Ceramics International (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Polymer derived ceramics with β-eucryptite fillers: A novel processing route to negative and near zero expansion materials

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ARTICLE INFO

Keywords:
Polymer derived ceramics
Negative thermal expansion
Pyrolysis

ABSTRACT

A polymer derived ceramic with near-zero or negative thermal expansion was manufactured from a powder mixture consisting of β-eucryptite fillers having a negative thermal expansion, and a polymethylsilsesquioxane preceramic polymer. The composite starting material was manufactured by ball-milling and warm-pressing and pyrolysis in inert atmosphere. The thermal expansion behavior of the composite material was controlled via the filler volume fraction and via the pyrolysis temperature. An influence of the filler material on the pyrolysis process was found.

1. Introduction

Over the last 60 years or so a class of material attracted increasing interest because of its opposite behavior to that of materials with common thermal expansion. These materials, which contract during heating, are known as negative thermal expansion materials (NTE-materials); among them is the synthetic mineral β-eucryptite, a representative of the Li_2O-Al_2O_3-x·SiO_2 compositional family.

The material system Li_2O-Al_2O_3-x·SiO_2 provides several phases with a negative or a very low coefficients of thermal expansion (CTE), which have already gained enormous industrial interest, i.e. to produce zero-expansion glass-ceramics such as CERAN® or ZERODUR®, both by Schott AG, Mainz, Germany [1]. The lowest CTE among the members of this system was reported for the composition Li_2O-Al_2O_3–2·SiO_2 (β-eucryptite). Its crystallographic structure might be addressed as a Li-stuffed derivative of high-quartz; it allows to form a solid solution with SiO_2.

Composites of β-eucryptite with different ceramic and metal matrices with a tailored CTE have already been reported, i.e. for a copper matrix to combine a low CTE with high thermal conductivity. Those applications have potential as electronic packaging and electronic heat sinks [2]. A composition of this materials with a volume fraction of 45% β-eucryptite and 55% copper possesses a CTE of $11\times10^{-6}\ K^{-1}$; in comparison: the CTE of plain copper is $16.6\times10^{-6}\ K^{-1}$ [3].

For ceramic composites with a near zero CTE the use of oxides as matrix materials was reported. For example, a composite combining yttria partially stabilized zirconia with 55 wt% or 65 wt% of β-eucryptite exhibited a CTE of $1.45\times10^{-6}\ K^{-1}$ and $-0.52\times10^{-6}\ K^{-1}$, respectively, and a relative high bending strength of 220 MPa for 55 wt% β-eucryptite filled material. A maximum strength was achieved, when the grains of the NTE material were embedded in a continuous matrix of high strength grains [4,5].

This paper deals with a new approach for the manufacturing of ceramic composites with negative CTEs by using preceramic polymers. Among the different preceramic polymers the polysilsesquioxanes, also known as silicones, are commercially available in a wide compositional range. These materials are in a liquid or in a solid state, meltable or soluble in organic solvents and may be crosslinked for the transition from the thermoplastic into the thermoset state. They show a high ceramic yield – often above 70% – when pyrolyzed in inert atmosphere. During pyrolysis to form polymer derived ceramics (PDCs) these materials suffer from porosity formation and a high linear shrinkage; both can be compensated or minimized by the introduction of fillers. An overview can be found, e.g. in [6,7].

The use of preceramic polymers as matrix material allows the application of polymer processing technologies for the manufacturing of PDCs with NTE fillers. The adjustment of the volume ratios of the preceramic polymer matrix and the β-eucryptite filler, and the pyrolysis regime (temperature, pyrolysis atmosphere) are crucial parameters affecting the CTEs of the resulting polymer derived ceramic material.

In this paper the preparation of a polymer-derived ceramic with β-eucryptite NTE filler particles is demonstrated and the resulting thermal expansion properties are discussed. Particular attention is paid to the filler's influence on the thermal transformation of the preceramic polymer during pyrolysis.

