

## Microstructure of the microwave fast-sintered MgAl<sub>2</sub>O<sub>4</sub> ceramics

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Polycrystalline MgAl<sub>2</sub>O<sub>4</sub> spinel is considered as one of the major candidates for various applications that require a combination of properties including high optical / IR transparency and excellent mechanical performance, particularly in harsh environments. Among many different techniques to produce translucent or transparent spinel, the two-stage method based on the pressureless or hot press sintering with subsequent hot isostatic pressing (HIP) proved itself the most successful. But high pressure ( $\geq 150$  MPa) and high temperature ( $\geq 1600$  °C) commonly used in HIP greatly limit the potential of its use.

Recently, a significant attention has been attracted to the investigation of very rapid ("flash") sintering of ceramics achieved by applying a dc or ac voltage to the sample [1]. In these experiments, many (mostly oxide) ceramics have been sintered nearly to full density in several seconds. In particular, in [2] the MgAl<sub>2</sub>O<sub>4</sub> spinel was flash sintered to a relative density of 97.9 % at the applied DC field of 1000 V/cm. This paper reports on the fast microwave sintering of MgAl<sub>2</sub>O<sub>4</sub> ceramics to nearly full density under high-rate heating and zero isothermal hold time.

Magnesium aluminate spinel powder was produced from isopropoxide MgAl<sub>2</sub>(OPr<sup>i</sup>)<sub>8</sub> by method described in detail elsewhere [3]. Specific surface area of powder was about 100 m<sup>2</sup>/g after calcining in air at T = 900 °C. Samples with 15 mm dia and 2.5 mm thickness were uniaxially pressed at 300 MPa to a relative density of 39 % of the theoretical value. Some samples were impregnated with yttrium oxide which was introduced by dipping them into 0.5 mol/l water solution of Y(NO<sub>3</sub>)<sub>3</sub> with consequent heating in air at 70 °C. The content of Y<sub>2</sub>O<sub>3</sub> in these samples was equal to 0.8–1.0 % wt.

Samples were heated in the applicator of a gyrotron system with a microwave power up to 6 kW at a frequency of 24 GHz with a feedback computer control of the power. The details of the experimental scheme can be found in [4]. Samples were heated at 2–4 MPa pressure of the residual air at a rate of 50 °C/min up to 1250 °C and then at rates of 15...200 °C/min to the preset maximum temperature of sintering, T<sub>max</sub>, in the range of 1400–1780 °C. When the preset T<sub>max</sub> was reached, the microwave power was switched off automatically and a sample cooled down along with the thermal insulation.

Shown in Fig. 1 are the relative densities of the pristine and Y-doped samples heated at a rate of 100 °C/min as the function of the temperature T<sub>max</sub>. The relative density of the Y-doped samples exceeded 99 % at all rates of heating to T<sub>max</sub>  $\geq$  1500 °C, whereas it was about 98 % for the pristine samples at T<sub>max</sub>  $\geq$  1600 °C. The relative densities of doped and pristine samples sintered conventionally in the similar regimes at T<sub>max</sub> = 1500 °C were only 92.2 and 89.1%, respectively.

The density of Y-doped samples starts to exceed the density of pristine samples at T<sub>max</sub> above 1400 °C.

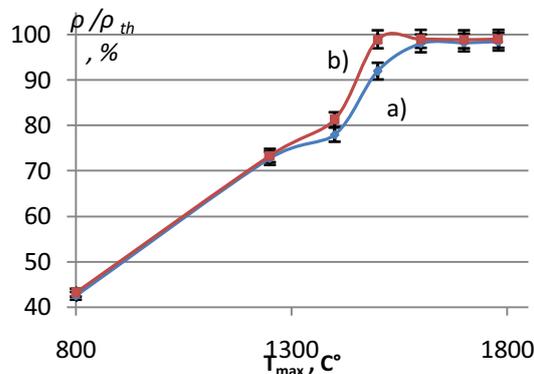


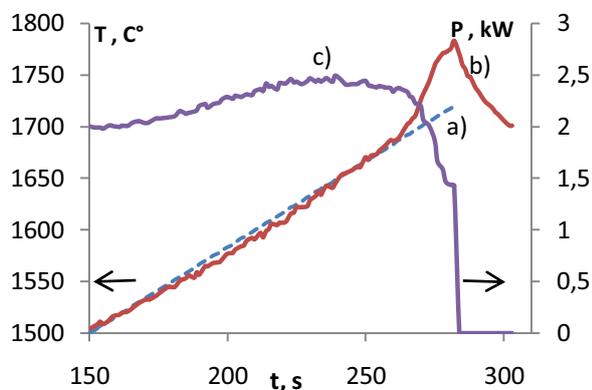
Fig. 1. Density of pristine (a) and Y-doped (b) samples heated at a rate of 100 °C/min to the temperature T<sub>max</sub>

The densification enhancement of Y-doped samples is explained by the changeover to the transient liquid phase sintering, as it is clear from the data on T(t) and P<sub>mw</sub>(t) behavior at the final stage of heating. It can be seen that at T  $\geq$  1600 °C the microwave power P<sub>mw</sub> required to sustain the prescribed heating rate does not increase (as it should due to the growth of the heat losses from the sample, which are proportional to T<sup>4</sup>) and even falls down towards the end of the process (Fig. 2). The decrease in the microwave power can only be explained by a sharp increase in the microwave absorption coefficient, i.e. in the effective high-frequency conductivity of the material of the sample, which is associated with the development of the thermal instability. The onset temperature of the instability decreases with an increase in the microwave power deposited per unit volume of sample.

