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Study of pore closure during pressure-less sintering of advanced oxide ceramics

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ABSTRACT

Capsule-free hot isostatic pressing (HIP) represents a cost-effective variant to classical HIP allowing production of ceramics with top properties. For successful application of capsule-free HIP it is necessary to close all pores to prevent infiltration of the high-pressure gas into ceramics. This occurs when the sample completely transits from 2nd to 3rd stage of sintering, i.e. all open pores get closed at a density called critical density. A robust experimental study of this transition for several materials (alumina, magnesia-alumina spinel, tetragonal and cubic zirconia) has been carried out and compared with three theoretical models. From theoretical models it follows that critical density is a material parameter depending only on dihedral angle and being independent of particle size, green density and pore size distribution. It varies from 88.1% to 93.7% of theoretical density for studied materials and used models. Measured critical densities agree well with models by Beere and Carter & Glaeser for cubic systems (spinel and cubic zirconia). However, they do not match very well experimental data for alumina (hexagonal system) being in agreement with other open sources data. The sophisticated model by Svoboda et al. significantly underestimates the critical density for all systems. The reason of disagreement is analyzed in detail and several hypotheses explaining differences between the model and reality are proposed. It is recommended to use Beere's and Carter's & Glaeser's models for prediction of critical density, while the model by Svoboda et al. characterizes rather the stage of pore closing initiation.

1. Introduction

Material science faces demands on advanced materials with excellent and specific properties. Development of such materials utilizes a wide spectrum of methods. It is very well known, that material properties are predominantly determined by their microstructure, therefore the ability of tailoring microstructure is intensively examined. In case of sintering of ceramics, application of proper precisely given sintering conditions is necessary for producing materials with required microstructure (grain size, porosity, etc.).

Sintering occurs in three stages, which are characterized by specific microstructure features: (i) necks formation, (ii) open porosity network and (iii) closed porosity [1]. For sintering techniques needing airtight surface of the specimen, such as capsule-free hot isostatic pressing (HIP), the pressure-less presintering is used to reach the final sintering stage [2,3] with closed porosity. Such presintering allows replacing of technologically difficult encapsulation process necessary in standard HIP by capsule-free HIP. The leading idea of capsule-free HIP is following: pressure free sintering is carried out up to point of complete transition from open to closed pores and then subsequent HIP is applied to reach full density. If the HIP is applied before complete closing of pores, pressurized gas penetrates through open pore tunnels into the material and cancels the positive effect of the external gas pressure on forces acting between grains. Moreover, after closure of pores the trapped gas prevents them from their shrinking. If the HIP is applied significantly later than the pores get completely closed, the benefits of the HIP are reduced. Thus, exact determination of the complete pore closure represents a key step in processing.

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HIP provides significantly finer grain structure in final product than in case of mere pressure-less sintering [4]. Pore closure triggers accelerated grain growth [5], leading to deterioration of numerous functional properties (optical transparency [6], mechanical properties [7], etc.). Therefore it is extremely important to reduce temperature and time in this last stage and utilize the mechanical driving force provided by HIP as much as possible. Thus the complex study and understanding of the transition between the open and closed porosity stage is highly required.

According to the authors' best knowledge there are only few theoretical models [8–11] dealing with pore closure phenomena and no relevant experimental research, which confirms or disproves these theoretical models. For every examined material numerous experiments have to be executed, which makes the efforts highly time and material consuming.

Every theoretical model must simplify reality and must target only to specific problems. Therefore recent models assume periodic structures and use as unit cells e.g. tetracaidekahedrons (as Coble [12] proposed in the model for the second stage of sintering). The instability of cylindrical open pores is well described by Rayleigh [13] criterion and all recent models utilize this criterion directly or in a modified way.

Confrontation of the theoretical models with experimental data for various oxide ceramic materials (alumina, cubic & tetragonal zirconia and magnesia-alumina spinel) is the main goal of this paper, which should contribute to understanding of sintering behavior and processing optimization of advanced ceramics.

2. Theoretical models

The first theoretical approach dealing with pore closure is a simple, strictly geometrical theory by Budworth [8], which defines transition from open to closed porosity at about 92% of relative density independently on material properties. The idea is based on idealized polyhedral grain structure consisting of tetrakaidecahedrons and idealized tubular pore structure situated on grain edges. Cylindrical pores meet at the vertices and have dihedral angle 180°. Such an assumption is far from the reality as the dihedral angle is always smaller than 180° due to grain boundary – pore surface interaction.

