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Polymer-derived ceramic tapes with small and negative thermal expansion coefficients

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ABSTRACT

A polysiloxane filled with ß-eucryptite and/or SiC was used for the processing of polymer derived ceramic tapes. The combination of both fillers in varying proportions allowed to tailor the overall bulk thermal expansion and the flexural strength of the resulting composite materials simultaneously. Incorporation of SiC increased noticeably the flexural strength of the samples and influenced the phase changes resulting from the interactions between the β-eucryptite filler and the polymer derived ceramic matrix. Changes in the phase composition and changes of the unit cell parameters of β-eucryptite because of the formation of solid-solutions with silica originating from the SiO_2 constituent of the polymer derived ceramic matrix were observed by Rietveld refinement. Tapes resulting from this process possess a sufficient mechanical stability and their coefficient of thermal expansion can be adjusted from slightly positive to moderate negative values.

1. Introduction

For over 50 years fabrication of high-performance ceramic materials via the pyrolysis of preceramic polymers draws attention. This approach allows to manufacture oxide and non-oxide ceramics without the limitations associated with conventional processing techniques. However, the processing of polymer-derived ceramics is limited due to high shrinkage during heat treatment, and uncontrolled crack and porosity formation, often resulting in non-sufficient mechanical properties.

A strategy to reduce shrinkage and reduce porosity during pyrolysis is the introduction of inert or active fillers in the polymer precursor, developed by Greil in 1995 [1]. Inert fillers serve as spaceholders and do not take part in chemical reactions during pyrolysis. Active fillers, however, react with decomposition products of preceramic polymers and/or the pyrolysis atmosphere. The reaction products help to decrease the shrinkage by forming new phases and they enable near-net-shape processing [2].

Due to their rheological properties some of the preceramic polymers may be suitable for tape casting. Manufacturing of polymer derived ceramic (PDC) tapes using a slurry consisting of a preceramic polymer filled with particles was demonstrated for Si-SiC [3], Si_3N_4-Al_2O_3 [4] or ß-SiC and resulting SiAlON formation [5].

A new context for tape casting is the use of fillers with negative thermal expansion coefficients. Bulk composites, combining materials with positive and negative thermal expansion have been extensively studied in last 20 years because of their technical applicability in fields, where high dimensional stability is required, i.e. in high-precision optics, electronic devices or cooking ware [6]. Combination of preceramic polymers and negative thermal exoansion (NTE) fillers may allow to simplify fabrication routes and to avoid handling steps at high temperatures [7].

A NTE filler used in [7] is β-eucryptite. It belongs to the system $Li_2O{\cdot}Al_2O_3{\cdot}xSiO_2$ with x = 2 giving its stoichiometric composition. It has the structure of β-quartz, which is stabilized by the incorporation of Li^+ ions. The charge is balanced by replacing half of Si^{4+} through Al^{3+}. In the structure Si and Al atoms are ordered in layers, alternating perpendicular to the c axis. Li atoms are situated in the structural channels, running parallel to the c axis [8].

The similarity between the eucryptite and the quartz structure enables the formation of solid solutions, which exist in the system Li_2O-Al_2O_3-$x{\cdot}SiO_2$ in a compositional range of $2 < x \leq 3.8$ [9]. When the SiO_2 content oversteps this range, the phase transformation into β-spodumene with an orthorhombic structure takes place at temperatures above 950 °C. The lowest negative coefficient of thermal expansion among the members of this system has β-eucryptite, and the coefficient of thermal expansion (CTE) increases with an increasing SiO_2 content, reaching a positive value prior to the eucryptite-spodumene transformation. The change of the SiO_2 fraction influences the lattice parameters of the eucryptite-based phase, and the a/c relation can be used for an approximation of the phase composition [9].

The reason why β-eucryptite filled composites show low mechanical

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properties is a high level of residual stresses in this material. They are formed due to an anisotropic thermal expansion: while the structure expands along the crystallographic a-axis with an increasing temperature, it contracts along their crystallographic c-axis, which results in an overall slightly negative CTE [10]. It was assumed, that a much lower negative value of the CTE found in compacted eucryptite samples compared to theoretical values derived from the elemental cell of the eucryptite results from microcracks in the polycrystalline material [11].

To improve the mechanical properties of NTE composites with β-eucryptite and to preserve an overall low or negative thermal expansion additional fillers possessing high strength may be added. A combination of aluminium borate whiskers and β-eucryptite particles, e. g., allowed to increase the Youngś modulus of an aluminium alloy matrix from 63 GPa to 100 GPa and to reduced the overall CTE compared to the CTE of the matrix from 23,78·10^{-6} K^{-1} to 13,5·10^{-6} K^{-1}. Because of the low mechanical strength of β-eucryptite the main contribution to the strength increase is due to aluminium borate whiskers [12].

Among different ceramic systems the combination of β-eucryptite and silicon carbide (SiC) showed very good mechanical properties. A variation of the filler proportion allowed to increase the Youngś modulus of the resulting composite (β-eucryptit/SiC proportion 73/27 vol %) from 102 GPa to 150 GPa, and a low CTE of 0.32·10^{-6} K^{-1} in the temperature range between −150 °C and 450 °C was retained [13].

The aim of this work is to demonstrate the feasibility of polymer derived ceramic tapes by using a polysiloxane-type preceramic polymer filled with ß-eucryptite as a NTE filler and SiC as a second filler. The combination of both fillers is supposed to provide higher strength to the resulting polymer-derived ceramic tapes and a control of the overall CTE by the variation of the filler composition.

