodale particle size distribution (PSD). Hodge [1] has concluded, that alumina with bimodale PSD enable development of more uniform microstructure with coarser grains than alumina with narrow PSD. PSD of alumina Alcoa CL 2500 is presented in Fig. 1.

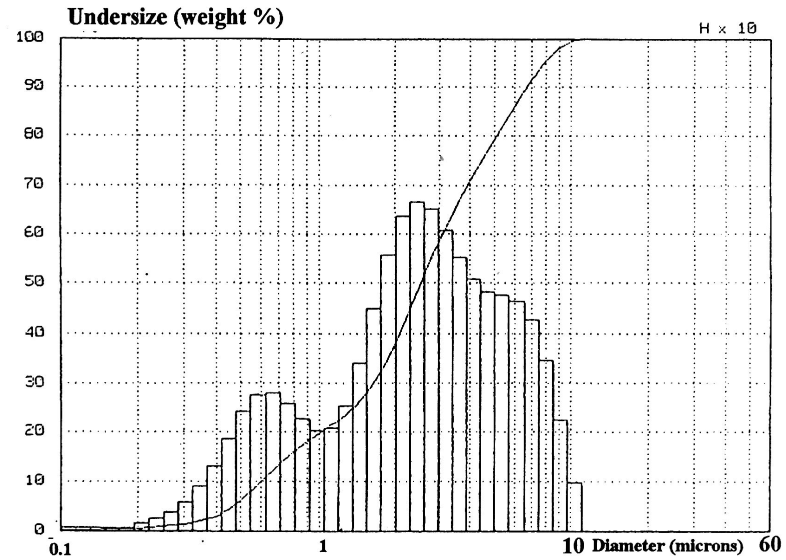

Fig. 1. Particle size distribution of alumina Alcoa CL 2500.

Median size:	*2.54 microns*		
Diameter for 90%:	*6.71 microns*	*and 10%:*	*0.60 microns*
Specific surface area:	*10139* cm^2/g		
200< Concentration < 400:	*317*		

Our intention to use additives was to promote the densification and grain growth between the liquid phase sintering process. The influence on desired microstructure development is positive in all cases (Figs. 2 and 3). SiO_2 content is the same in both additives, a part of CaO has only been exchanged with MgO to study the influence of these two oxides on microstructure.

The grains in the case of liquid phase with MgO content are smaller (Fig. 2 and Table 1). The finer microstructure in this case may be caused by precipitation of MgO on grain boundaries, and a slightly higher viscosity of MgO contained in the liquid phase.

The additive composition has no effect on densification but an important one on microstructure. A coarser microstructure, with large oriented corundum grains, and intragranular porosity and pores in the contacts of grains, is developed in the case with CaO and SiO_2 additives.

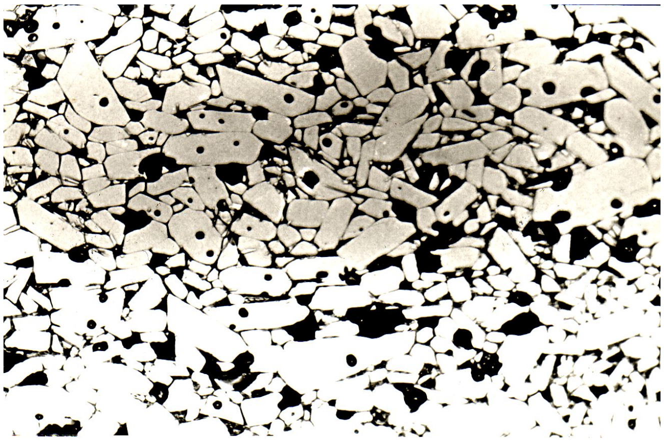

Fig. 2. Microstructure of sample 1, sintered 4 hours at 1700 °C, magnification: ×270.

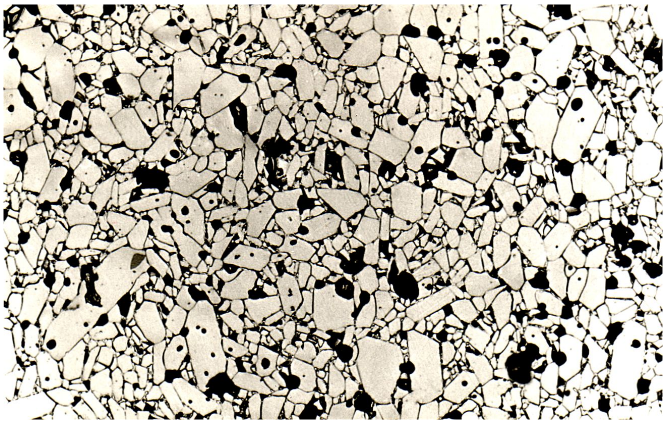

Fig. 3. Microstructure of sample 2, sintered 4 hours at 1700 °C, magnification: ×270.

4. Conclusions

The coarse grain starting alumina can be sintered to above 95% of the theoretical density with the additives from the CaO-MgO-SiO_2 or only from the CaO-SiO_2 system at 1700 °C.

The grain growth is influenced by composition of additives. Large grains are obtained with the additive from the CaO-SiO_2 system. In this case, after sintering at 1700 °C for 4 hours, grains above 15 μm are obtained. The alumina ceramics with these characteristics (grains above 15 μm large and density more than 95% of theoretical value) are suitable for the MoMn metallization.

The finer microstructure of the ceramics with MgO in additive composition can be improved with prolonged sintering.

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DODACI Al_2O_3 ZA KRUPNOZRNATE KERAMIKE ZA METALIZACIJU

Spojevi metal–keramika mnogo se upotrebljavaju kao trajni vakuumski spojevi. MoMn metalizacija se često upotrebljava radi velike čvrstoće, malih dielektričnih gubitaka i sl. Za tu metalizaciju nužne su krupnozrnate keramike koje se proizvode sinteriranjem Al_2O_3 s raznim dodacima koji pospješuju rast zrna u tekućoj fazi tijekom sinteriranja. U ovom radu opisuju se keramike s dodacima $CaO–SiO_2$ i $CaO–MgO–SiO_2$.