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# Grain growth suppression in alumina via doping and two-step sintering

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**Abstract**

Efficiency of two-step sintering on grain growth elimination in the final stage of sintering of polycrystalline alumina has long been considered questionable. The published works failed either to suppress the grain growth entirely or to achieve the relative densities above 99% where the grain growth is the most severe. This paper reports on successful grain growth elimination in the final stage of sintering of a sub-micron alumina ceramics by a combination of the two-stage sintering and doping with metal oxides (MgO, $ZrO_2$ or $Y_2O_3$). Relative densities up to 99.7% were achieved. Neither doping of aluminas sintered under conventional conditions nor the two-step sintering of pure alumina alone resulted in entire grain growth suppression in the final stage of sintering. A combination of the two-step heating regime with suitable doping (500 ppm MgO added as $MgAl_2O_4$ nanopowder) led to complete grain growth suppression at relative densities above 99%.


*Keywords:* A. Grain growth; A. Sintering; B. Grain size; Alumina ceramics; Microstructure – final

## 1. Introduction

Microstructure refinement in advanced ceramic materials is frequently related to improvement of mechanical properties [1–4]. Moreover, it often provides additional functionalities, such as transparency in visible and infrared wavelength range [5,6]. Many densification techniques, mostly pressure assisted processes such as hot pressing [7], hot isostatic pressing [8], spark plasma sintering [9–11], or pressure-less techniques such as microwave assisted sintering [12] and two-step sintering [13–15] were therefore applied in order to achieve full densification, while simultaneously suppressing grain growth in the final stage of sintering. Among them, two-step sintering [16] is of particular interest due to its simplicity, and possibility to achieve complete densification at relatively low temperature without application of pressure: its capacity has been demonstrated for a range of various systems [17–24]. Few works dealing with two-step sintering of alumina report on certain refinement of microstructure in comparison to conventional sintering. However, entire grain growth elimination was not achieved [13–15]. In our previous work we showed that a combination of two approaches, i.e. two-step sintering, and doping with suitable oxide additives, such as MgO, $Y_2O_3$ or $ZrO_2$ can result in suppression of the grain growth in the final stage of sintering [25].

Positive effect of the used additives on the microstructure refinement comes as no surprise: the impact of yttria, zirconia, and magnesia doping on densification and grain growth during the two-step sintering [25], and spark plasma sintering followed by hot isostatic pressing of doped polycrystalline alumina with submicron grains [26] as well as the change of activation energy of sintering through doping with various metal oxides [27] has been demonstrated previously.

The MgO is usually considered as the most effective agent for alumina grain growth suppression probably due to solute drag (or pinning) mechanisms. Bennison et al. [28] suggested that MgO reduces the grain boundary mobility as a solute in the corundum crystal or segregated preferentially in the grain boundaries, depending on the type and amount of present impurities. Jo et al. [29] attributed the effect of magnesia to

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roughening of originally atomically smooth alumina faces. The grain growth is then not controlled by interface reaction, but by diffusion, and increased number of grains which can grow impinge each other, resulting in final grain size decrease. The roughening of atomically smooth surfaces explains also the enhanced densification rate, because the diffusion can progress much faster in the systems with disordered grain boundaries [29]. The important role of grain boundary structure of doped alumina was also proved by Dillon et al. [30]. They showed that doping of $Al_2O_3$ with different elements can alter grain boundary structure which than has huge influence on the grain grow kinetics of particular grain boundaries. Another important effect of MgO addition may be the easier way to find the kinetics window for TSS compared to pure alumina due to reduced sensitivity of microstructure to time–temperature regime applied during sintering. Reduced influence of the conditions applied during sintering on the mean size of alumina grains in MgO-doped alumina sintered by SPS comparing to pure, undoped alumina was reported by Struer et al. [31]. Doping with MgO thus could partly eliminate the strong influence of temperature observed in undoped two-step sintered alumina [13], and to eliminate the necessity of careful temperature control required for successful densification in a two-step regime.

