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High-Temperature Elastic Properties of Ceramics in the System MgO-Al_2O_3-SiO_2 Measured by Impulse Excitation

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Abstract. Young's moduli of talc-based ceramics from the system MgO-Al_2O_3-SiO_2 are measured for temperatures up to 1000 °C via impulse excitation. It is shown that, after pressing at 50 MPa and firing at 1280 °C, MgO-rich compositions exhibit higher porosity and lower Young's moduli (approximately 20–30 % lower than predicted via micromechanical relations). The Young moduli of materials with less MgO decrease with temperature, but those of MgO-rich ceramics increase with temperature and exhibit a large hysteresis between heating and cooling. Lower absolute values are mainly due to increased porosity, but the reason for the modulus increase with temperature and the hysteresis is the higher enstatite content in the MgO-rich compositions. For a special composition the Young's moduli are more or less temperature-independent and without significant hysteresis effects, probably due to the low content of enstatite and the high content of sapphirine.

Introduction

Talc-based ceramics from the system MgO-Al_2O_3-SiO_2, in particular cordierite ceramics, are well known for their good mechanical properties, heat resistance and especially their low thermal expansion [1], which makes them ideally suited for high-temperature applications in which high thermal shock resistance is required. One of the most famous applications are automotive catalyst supports and diesel particulate filters [2,3], but they are used for many other applications as well. For all these the elastic constants are key properties and should be reliably known at high temperatures, because they are important indicators of high-temperature strength and affect thermal shock resistance. However, due to the complexity of these materials their high-temperature elastic properties have not been studied in great detail so far. This paper is an attempt to tackle with this problem from the viewpoint of micromechanics. Based on phase compositions and phase moduli, room temperature values of the effective Young's moduli are predicted via micromechanical relations and compared to values measured via impulse excitation. Characteristic features of the temperature dependence are discussed with respect to phase composition and microstructure.

Experimental

Raw Materials. The raw materials used in this work are kaolin (Sedlec Ia, Czech Republic), alumina (Almatis CT 3000 SG, Germany), talc (natural talc, Australia) and a premixed and granulated precursor powder (denoted here CT0) for commercial cordierite products. According to X-ray fluorescence (XRF) analysis, the kaolin contains 36.9 wt.% Al_2O_3 and 47.4 wt.% SiO_2, the talc 33.1 wt.% MgO and 64.4 wt.% SiO_2 (other oxides below 1 wt.%). The alumina is more than 99 % pure α-Al_2O_3. Particle sizes (median diameters), measured via laser diffraction, are 3.3 μm (kaolin), 9.0 µm (talc) and 0.9 µm (alumina). The premixed precursor powder CT0 had a median particle size of 5.4 µm, but the granule size was around 500 µm. The magnesia content of this powder (7.2 wt.%) is below that of stoichiometric cordierite (13.8 wt.%). Therefore, talc-rich raw material mixtures (denoted CT1, CT2, CT3) were prepared by adding more talc to the CT0 composition (resulting in batches containing 11.7, 23.2 and 33.7 wt.% of additional talc), thereby decreasing the relative alumina content. Another mixture (denoted KTA) was prepared by mixing kaolin, talc and alumina in the weight ratio 37 : 41 : 22, see [4]. In order to ensure complete homogenization, this mixture was prepared in the form of aqueous suspensions, ball-milled for 12 h, cast on plaster blocks, dried at 105 °C, crushed and dry-milled to obtain a granulate for pressing. MgO, Al_2O_3 and SiO_2 contents are 7.2–17.7, 38.9–24.4 and 49.3–55.0 wt.% for CT0, CT1, CT2 and CT3, respectively, and 11.4, 44.6 and 42.6 wt.% for KTA (contents of other oxides < 1.2 %).

