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Impact of powder morphology on quality of low-pressure injection moulded reaction-bonded net shape oxide ceramics

Nadja Schlechtriemen, Regina Knitter, Jürgen Haußelt, Joachim R. Binder *

Institute for Applied Materials (IAM-WPT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

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Abstract

Low-pressure injection moulding is a very efficient process for net shape manufacturing of ceramic micro parts. In order to obtain sintered ceramic specimens without shape distortion or damages, density gradients in the green bodies have to be avoided. Especially feedstocks with a solid loading near the critical powder volume content often tend to segregate the binder while flowing. However, the value of critical powder content can be significantly influenced by particle size, particle size distribution and particle morphology. This paper compares two powder mixtures of identical chemical compositions with different specific surfaces and morphology and evaluates their workability for low-pressure injection moulding. The aim of this paper is to identify the influence of morphology on feedstock rheology as well as on accuracy, mechanical properties and microstructure of net shape manufactured reaction-bonded zircon ceramics.

Keywords: Injection moulding; Powder morphology; Rheology; Net shape manufacturing

1. Introduction

The accuracy of ceramic devices can be enhanced by reducing the tolerance of sintering shrinkage and/or reducing the total shrinkage.[1] One of the proposed approaches to achieve net shape fabrication of ceramic components is a reaction-bonding process, which enables a reduction of total sintering shrinkage by volume expansion reactions. Common reaction-bonded ceramics are reaction-bonded silicon nitride (RBSN)[2–4] and reaction-bonded aluminium oxide (RBAO).[5,6] In contrast to these common reaction-bonded processes a complete compensation of the total sintering shrinkage can be realized by using intermetallic compounds such as $ZrAl_3$ or $ZrSi_2$. During oxidation, the increase in volume of these intermetallic compounds is much higher than that of metals. Therefore, the use of intermetallic phases allows the fabrication of dense reaction-bonded ceramics without any oversizing in the ternary system of Al_2O_3–SiO_2–ZrO_2.[7,8]

Besides reducing sintering shrinkage, accuracy can also be enhanced by an improved tolerance of sintering shrinkage, using particularly reliable and highly accurate shaping processes. Especially for manufacturing ceramic micro parts, a good interaction between material properties and shaping methods is essential. For the production of ceramic micro parts, low-pressure injection moulding (LPIM) has already proven to have excellent moulding capabilities and provides a high surface quality.[9–11] A combination of reaction-bonding net shape oxide ceramics and low-pressure injection moulding enables the economical production of ceramic micro devices with complex geometries and high aspect ratios.[12]

The required powder content for feedstocks of reaction-bonded net shape oxide ceramics to achieve zero shrinkage can be calculated as follows:

$$\tilde{V}_p = \frac{\rho_s \sum_{i=1}^{n} \tilde{m}_i/\rho_i}{\sum_{i=1}^{n} \tilde{m}_i(1+\Delta\tilde{m}_i)} \quad (1)$$

$\tilde{V}_p$ is the powder volume fraction; ρ_i is the density of reactant (g/cm^3); ρ_s is the sintering density of ceramic product (g/cm^3); m_i is the mass fraction of reactant (g/cm^3); Δm_i is the relative mass change of reactant.

To prepare a feedstock which is e.g. solely based on $ZrSi_2$, a powder content of about 50 vol.% is required to achieve zero shrinkage. Any addition of sintering additives, such as Al_2O_3 and MgO or the addition of ZrO_2 to adjust the Zr to Si ratio,

* Corresponding author. Tel.: +49 721 608 24743; fax: +49 721 608 24612.
E-mail address: joachim.binder@kit.edu (J.R. Binder).

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increases the powder content. For a composition with a Zr to Si ratio of 0.8, including 5.0 wt.% Al_2O_3 and 0.5 wt.% MgO, 61.3 vol.% powder are required to achieve zero shrinkage.

However, particularly when nearing the critical powder volume content, the feedstock rheology reacts increasingly sensitive to particle size, particle size distribution, and particle morphology. This paper describes the influence of powder morphology on the rheological properties and the workability of feedstocks for low-pressure injection moulding of reaction-bonded oxide ceramics. The reliability of the two compositions was compared by investigating the mechanical properties, the accuracy and the microstructure of injection moulded and reaction-sintered specimens.