Models of Beere [9] and Carter & Glaeser [10] incorporated the grain boundary – pore surface interaction in their calculations and derived the dependence of critical density (i.e. relative density of transition from open to closed porosity stage) on dihedral angle. Beere presented a model of grain edge porosity covering a wide range of surface to grain boundary energy ratios characterizing various materials. The model is based on energetics of the system and predicts shape, mean surface curvature and stability of pores. The geometry of pore structure is no more mere cylinder, and porosity has a complex shape. The equilibrium shape of grain edge pores is calculated for idealized tetrakaidecahedron grain structure and the energy calculations are carried out for a unit cell corresponding to one grain corner.

Carter's & Glaeser's model is focused on application of Rayleigh instability criterion to intermediate stage of sintering. They considered condition for collapsing of a tubular pore channels along n-grain junctions (for our purposes and ability to compare with other models n was set to 3) as a function of dihedral angle. This model is an extension of Budworth's model incorporating geometrical dependence of critical density on dihedral angle.

The latest approach by Svoboda et al. [11] examined the influence of different periodic structures and dihedral angles and proposed a model showing that for low dihedral angles open porosity resembles interconnected pillow-shaped gaps between grain neighbors. This model computes equilibrium pores for various combinations of porosity and dihedral angle for simple cubic, bcc and fcc structures and provides a deeper insight into pore closure phenomena than previous models.

3. Experimental

3.1. Materials

Eight commercial powders of alumina, t-zirconia, c-zirconia and magnesia-alumina spinel were used for green body preparation. The parameters of powders are presented in Table 1. Whereas alumina and magnesia-alumina spinel are single phase materials with well-defined theoretical density (3.99 g/cm^3 for alumina [14,15], resp. 3.58 g/cm^3 for $MgAl_2O_4$ [16,17]), theoretical densities as well as lattice structure of yttria stabilized zirconias varies according to content of yttria and temperature. From equilibrium phase diagram it follows that for sintering temperatures above 1100°C ZrO_2 doped by 8 mol% Y_2O_3 is cubic and ZrO_2 doped by 3 mol% Y_2O_3 is a mixture of tetragonal and cubic phases with fractions depending on annealing temperature [18]. Since the variation in the phase composition due to temperature and also kinetic reasons causes only minor deviations in the theoretical densities (lower than 0.3%) [18], we employ commonly used literature values of theoretical densities: 6.08 g/cm^3 for ZrO_2 doped by 3 mol% Y_2O_3 [19,20] and 5.99 g/cm^3 for ZrO_2 doped by 8 mol% Y_2O_3 [21,22].

3.2. Green body preparation and microstructure

All powders were compacted to cylinder-like shapes by cold isostatic pressing (CIP) (Autoclave Eng., USA) using rubber moulds. Two different pressures were applied: 100 MPa for the first lot and 300 MPa for the second lot, which leads to different microstructures of green bodies made from the same powder.

After pressing, green bodies were annealed at 800°C/1h to ensure a sufficient strength for manipulation. Discs of diameter 30–32 mm and height 10–12 mm were cut to few smaller samples and polished on sand paper (polishing is not necessary, but it provides better handling during density measurements).

Pore size distribution in annealed green bodies was measured by mercury intrusion porosimetry (Pascal 440, Porotec, Germany). Assuming a reliable reproducibility, samples for measurement of porosity in green bodies were prepared in the same way as those for sintering. The maximum detectable pore diameter as well as the most frequent one were chosen as the quantitative parameters describing the porosity. The green density was measured by Archimedes method (EN 623-2) in distilled water. Three measurements of each sample were performed to establish the standard error.

3.3. Sintering and density measurements

Pressure-less sintering was performed in air in a resistance furnace with $MoSi_2$ heating elements (Heraeus, Germany). Samples were sintered without dwell at various temperatures (1300–1500°C) to achieve the total volume fraction of open pores V_o close to 0%. The heating rate was 10°C/min up to 800°C followed by 5°C/min, cooling rate was 25°C/min. At least 10 samples were sintered at various temperatures for each material and CIP pressure. Density of green bodies and sintered samples as well as ratio of open and closed porosity was determined using Archimedes method.