Another group of dopants is represented by metal oxides, which strongly segregate at alumina–alumina interfaces, such as yttria and zirconia. Due to its limited solubility in alumina crystal lattice (~10 at ppm) yttrium segregates to alumina/alumina interfaces [32,33]. Large yttria cations segregated at the interfaces block the motion of $Al^{3+}$ and $O^{2-}$ ions along grain boundaries, which results in reduced grain-boundary diffusivity and decreased densification rate [34]. Nevertheless, the mechanisms responsible for observed microstructure refinement were not determined unambiguously [35]. Flattening of the sintering trajectory was observed in yttrium doped alumina sintered under conventional conditions, which reflected the fact that the doping decreased the grain growth rate more than the densification rate [36]. Similar effect on grain growth of $Al_2O_3$ was observed also by minor (up to 1000 ppm) $ZrO_2$ addition, and it was attributed to the segregation of $Zr^{4+}$ ions at the grain boundaries due to elastic strain caused by a misfit in ionic radii of zirconium and aluminium ions [37].

However, despite the success in terms of grain growth suppression achieved by the combination of a two-step sintering regime and doping with oxide additives reported in our previous work, full applicability of the two-step sintering for alumina, i.e. the ability to achieve complete densification (relative density > 99.5% t.d) with no grain growth in the final stage of sintering has remained questionable. The inhibition of grain growth was confirmed in the relative density range only up to ~98.5% t.d. However, the behaviour of the system at relative densities between 98.5% and 100% t.d., i.e. in the interval where the grain growth rate is usually the highest [27], was not mapped, as we failed to sinter studied materials to higher densities. In the present work the powder preparation method was modified by enhancing the homogenisation in order to reduce the amount of aggregates in doped powders. Conventional sintering experiments were also carried out both with doped and undoped samples in order to separate the effect of doping from the influence of two-step sintering regime on microstructure development. Both conventional, and two-step sintering regimes were optimised in order to obtain fully dense materials (> 99% t.d.), and then the parameters of sintered microstructures (relative density, and the mean grain size) were compared. Sintering trajectories were constructed and compared, with special attention paid to the mean grain size of fully dense materials. The efficiency of additives and the two-step sintering regime on grain growth inhibition were discussed and evaluated. The influence of a doping method (the way how the dopants were introduced) on densification behaviour was also analysed.

## 2. Materials and methods

High purity 99.99% commercial alumina powder (α-$Al_2O_3$, Taimicron TM-DAR, Taimei Chemicals Co., Ltd., Tokyo, Japan, primary particle size 150 nm and specific surface area 13.7 $m^2\ g^{-1}$, the values determined by the producer from SEM micrographs and BET analysis, respectively) was used as a starting material. Doped powders (500 ppm (mole) of Mg and Y or 250 ppm Zr with respect to $Al_2O_3$) were prepared by mixing 100 g of the alumina powder with respective amounts of suitable precursors: $Mg(NO_3)_2 \cdot 6H_2O$ (p.a., Lachema Brno, Czech Republic), zirconium acetate, and $Y(NO_3)_3 \cdot 6H_2O$ (99.8% purity, Sigma Aldrich). Zirconia was added in a lower amount than the other two dopants: formation of zirconia inclusions as a secondary phase was observed already at 500 ppm addition [25,38]. The presence of a second phase is undesirable in term of prospective application in preparation of fine-grained transparent alumina. The mixture was homogenised in a polyethylene jar in isopropanol (p.a., Sigma Aldrich) with high purity alumina milling balls for 20 h. The effect of prolonged homogenisation (20 h compared to 2 h in our previous study [25]) on elimination of aggregates was already evaluated by the sedimentation method [39], and in this work it should be proved by the study of densification. The water solution of ammonia was then added in order to precipitate respective hydroxides ($Mg(OH)_2$, $Y(OH)_3$, $Zr(OH)_4$). The mixtures were then further homogenised for 4 h to complete the hydrolysis, and the solvent was removed in a vacuum evaporator. The powders were crushed with a pestle in an agate mortar, sieved through a 100 μm polyethylene sieve, calcined for 1 h at 800 °C in air, and sieved again to obtain a reasonably free flowing powder. The powder was stored in a laboratory drying cabinet at 100 °C in order to avoid aggregation of the powder caused by water absorption [40]. The specimens containing MgO, $Y_2O_3$ and $ZrO_2$ are denoted as AM, AY, and AZ, respectively. To ensure proper comparison with the doped powders, the reference alumina powder (denoted as A) was treated in the same way (milling in isopropanol for 20 h, addition of ammonia, milling for 4 h, removing the solvent, sieving, and calcination for 1 h at 800 °C).

To avoid calcination, which was found to impair densification of alumina powders [25], an alternative way was devised for preparation of the MgO-containing mixtures. Doped powders were prepared by mixing the Taimicron TM DAR