Sample Preparation and Measurement Techniques. Bar-shaped specimens with dimensions 100 x 20 x approx. 10 mm were prepared by pressing (50 MPa) and subsequent firing at 1280 °C (heating rate 1 °C/min, dwell time 1 h). Bulk density and apparent porosity were characterized via the Archimedes method and the phase composition was determined by X-ray diffraction (XRD) using Cu-K_α radiation (PANalytical X'Pert PRO and High Score Plus, The Netherlands). Elastic properties were measured according to ASTM E-1876 from resonant frequencies of flexural vibrations obtained via impulse excitation (RDFA HT 1600, IMCE Belgium) up to 1000 °C.

Results and Discussion

Phase Composition and Young's Modulus Prediction. Table 1 lists the phase composition of the cordierite-containing ceramics after firing at 1280 °C, as determined via XRD, as well as the theoretical densities and Young moduli of the constituent phases at room temperature. For alumina, cordierite, cristobalite and mullite the Young moduli have been calculated from the stiffness tensor components of the monocrystals [2,5-8]. Due to the low firing temperature, the glass phase content is low (below 20 %). Assuming a glass composition corresponding to stoichiometric cordierite, the density is approximately 2.60 g/cm^3 [9] and the Young modulus of the $MgO-Al_2O_3-SiO_2$ glass phase can be estimated very roughly using empirical additivity rules and factors [10], resulting in a values of approximately 90 GPa. The Young modulus of (proto-) enstatite can be estimated based on the fact that the Young's modulus of steatite ceramics is below 100 MPa [1], and the Young's modulus of sapphirine has been adapted to make the value measured for the porous sapphirine-rich composition KTA lie below the corresponding upper Hashin-Shtrikman bound (see below). The density values can be used to transform weight fractions into volume fractions.

Table 1. Phase composition in wt.% of cordierite-containing ceramics after firing at 1280 °C, as determined via X-ray diffraction (semiquantitative analysis, crystalline phases only), as well as densities and Young's moduli of the constituent phases (values denoted * are estimated, see text).

Phase	CT0	CT1	CT2	CT3	KTA	Density [g/cm^3]	Young modulus [GPa]	Ref.
Alumina	20	12	7	7	4	3.99	400	[5]
Cordierite	56	55	34	29	43	2.63	141	[2]
Cristobalite	4	5	5	4	9	2.32	65	[6]
Enstatite	-	13	29	36	8	3.19	100 (*)	[1]
Mullite	13	9	7	6	10	3.14	225	[7]
Sapphirine	-	-	14	14	22	3.45	160 (*)	n.a.
Spinel	7	6	4	4	4	3.58	258	[8]

The theoretical (true) densities of the cordierite-containing ceramics listed in Table 2 are relatively independent of composition. The average value of 2.91 g/cm^3 is in good agreement with literature data for cordierite ceramics [3]. The total porosities calculated from these theoretical densities and the measured bulk densities are in the range 14–25 %. Based on the volume fractions and Young's moduli of the different phases, see Table 1, the effective Young's modulus of the solid phase (multiphase composite) can be calculated via the Paul bounds (Voigt-Reuss average) [11], while the upper Hashin-Shtrikman bound (HS+) restricts the Young's modulus for a certain porosity and our exponential model (exp.) [12,13] gives a rough prediction of the latter. The measured values listed in Table 2 show that the prediction is too high by 20–30 %. However, with regard to the many approximations and estimates required, this prediction must be considered satisfactory.

Table 2. Microstructure and properties of cordierite-containing ceramics after firing at 1280 °C, theoretical predictions (all values calculated for an intermediate glass content of 10 wt.%; the symbol ± denotes the deviation for 0 and 20 wt.% of glass, respectively) and experimental results.