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http://dx.doi.org/10.1016/j.ceramint.2016.12.099
Received 14 October 2016; Received in revised form 6 December 2016; Accepted 19 December 2016
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Please cite this article as: Fedorova, A., Ceramics International (2016), http://dx.doi.org/10.1016/j.ceramint.2016.12.099

2. Experimental

2.1. Materials processing

The filler β-eucryptite was synthesized from the commercially available raw materials Li_2CO_3, $Al(OH)_3$ and SiO_2 (all by Merck KGaA, Germany) according to the procedure described in [8]. The starting powders were mixed a ceramic mortar to form the stoichiometric composition of eucryptite (LiO_2: Al_2O_3: SiO_2 molar ratio 1:2:2). Isopropanol was added to improve the homogeneity of the components; the volume ratio of the solid powder to isopropanol was adjusted to 2:1. The mixture was transferred to a planetary ball mill (Retsch PM 400, Germany) together with silicon nitride mixing balls with 5 mm in diameter. After a 24 h mixing procedure and subsequent drying at room temperature the mixture was re-milled and thermally treated in air at 700 °C for 4 h and then at 1300 °C for another 4 h to achieve a maximum amount of β-eucryptite. X-ray powder diffraction analysis of the material proved a high purity of the as-received β-eucryptite, however the X-ray powder patterns indicated a small amount of impurities within the synthesized material. For the measurement of the thermal expansion, part of the powder was separated after heat treatment at 700 °C and subsequently compacted with a pressure of 150 MPa and a holding time of 30 s. The diameter of these specimens was 30 mm. These compacted bodies were cut into specimens with a size of 25 mm×2.5 mm×5 mm and heat treated at 1300 °C for 4 h.

For the manufacturing of the NTE composite materials a commercially available polysilsesquioxane (Silres MK, Wacker Siltronic GmbH, Burghausen, Germany) was mixed with β-eucryptite as NTE filler, and a filler volume fraction of 40%, 50% and 60% was adjusted. The powders were sieved to pass through a 500 µm mesh net and mixed in a ball mill with alumina balls with 10 mm in diameter. The powders were then warm-pressed at a pressure of 35 MPa at 200 °C in a round mold with 40 mm in diameter. The green compacts were cut to obtain a desirable geometry for CTE analysis, and they were subsequently pyrolyzed in argon or in nitrogen for 1 h in a temperature range from 800 °C to 1100 °C.

2.2. Materials characterization

In order to get information about the influence of the filler material on the pyrolysis course, plain non-crosslinked polysilsesquioxane (MK) samples and MK cross-linked at 200 °C were investigated. MK and non-crosslinked MK/filler mixtures are labeled as "untreated", MK and MK/filler mixtures after heat treatment at 200 °C are labeled as "crosslinked" and specimens after pyrolysis in Ar or in N_2 are labeled as "pyrolyzed".

The pyrolytic transformation from the MK/filler mixture to the polymer derived ceramic material was characterized with a simultaneous thermal analyzer (STA 449 F3 Jupiter, Netzsch, Selb, Germany). About 50 mg of the non-pyrolyzed, warm-pressed samples were transferred into high purity aluminum oxide crucibles (purity level 99.7% Al_2O_3) and investigated under argon (99.99%) and under nitrogen (99.99%) atmosphere. The flow rate was 50 ml min^{-1}; the heating rate was 10 K min^{-1}, data were recorded from 25 °C to 1150 °C.

Mass spectrometry was conducted for the crosslinked, filler-free polymer (MK (200 °C) and for MK/filler mixtures with a sector field mass spectrometer MAT 95 (Finnigan, Bremen, Deutschland). The specimens were held at room temperature for 30 s, then heated up to 200 °C within 2 min and held at this temperature for another 30 s.