2. Experimental

2.1. Materials and processing

A commercially available polysiloxane with the trade name Silres MK (Wacker AG, Germany) was used to prepare slurries with 50 vol% of filler materials. As fillers β-eucryptite and silicon carbide (SinSic 07, ESK-SiC GmbH, Germany) were used. β-eucryptite was synthesized via a solid-state route, details were described in [7]. Respective shares of fillers were varied: two single filler slurries and three slurries with different filler volume ratios were mixed (see Table 1). Single filler slurries will be further addressed as Euc and SiC. The notations Euc:SiC 2:1, Euc:SiC 1:1, Euc:SiC 1:2 correspond to eucryptite:SiC filler volume ratios of 2:1, 1:1, 1:2 respectively. Two catalysts were used to ensure cross-linking: oleic acid (VWR International, Germany) for the temperature range below 100 °C and aluminium acetylacetonate (Al (acac)$_3$, Merck, Germany) for the temperature range above 100 °C, for details please see [3].

First, the preceramic polymer was dissolved in 2-propanol, the volume ratio of the solid powder to isopropanol was adjusted to 1:1 to achieve optimal viscosity. As a next step, a desired amount of fillers was added to the mixtures followed by further agitation for 15 min. Subsequently, both catalysts were added to the slurries and the resulting mixtures were homogenized for 18 h by rotation in a closed container. Then the slurries were treated for 10 min with an ultrasonicator (Hielscher Ultrasonics GmbH, Germany) followed by mixing in a planetary centrifugal mixer (ThinkyMixer, ARE-250, Thinky Corporation, Japan) for 20 min at 2000 min^{-1}.

Table 1
Compositions for tape casting.

	Composition (vol%)				
	Euc	Euc:SiC 2:1	Euc:SiC 1:1	Euc:SiC 1:2	SiC
MK resin	49.5	49.5	49.5	49.5	49.5
β-eucryptite	49.5	33.75	15.75	14.75	–
SiC	–	15.75	15.75	33.75	49.5
Al(acac)$_3$	0.5	0.5	0.5	0.5	0.5
Oleic acid	0.5	0.5	0.5	0.5	0.5

Slurries were cast manually with a manually operated tape casting bladeonto a non-adhesive polyethylene terephthalate support tape, fixed on a plain glass plate prior to the casting process. The green-tape thickness was adjusted to 2.5 mm. For the slurry with the single filler SiC a modified method was applied due to enhanced tendency of crack formation: the green-tape thickness was decreased to 1.5 mm and after the cross-lining step a second layer with the same thickness was applied by overcasting.

After drying for 24 h the tapes were cut into sheets of a size of 25 mm × 25 mm or into specimens with dimensions required for specific characterization method. Cross-linking was carried out stepwise by heating to 40 °C, 60 °C, 90 °C, 120 °C, 160 °C, 200 °C with a heating rate of 1 K miñ^1, and each cross-linking step lasted for 4 h. The tapes were pyrolyzed subsequently at temperatures between 800 °C and 1100 °C under a constant argon flow. Heating and cooling rates were adjusted to 1 K miñ^1 and 3 K min^{-1}, respectively.

2.2. Characterization

For particle size measurements, a laser diffraction technique was applied using a particle size analyser of the type Mastersizer 2000 (Malvern Instruments GmbH, Germany). The filler materials were dispersed in water prior to the measurements.

Rheological measurements of the polymer/filler slurries were carried out using a rotational viscometer Physica MCR 301 (Anton Paar GmbH, Austria). The viscositiesy were measured at room temperature (25 °C) as a function of the shear rate in rotational mode with shear rates varying from 0.1 s^{-1} to 100 s^{-1}.

Simultaneous thermal analysis (STA) including thermogravimetric analysis (TG) and differential thermal analysis (DTA) of the non-pyrolyzed and already cross-linked substrates was carried out with a simultaneous thermal analyzer (STA 449 F3 Jupiter, Netzsch, Germany) in argon atmosphere in a temperature range between 20 °C and 1100 °C. For measurements of the coefficient of thermal expansion pyrolyzed samples with dimensions of 25 mm × 8 mm × 2 mm were used. Measurements were carried out with a heating rate of 5 K min^{-1} up to 1000 °C for samples pyrolyzed at 1000 °C and 1100 °C and up to 800 °C and 900 °C for those samples pyrolyzed at 800 °C and 900 °C, to ensure to not exceed the pyrolysis maximum temperature. Measurements were carried out in argon atmosphere with a Netzsch 420C dilatometer (Netzsch, Germany) equipped with an Al$_2$O$_3$ pushrod and sample holder. Prior to actual measurements a calibration measurement with an alumina standard was conducted to obtain a calibration curve, which was later automatically used by the Proteus software (Proteus 6.0.0, Netzsch, Germany) to correct the shrinkage data. To preserve contact between the sample and the pushrod a nominal load of 25 cN was applied during heating.

To characterize crystalline phases formed during pyrolysis, x-ray analysis was performed using an x-ray diffractometer Empyrean (PANalytical GmbH, Germany) with Cu-Kα radiation in a theta-2 theta (Bragg-Brentano) setup. The identification of crystalline phases was carried out with the software package HighScore Plus 3.0.4 (PANalytical, Netherlands) and the software package TOPAS Academic V4.1 (Coelho Software, Australia) was used to calculate the relative amounts of crystalline phases.

During the Rietveld refinement the instrument contribution to the line broadening was described by the fundamental parameters approach [14]. Instrument related parameters (X-ray tube emission profile, axial beam divergence and slit contributions) were refined in a Pawley fit to a LaB$_6$ (10 μm grain size, Sigma-Aldrich, Germany) sample diffractogram. These instrument parameters were then fixed in the Rietveld analysis of the respective specimens. For each sample global