2. Experimental

The two investigated powder mixtures with a Zr to Si ratio of 0.8 were composed of the main constituents $ZrSi_2$ (H.C. Starck) as the reactive component and monoclinic ZrO_2 (TZ-0, Tosoh). $ZrSi_2$ was pre-processed in an agitator bead mill to adjust the specific surface from approx. 1 m^2/g (as delivered) to the selected level of approx. 6 m^2/g. 5 wt.% γ-Al_2O_3 and 0.5 wt.% MgO (Merck) were added as sintering additives. To reduce the specific surface area for one of these compositions, the metal oxides – a powder mixture of ZrO_2, Al_2O_3, and MgO – were calcined in a chamber furnace (RHF1400, Carbolite) at 1300 °C for 10 h. The metal oxides and the intermetallic compound were homogenized in 100 g batches in a planetary ball mill (Pulverisette 5, Fritsch) with 100 g of ZrO_2 milling spheres (10 mm diameter) in 2-propanol (100 g) for 24 h. After the evaporation of the solvent the powder was ready for feedstock preparation. The powder mixtures were characterized by physisorption (Flow Sorb II 2300, Micromeritics) to measure the specific surface area and by scanning electron microscopy (Zeiss Supra 55). Phase analysis of the powder was carried out by X-ray powder diffractometry (XRD) using Cu Kα radiation (Siemens D 5000). The bulk density and the tap density of the powder mixtures were measured using a jolting volumeter (STAV2003, JEL). In addition, the powders were investigated by thermal gravimetric analysis (STA 449C, Netzsch) at temperatures up to 1450 °C and a heating rate of 5 K/min.

To produce 350 cm^3 of the feedstock, the binder was molten within a 1000 ml vessel at 100 °C in a heating cabinet. The binder consisted of a mixture of 7.5 wt.% Siliplast LP13 in 92.5 wt.% Siliplast LP65 (Zschimmer&Schwarz). Subsequently, the powder was incorporated into the feedstock by means of a heatable agitator (DISPERMAT©, Getzmann) with an 80 mm diameter agitator stirrer under vacuum at 110 °C. The maximum speed was 1250 rpm. Rheology was measured in a plate–plate system (PP25) of a rotating rheometer (MCR 300, Paar-Physica) with a gap of 0.5 mm. The temperature of measurement was 85 and 90 °C, respectively. Viscosity was measured under shear stress control up to 3000 Pa. The resulting flow curve was fitted with Eq. (2), which describes the flow behaviour of non-Newtonian suspensions according to the theory of Herschel–Bulkley[13]:

$$\tau = \tau_{HB} + c \cdot \dot{\gamma}^p \quad (2)$$

where τ is the shear stress and τ_{HB} is the yield stress according to Herschel–Bulkley in Pa. $\dot{\gamma}$ is the shear rate and c is the consistency index (also referred to as Herschel–Bulkley viscosity η_{HB}) in Pa s. The Herschel–Bulkley index p indicates shear thickening or shear thinning behaviour, for $p > 1$ or $p < 1$, respectively. Even if p reaches the value of 1, Bingham flow behaviour ($\tau_{HB} > 0$) or Newtonian behaviour ($\tau_{HB} = 0$) is still indicated.

The dependence of viscosity η on temperature at a shear stress of 100/s was measured from 105 °C down to 75 °C or from 120 °C down to 60 °C. The resulting behaviour of viscosity was fitted with Eq. (3) to determine the flow activation energy E_A of the feedstock according to Arrhenius.[13]

$$\ln \eta = \ln c + \left(\frac{-E_A}{R}\right) \cdot \left(\frac{1}{T}\right) \quad (3)$$

R stands for the gas constant, c for a material specific constant and T for the temperature in K.

The test specimens were manufactured by means of a LPIM-machine (GC-MPIM-2-MA, Goceram). After moulding, the paraffin was removed from the specimen during thermal debinding at 500 °C for 10 min (HT6/28, Carbolite). For this purpose the samples were placed on an alumina powder bed. Subsequent reaction-sintering was carried out at 1575 °C for 4 h in a high-temperature furnace (KaVo Everest© therm, KaVo Dental). The microstructures of the sintered ceramics were investigated by scanning electron microscopy on polished samples.

In order to characterize the mechanical properties, 45 test specimens of each composition were produced to investigate the biaxial bending strength in direct comparison. The samples were ground down to the desired dimension with a grit of 91 μm and were finished by lapping with a SiC-suspension of 9 μm. The overall dimensions of the specimens were assessed and their density was measured in ethanol using the Archimedes principle. Before measuring the mechanical properties, the samples were dried for 30 min at 150 °C in a heating cabinet (UT 6, Heraeus). The biaxial bending test was carried out in a universal testing machine (UTS 10, Zwick), using balls with $d = 3$ mm, a punch with $d = 1.5$ mm and a traverse speed of 0.2 mm/min. The bending strength was calculated according to ISO 6872.[14] Additionally the Vickers hardness (HV10) and the fracture toughness K_{IC} were determined for both compositions by means of the indenter method.[15]

A milled aluminium structure (Fig. 1) was chosen as master model for an accuracy test pattern.[12] The replication quality was qualified by comparing the dimensions of the master model and the green body. The accuracy of the whole process was evaluated by comparing the dimensions of the master model and the sintered specimen. For this the dimensions of the aluminium structure, green bodies and sintered samples were measured under a stereo microscope (Aristomet, Leica) equipped with a digital stage and a sensor control display (Leica). The z dimension (height) was measured with an attached mechano-optical scanning device (Heidenhain). The replication quality and accuracy of the moulded sample was evaluated by measuring the five pyramids of the micro part. Their widths (x, y) and heights (z)