Due to limitations of in temperature with this equipment mass spectroscopy at higher temperatures were conducted with a quadrupole mass spectrometre (Quadrex 200, Laybold Heraeus, 70 eV, electron impact) coupled with a mass loss analyzer. All measurements were carried out under helium (purity of 99.999%) with a flow rate of 25 ml min^{-1}. The samples were heated in alumina crucibles up to 1200 °C with a heating rate of 10 K min^{-1}. Data recording was carried out over the entire temperature range.

Dimensional changes during pyrolysis were measured with a Netzsch 420C dilatometer (Netzsch GmbH & Co. KG, Selb, Germany) equipped with an alumina pushrod and an alumina sample holder. The measurements were performed in argon and in nitrogen atmosphere with a heating rate of 5 K min^{-1} up to 1200 °C. Compacted samples of pure β-eucryptite were measured with a heating rate of 5 K min^{-1} up to 1000 °C in argon. Prior to a series of dilatometer measurement a calibration measurement with an alumina standard was conducted, and the resulting calibration curve was implemented in the analysis procedure of the Proteus software package (Proteus 6.0.0, Netzsch GmbH & Co. KG, Selb, Germany) for proper data correction. To preserve the contact between the sample specimens and the pushrod of the dilatometer a nominal load of 25 cN was applied during heating.

X-ray powder diffraction analysis (XRD) was carried out with the as-receieved β-eucryptite powder and with powdered MK/filler specimens pyrolyzed at different temperatures using an X-ray diffractometer Empyrean (PANalytical GmbH, Kassel, Germany) with Cu-Kα radiation. The identification of crystalline phases and its amounts was conducted with the software package HighScore Plus (HighScore Plus 3.0.4, PANalytical, Almelo, Netherlands) and the software package TOPAS (TOPAS-Academic V4.1, Bruker, Karlsruhe, Germany).

The microstructure of the samples was characterized with a scanning electron microscope (SEM; XL30 FEG ESEM; FEI/Philips Hillsboto, USA) and with a computer tomograph (nanotom, phoenix|x-ray, Wunstorf, Germany). Prior to SEM characterization the samples were sputtered with gold (K550 Sputter Coater, Quorum Emitech, Qourum Technologies Ltd., Lewes, UK).

3. Results and discussion

3.1. β-Eucryptite filler synthesis

The XRD patterns of the as-synthesized β-eucryptite powders showed high purity with respect to the crystalline phases. Beside β-eucryptite, traces of lithium silicate Li_2SiO_3 (0.8 wt%), lithium pentaaluminium oxide $LiAl_5O_8$ (0.7 wt%) and γ-eucryptite (2.2 wt%) were identified, Fig. 1.

Since the XRD powder patterns of the filler-loaded materials did not show any additional crystalline phases in the temperature range up to 1100 °C, they are not shown here. Changes were observed with the [1,4] reflex and are discussed in detail in a forthcoming paper.

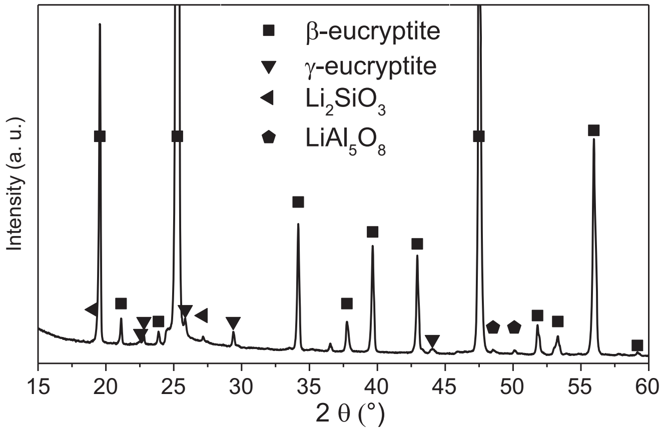

Fig. 1. X-ray powder patterns of the as-synthesized β-eucryptite powder after firing at 700 °C, re-milling and firing at 1300 °C in air; each firing step 4 h.

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