The mechanism of fast densification caused by the development of thermal instability has been suggested in [4, 5]. In brief, if the temperature and the density of the deposited power are high enough, the particle surface pre-melts at a temperature well below the melting point of the bulk of grains due to the abundance of impurities and defects in the near-surface layer. All the mechanisms inherent in liquid phase sintering become activated in the transient quasi-liquid medium, leading to an accelerated densification.

The crucial role of the liquid phase formation in the process of fast microwave MgAl<sub>2</sub>O<sub>4</sub> ceramics sintering is confirmed by the study of the microstructure of the sintered samples. As seen from the SEM image of the unpolished surface of a sample sintered at T<sub>max</sub> = 1500 °C (Fig. 3a), it has a dense and uniform microstructure with an average grain size of about 150 nm, close to the initial particle size. At higher temperature, T<sub>max</sub>  $\geq$  1600 °C,

intense abnormal grain growth (AGG) takes place, much more pronounced in the Y-doped samples (Fig. 3b). It is well-known that AGG is typical for liquid phase sintering. The morphology of the microstructure suggests that the growth of large-size grains occurs by some collective effects rather than by the ordinary mechanism based on the grain boundary mobility of individual particles.



**Fig. 2.** Time dependence of the preset (a) and actual (b) temperatures, and microwave power (c) during heating of an Y-doped sample at a rate of 100 °C/min to  $T_{\max} = 1780^{\circ}\text{C}$

The formation of the liquid phase at the high temperature stage of sintering is confirmed also by the effect of fast segregation of Y atoms at the boundaries of the growing grains (Fig. 3c). From the pattern and scale of Y atoms distribution, seen in the SEM images as white

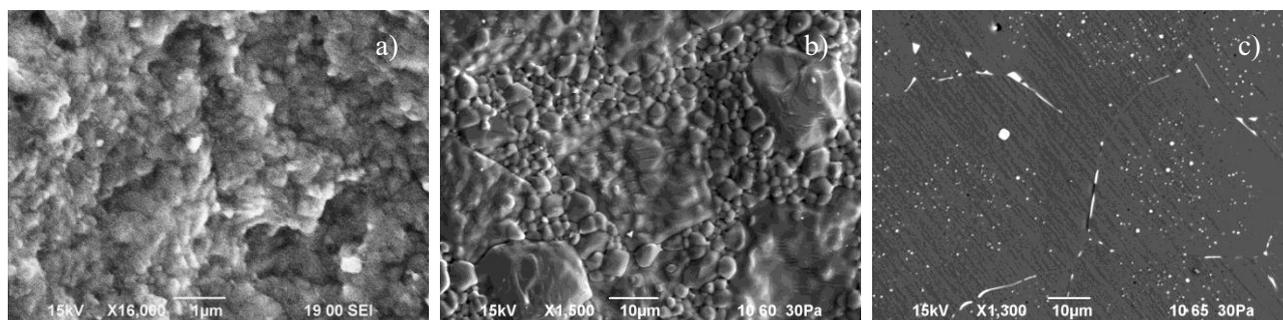
lines along boundaries, the grain boundary mobility can be estimated, which, as it turns out, exceeds the value measured from normal grain growth in dense stoichiometric  $\text{MgAl}_2\text{O}_4$  ceramics [6] by a factor of  $10^2 - 10^3$ .

The X-ray phase analysis revealed small amounts (about 1–2 wt. %) of Y-Al-O compositions in the fast microwave sintered Y-doped samples: the  $\text{Y}_4\text{Al}_2\text{O}_9$  phase is present in the samples heated to 1250 °C, and YAG – in the samples heated to 1780 °C. The composition  $\text{MgAl}_2\text{O}_4 - \text{YAG}$  has an eutectic temperature of 1775 °C at conventional heating under normal pressure. It is known that microwave heating can decrease the temperature of some phase transformations and solid state reactions [7]. One can not exclude a similar effect of the microwave heating on the reduction of the eutectic temperature of the given composition resulting in the earlier formation of the liquid phase.

The reason why the abnormal grain growth is also observed during the fast microwave heating of the pristine spinel needs further investigation.

In conclusion, we have demonstrated fast microwave sintering of  $\text{MgAl}_2\text{O}_4$ -ceramics to nearly full density in less than two minutes without any isothermal hold. The results of the microstructure study on the sintered samples show that the fast microwave densification of  $\text{MgAl}_2\text{O}_4$ -ceramics takes place by the transient liquid phase formation.

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**Fig. 3.** Microstructure of unpolished surface of Y-doped  $\text{MgAl}_2\text{O}_4$  sample sintered at 1500 °C (a) and at 1780 °C, unpolished (b) and polished surfaces (c)

## References

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