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Novel synthesis and applications of yttrium silicates from a silicone resin containing oxide nano-particle fillers

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Abstract

In this paper, a novel method for the synthesis of yttrium silicates is presented. Such silicates are well known to be promising materials for protecting various substrates against high temperature oxidation, but they can typically be produced only after quite complicated processing. The use of preceramic polymers, in which a silicate article is obtained by direct thermal treatment in air of nano-composites consisting of silicone resins containing suitable oxide nano-particles, is a valid alternative, since the desired phases, i.e. Y-monosilicate ($Y_2O_3{\cdot}SiO_2$) and Y-disilicate ($Y_2O_3{\cdot}2SiO_2$) can be obtained by treatments at low temperature (1000–1400 °C). Y-disilicate could be employed for the manufacturing of dense and thick coatings on SiC foamed substrate, by simply dipping the substrates into silicone suspensions, before ceramic conversion. Y-monosilicate, that could be also useful for coatings, was found to exhibit promising characteristics, when doped with Eu_2O_3, making it of interest for application as red phosphor for LEDs.

Keywords: B. Nanocomposites; D. Silicate; E. Thermal applications; E. Functional applications

1. Introduction

Among oxide ceramics, silicates are well known to possess a high thermal and chemical stability, due to their characteristic partially covalent bonding and limited ionic interdiffusion. Such features, however, pose some difficulties in the overall processing, since they are related to a poor solid state sinterability [1,2]. Silicate ceramics with limited secondary glassy phases are generally obtained by spark plasma sintering [2–4] or chemical vapor deposition [5,6], i.e. by processes so complicated and expensive that extensive applications are greatly limited.

The present paper aims at providing a novel method for the synthesis of yttrium silicates based on the use of silicone resins containing oxide nano-particle fillers. Silicone/oxide nano-composites have been recently proven to be valid precursors for silicates of high technological relevance, such as mullite ($3Al_2O_3{\cdot}2SiO_2$), wollastonite ($CaO{\cdot}SiO_2$) and zircon ($ZrO_2{\cdot}SiO_2$) [7–12]. Silicones act as sources for silica, reacting easily with the nano-sized dispersed phase due to the quasi molecular mixing that can be achieved during the forming of the component. In fact, filler incorporation is greatly favored by the easy dissolution of silicones in common solvents, such as acetone or isopropyl alcohol, leading to solutions in which nano-particles can be put in suspension. Fine nano-composite powders, obtained by gentle grinding of the solid residue left upon drying of suspensions, can be employed for the final shaping, carried out by cold or warm pressing or even by extrusion [13]. The produced preceramic article, can be then directly transformed into a ceramic component by controlled treatment in air. Although some shrinkage occurs, a proper formulation of fillers allows the production of dense (especially in conjunction with the presence of some sintering aids) and uncracked samples [9,12], with no significant shape distortion. If compared to the sol–gel route, the PDCs route is characterized by a generally higher ceramic yield and a better control of the viscosity of the precursors, which in turn could give a much more limited global shrinkage of the materials during their processing and, above all, the possibility of applying conventional plastic shaping technologies for an easy manufacturing of ceramic components.

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Yttrium silicates are subjected to a the growing interest for materials suitable for high temperature applications [14]. Yttrium monosilicate, $Y_2O_3{\cdot}SiO_2$ (or Y_2SiO_5, Y_2O_3/SiO_2 molar ratio equal to 1, later called Y-MS), and yttrium disilicate, $Y_2O_3{\cdot}2SiO_2$ (or $Y_2Si_2O_7$, Y_2O_3/SiO_2 molar ratio equal to 0.5, later called Y-DS) are relatively new refractory silicates. Y-MS is practically monophasic, being subjected only to a dislocative (i.e. martensitic) transformation between the X1 phase (low temperature phase) and the X2 phase (high temperature phase) [15]. Y-DS, on the other hand, features many polymorphs (y, α, β, γ, δ, z) [16,17]; all the forms are stable in a certain temperature range, but high temperature polymorphs may be retained at room temperature, due to extremely slow phase transformations [15]. A particular polymorph may be associated to a specific processing procedure [17]: for instance, whereas sol–gel processing favors the formation of the α-phase [18,19], hydrothermal synthesis is known to promote the development of the y-phase [20].

For intermediate compositions (Y_2O_3/SiO_2 molar ratio between 0.5 and 1), mono- and disilicate may coexist in their relative polymorphs [15]. The interest for yttrium silicates is due to the high melting points and, above all, their relatively low coefficients of thermal expansion and Young's modulus values, which afford to these ceramics a good thermal shock resistance [14]. In the case of Y-DS, the coefficient of thermal expansion is very close to that of SiC ceramics, so that it has been widely recognized as a promising anti-oxidation coating phase [14,15,21]. Typically, the production of these coatings rely on quite complicated processing procedures, such as plasma spraying or CVD [14,15,21].

