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Mechanical properties of zirconia core-shell rods with porous core and dense shell prepared by thermoplastic co-extrusion

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ABSTRACT

Bi-layered zirconia rods of core-shell geometry with a porous core of different core porosities and a dense shell of various shell thicknesses were investigated. Core-shell structures were successfully prepared by thermoplastic co-extrusion of assembled feedrods. For comparison, non-layered rods with different porosities and tubes were also prepared. Mechanical properties of sintered core-shell rods were determined and compared with the properties of non-layered rods and tubes. Increasing porosity in the core of the core-shell rods decreased Young's modulus and the dense shell improved the fracture resistance of the core-shell rods against bending loading. The fracture force of core-shell rods was in all cases considerably higher than the fracture force of non-layered porous rods or tubes with the same Young's modulus. The fracture behaviour of core-shell rods and tubes was analysed and correlated with the calculated stress distribution in these structures. The principle of the core-shell concept was described and discussed.

1. Introduction

Steadily increasing requirements on the mechanical performance of ceramic materials that often go beyond the possibilities of single-phase homogeneous ceramic materials have led to the development of new concepts of material structures and composites. The bi-layered structure with core-shell geometry is a simple structural concept that can provide bodies with modified mechanical as well as functional properties. The core-shell structures can be prepared in the shape of axially symmetric bodies, e.g. rods or tubes, where a shell (outer layer) surrounds concentrically a core (inner layer). The core and the shell can be prepared with different ceramic materials [1–5], the same material but with different internal structures [6–9] or by a combination of both. The properties of composites do not depend simply on the composition of individual phases but they are also related to the mutual interactions between phases [10–13]. Insight into these interactions caused by individual phases is important for understanding the composite properties and makes a successful design and development of new structures and composites possible. Core-shell composites (as rods or tubes) can be prepared by many processing methods, e.g. the sacrificial template method [8,9], cold isostatic pressing [14], electrophoretic deposition [15–17], freeze casting [6], foam extrusion [7,18] and co-extrusion [4,19–22]. Co-extrusion, in particular, has proved to be a useful fabrication method of ceramic core-shell rods and tubes because of the processing simplicity, perfect joining of the core and shell materials, and low-cost production [4,23,24].

To date, many researchers have reported on investigations into modified mechanical properties of ceramic composites with layered structures, particularly planar laminates [10,25–28] and multi-layered tubes [17,24,29,30]. Liang and Blackburn [29] prepared tubes with ZrO_2/Al_2O_3 and ZTA/Al_2O_3 alternating layers. Tubes with the number of layers ranging from 5 to 15 were crack-free, and ZrO_2/Al_2O_3 layered tubes exhibited the same or higher flexural strength compared with the flexural strength of pure ZrO_2 and Al_2O_3 tubes. Mani and Paydar [24] prepared 4-layer anode tubes for solid oxide fuel cells by a co-extrusion process, previously demonstrated in principle by Powell and Blackburn [23], but in addition, they also studied the effect of multilayer structures on mechanical properties. Co-extruded multilayer anode tubes had higher flexural strength and higher Weibull modulus, and thus they were of higher reliability compared with extruded single-layer anode tubes coated with an electrolyte by the conventional paint-

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ing method [24]. Chen et al. [30] studied the fracture behaviour of porous laminated alumina tubes with a pore gradient. The results showed the fracture behaviour varying with the amount of the pore-forming agent, regardless of the number of laminated layers. Another detailed analysis of crack initiation and propagation in laminated SiC/C tubes loaded in radial compression has been reported by Vandeperre and Van der Biest [17]. They have reported a crack deflection in the layered structure and an increase in the work of fracture. Although detailed descriptions of mechanical behaviour of multi-layered ceramic tubes exist, reports on the mechanical behaviour of bi-layered core-shell composites are rather exceptional [4,5]. Bueno et al. [5] have reported improved surface hardness and wear resistance of bi-layered ceramics (alumina coated tetragonal zirconia) and only recently, Kastyl et al. [4] have presented improved flexural strength of co-extruded bi-layered ZTA/Al_2O_3 core-shell rods.

Elastic modulus of ceramic parts is one of the mechanical properties of high interest from the structural point of view. Materials with high flexibility (i.e. low Young's modulus) represent reduced internal stresses in strain-controlled applications. For bioceramics, a low Young's modulus similar to the modulus of bone is desired [31,32]. The decrease in Young's modulus can be achieved by introducing a phase with lower Young's modulus or by introducing pores. Usually, Young's modulus can be lowered by half via creating a 25–30% porosity [33–36]. However, with increasing porosity the strength, too, rapidly decreases [8,37,38]. The dependence of both quantities, Young's modulus, E, and strength, σ, on porosity (up to a pore volume fraction of 0.5) can be satisfactorily described by the following empirical relations [36,38]:

$$E = E_0 \cdot exp\left(-a\phi_P\right) \tag{1}$$

and

$$\sigma = \sigma_0 \cdot exp\left(-b\phi_P\right), \tag{2}$$

where E_0 and σ_0 are Young's modulus and strength of fully dense (non-porous) bodies, respectively, ϕ_P is the volume fraction of pores, and a, b are coefficients connected with the pore structure. The steep decrease in strength due to introducing pores into the ceramics is the main restriction on the modification of Young's modulus in non-layered (one-component) bodies. Therefore, we have proposed an approach to lowering Young's modulus without sacrificing flexural strength by using core-shell structures with porous cores and dense shells.