Feature or property	CT0	CT1	CT2	CT3	KTA
Theor. density [g/cm^3] (calc.)	2.89 ± 0.04	2.85 ± 0.03	2.95 ± 0.05	2.99 ± 0.05	2.88 ± 0.02
Bulk density [g/cm^3] (meas.)	2.49	2.40	2.31	2.29	2.15
Total porosity [%] (calc.)	14.0	15.8	21.8	23.4	25.4
Apparent porosity [%] (meas.)	0.3	2.9	10.7	11.7	15.4
Young's modulus [GPa] (HS+)	123 ± 9	105 ± 6	85 ± 4	79 ± 6	79 ± 6
Young's modulus [GPa] (exp.)	118 ± 8	99 ± 6	76 ± 4	69 ± 5	67 ± 5
Young's modulus [GPa](meas.)	100	82	50	43	73

Temperature Dependence of Young's Modulus. Fig. 1 shows the temperature dependence of the Young modulus of the cordierite-containing ceramics prepared. It is evident that the absolute values decrease with increasing MgO content. This decrease is partly caused by increased porosity, but stronger than expected due to porosity effects alone (see Table 2). Moreover, while the base composition CT0 exhibits a decrease of Young's modulus with increasing temperature and negligible hysteresis, the MgO-rich compositions (CT1, CT2, CT3) exhibit an increase with increasing temperature and strong hysteresis effects between heating and cooling. Similar hysteresis effects have been found by other authors [14]. Considering the phase composition (Table 2) it is probable that the hysteresis is related to the content of enstatite which may exhibit phase transitions between low-and high-temperature polymorphs. On the other hand, the KTA materials exhibit intermediate Young's moduli that are more or less temperature-independent and without significant hysteresis effects, probably due to the low content of enstatite and the high content of sapphirine.

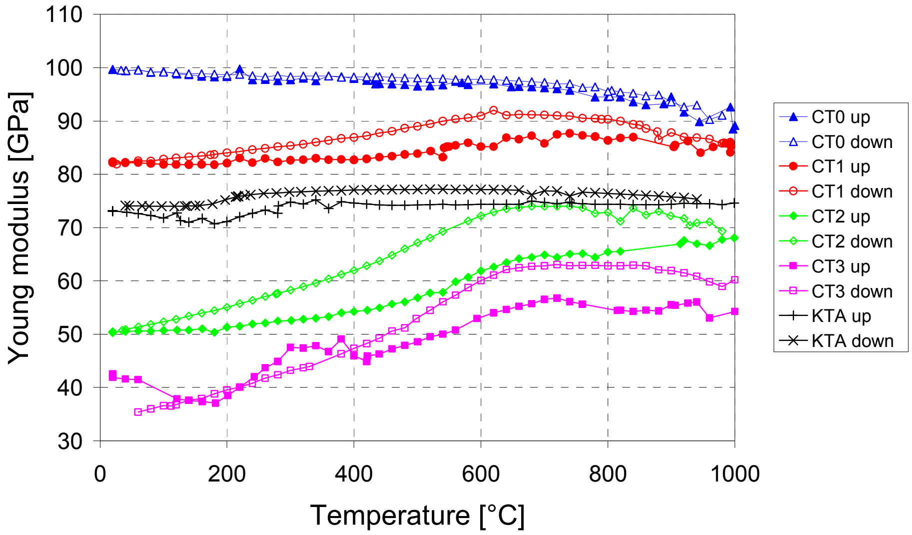

Figure 1. Temperature dependence of the Young modulus of cordierite-containing ceramics.

Summary

Young's moduli of talc-based ceramics from the system $MgO\text{-}Al_2O_3\text{-}SiO_2$ have been measured for temperatures up to 1000 °C via impulse excitation. It is shown that, after pressing at 50 MPa and firing at 1280 °C, compositions with increased MgO content exhibit higher porosity and lower Young's moduli (approximately 20–30 % lower than predicted via micromechanical relations). Moreover, while the Young moduli of the base materials decrease with temperature, the Young moduli of the MgO-richer ceramics increase with temperature and exhibit a large hysteresis between heating and cooling. While lower absolute values are mainly due to increased porosity, the reason for the modulus increase with temperature and the hysteresis seems to be the higher content of (proto-) enstatite in the MgO-rich compositions. For a special composition the Young's moduli have been found to be more or less temperature-independent and without significant hysteresis effects, probably due to the low content of enstatite and the high content of sapphirine.

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