In this paper, we will firstly discuss the possibility of effectively producing yttrium silicates from silicone resins filled with nano-sized oxide particles. Then we will show the potential of this processing method for the manufacturing of anti-oxidation coatings on SiC substrates as well as the possibility of producing powders exhibiting a red luminescence under visible/near-UV radiation, when doped with Eu oxide, that could be used in LEDs.

2. Experimental procedure

A commercial polysilsesquioxane (Silres R MK, Wacker-Chemie GmbH, München, Germany) was dissolved in isopropyl alcohol and mixed with Y_2O_3 nano-sized powders (purity >99.95%, diameter 30–50 nm, Inframat Advanced Materials, Manchester, CT), in two Y_2O_3/silicone weight proportions (3.16 and 1.58) for the production of Y-MS and Y-DS, respectively. The solid content, in all dispersions, was kept constant, at about 20%. The weight ratios were obtained considering both the Y_2O_3/SiO_2 molar ratios in the silicates, being 1/1 or 1/2, and the ceramic yield of the preceramic polymer, intended as amount of amorphous silica left after heat treatment in air (84 wt%) [7,9,11]. All the dispersions were homogenized by magnetic stirring for 10 min, and then ultrasonicated for 20 min to reduce the size of the residual particles agglomerates, thus obtaining homogeneous and stable dispersions. After the evaporation of the solvent in an oven at 90 °C in air, the material obtained was first finely ground with mortar and pestle, to a size of about 100 μm, then put on alumina trays and subjected to thermal treatment in air, with target temperatures varying from 900 to 1500 °C, with holding time of 1 h and heating rate of 10 °C/min. The phase development was investigated by means of X-ray diffraction (Bruker AXS, D8 Advance, Karlsruhe, Germany) operating with CuKα radiation (0.15418 nm). The diffraction patterns were analyzed by means of the Match! program package (Crystal Impact GbR, Bonn, Germany), supported by data from the PDF-2 database (International Centre for Diffraction Data – ICDD, Newtown Square, PA). The density of the powders was measured by gas pycnometry (Micromeritics AccuPyc 1330, Norcross, GA).

SiC open-celled foams (10 ppi ERBISIC-R foams, Erbicol SA, CH) were used as substrates for coating experiments. The foams, produced by the replica method, are comprised of α-SiC powder embedded in a β-SiC/silicon matrix, and possess a bulk average density of 2.83 g/cm^3 about 86 vol% porosity, and a cell size of approximately 3 mm [22]. Coatings were applied by dipping the foams in an water-based emulsion, following a procedure previously applied to mullite coatings on SiC foams [23]. A silicone/Y_2O_3 suspension was prepared by using a low amount of solvent (2.2 ml for 1 g of solid), then cast drop-by-drop in distilled water, under vigorous magnetic stirring, followed by ultrasonication for 10 min. Before casting, water had been added with a non-ionic surfactant (Pluronic P65, BASF Corporation, Florham Park, NJ), in a water/surfactant weight ratio equal to 30; the relative amount between the suspension and the water was chosen in order to have a water/solid (silicone + filler) weight ratio equal to 3.

SiC foams were dipped and extracted several times in the emulsion: the deposited layer, after each coating operation, was stabilized at 300 °C in air for 5 min (by direct insertion in oven), while the emulsion was kept homogeneous by applying sonication. Any excess of coating medium, forming thick drops at the cell corners of SiC foams, was removed after dipping by spraying compressed air. The ceramization of the coating layer, i.e. the conversion of the polymer and the filler into Y-DS, was achieved by applying three thermal cycles in air, each following two depositions. Every cycle lasted 1 h at the maximum temperature, and the sample was heated with a 2 °C/min rate. The temperature reached during the first heating cycle was 600 °C, whereas the second and the third heating cycles reached 1400 °C. A white, compact deposit was produced after the heat treatments. Morphological characterization was performed by optical stereomicroscopy and scanning electron microscopy (FEI Quanta 200 ESEM, Eindhoven, NL).

The formulation suitable for yielding yttrium mono-silicate (Y-MS) was used for the preparation of luminescent powders. Y_2O_3 nanoparticles were partially replaced by Eu_2O_3 nanoparticles (purity >99.9%, diameter 45–58 nm, Cometox Srl, Milan, Italy), for an amount of 5 mol%, thus giving the final composition of $(Y_{0.95}Eu_{0.05})_2SiO_5 = Y_{1.9}Eu_{0.1}SiO_5$ instead of Y_2SiO_5. The overall preparation procedure was the same than that adopted for pure yttrium silicate, except for firing, which was conducted at 1000–1300 °C (heating rate of 10 °C/min),