The present work extends our investigation into co-extruded core-shell rods with modified mechanical properties. In the previous paper [4] we have shown the benefits of a bi-material core-shell structure composed of dense ZTA core and dense alumina shell. In this paper, mechanical properties of bi-layered core-shell zirconia rods with porous core and dense shell are investigated and compared with mechanical properties of dense and porous non-layered rods and tubes. The aim of this investigation is to verify the possibility of lowering Young's modulus without sacrificing flexural strength by using the core-shell structure. Therefore, the research presented here is focused on evaluating the effect of core-shell geometry on Young's modulus and flexural strength of co-extruded core-shell rods with porous cores and dense shells.

2. Experimental procedure

2.1. Materials and preparation of samples

Zirconia powder stabilized with 3 mol% Y_2O_3 (TZ-3YS-E, Tosoh, Japan) with a specific surface area of 6.8 m^2/g was used for the preparation of ceramic samples (dense and porous rods, core-shell rods with porous core surrounded by dense shell and tubes). Tapioca starch (Farmer Brand, Thailand) with a particle size (d_{50}) of 15.5 μm was used as a pore forming agent and carbon black (Spheron 6000, CS Cabot, Czech Rep.) with a particle size (d_{50}) of 0.5 μm and a specific surface area of 20.5 m^2/g was used to produce a sacrificial core for tube manufacturing. A thermoplastic binder system was composed of ethylene-vinyl acetate (EVA) copolymer (Elvax 250, Du Pont de Nemours, USA) and paraffin wax (R-54/56, Slovnaft, Slovakia) [4,39–41]. Stearic acid (1.0067, Merck, Germany) was used as a surfactant. The composition of thermoplastic feedstocks is shown in Table 1. The thermoplastic feedstocks were prepared by mixing ceramic powder (or carbon black) with organic components in a two-blade high-shear kneader (HKD 0.6T, IKA-Werke, Germany) at a temperature of 120 °C for 2 h. Dense rods were extruded from basic zirconia feedstock (referred to as Z) and porous rods were extruded from zirconia feedstock filled with starch particles (referred to as ZST). Extrusion was carried out using a capillary rheometer (Galaxy V, Kayeness, USA) equipped with a conical nozzle with an inlet diameter of 9.55 mm and an outlet diameter of 3 mm that ended in a 12.5 mm long cylindrical part. The extrusion rate was 716 $mm^3 min^{-1}$, which corresponded to a shear rate of 4.5 s^{-1} in the cylindrical part of the nozzle. The extrusion temperature was 120 °C and the rod was extruded into distilled water with the water level 3 mm below the nozzle outlet. The temperature of the water was 23 °C in order to solidify the molten extrudate as quickly as possible and prevent any shape deformation of the extruded rods. The core-shell rods were co-extruded by piston extrusion of thermoplastic preforms called feedrods (assembled from both ceramic feedstocks used for the core and the shell). Co-extrusion conditions were the same as described for extrusion of non-layered rods. A detailed description of this approach (feedrod preparation and co-extrusion) can be found in our previous work [4]. The core-shell rods were co-extruded with starch filled feedstocks (ZST) in the core and surrounded by shell feedstock (Z). Co-extruded rods with 21.4, 30, or 40 vol% of starch in the core were referred to as ZST20-Z, ZST30-Z, or ZST40-Z, respectively. Thus, the core-shell rods were prepared with three different levels of porosity in the core and, moreover, with three different thicknesses of the shell. The shell thicknesses of the feedrods were 1.0, 1.5, and 2.0 mm, which corresponded to a theoretical shell thickness of 0.31, 0.47, and 0.63 mm after co-extrusion (applying a nozzle reduction ratio of 3.183). The ceramic tubes were co-extruded with carbon-based cores that were completely removed during sintering in air atmosphere, thus providing hollow tubes (referred to as CB-Z). All extruded and co-extruded rods were cut into 50 mm long test pieces.

The thermoplastic binder was removed in nitrogen atmosphere at a heating rate of 10 °C h^{-1} up to a temperature of 500 °C. Moreover, the heating rate was slowed down to 1 °C h^{-1} in the interval from 100 to 130 °C and a dwell time of 50 h at 130 °C was included. In order to obtain bodies with a sufficient handling strength, the debinding step was finished by heating up to 800 °C at a heating rate of 120 °C h^{-1}. During debinding, all the bodies were embedded in granular activated carbon (AY-5 12 × 30, Carbon Link, Wigan, U.K.) to obtain more homogeneous binder removal [42–44]. Samples containing starch (porous non-layered rods and core-shell rods) were additionally heat treated after debinding step at a rate of 50 °C h^{-1} up to a temperature of 900 °C in air atmosphere in order to completely remove all organic residues after the debinding process. Sintering took place in air atmosphere at a temperature of 1500 °C for 2 h. The heating to the sintering temperature was at a rate of 300 °C h^{-1} up to a temperature of 1200 °C and then at a rate of 100 °C h^{-1} up to 1500 °C.

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