Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

The effect of trace amounts of copper on the microstructure, stability and oxidation of macroporous silicon carbide

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ARTICLE INFO

Article history:
Received 9 October 2015
Received in revised form 26 February 2016
Accepted 29 February 2016
Available online xxx

Keywords:
Silicon carbide
Copper
Controlled oxidation
Porosity
Catalyst support

ABSTRACT

Trace amounts of copper have advantageous effects when creating macroporous silicon carbide monoliths to be used for combined diesel particle filter and catalyst support systems. These structures were produced from a slurry of silicon, graphite, aluminium and copper. Mixed with water, extruded and dried, the resulting bodies were pyrolyzed, sintered, and then partially oxidized, to yield a mechanically stable porous 4H-SiC microstructure with an average pore diameter of 20 μm and average accessible porosity of 57%. The Cu alloys with the Si and Al to create the sintered body via a liquid phase, and prevents the build-up of undesirable Al-containing ternary carbide crystals in the microstructure. The Cu promotes oxidation of SiC to form a 80 nm SiO_2 layer that serves as a good catalyst support. The accelerated oxidation can be intercepted by dissolving the Cu component from the monoliths with an acid solution.

1. Introduction

Diesel engines are known to be less CO_2 emissive than petrol engines, but a purification of the exhaust – in particular the particulate matter and NO_x gases – is needed. For some years, macroporous silicon carbide (SiC) was shown to be suitable for this purpose, acting as a combined particle filter and SCR catalyst support system [1]. In order to combine the two functionalities, the accessible porosity of the filter has to exceed 50%, and have a pore diameter greater than 15 μm. Silicon carbide is ideal for use as a filter and catalyst support due to its extreme hardness, high fracture toughness, and high chemical and thermal stability [2,3]. Macroporous SiC can be synthesised by reaction sintering and subsequent recrystallization [4–7]. A procedure for producing macroporous 4H-SiC with 65% accessible porosity and 17–20 μm pores was described and characterised in a previous submission by the authors [8]. The microstructure, crystal structure and amounts of by-product in these SiC monoliths were found to be highly dependent on the amount of aluminium (Al) additive present in the initial reaction mixture. Commercially available high porosity filters, such as those with an accessible porosity greater than 55%, are very friable. Current production methods for these filters take place at very high temperature and require several steps, which result in high energy consumption and production costs. Therefore, improvements in this area that also could lead to an enhancement in mechanical stability would be advantageous. In the present work the effect of adding trace amounts of elemental copper (Cu) together with Al in the initial mixture is presented, and is shown here to have distinctive and pronounced effects on mechanical stability, microstructure, prevention of undesirable by-products, and enhanced surface oxidation of the SiC monoliths. The intrinsic physical and chemical mechanisms resulting in this superior product (for use in industrial applications) were investigated, using material characterization methods such as PXRD, EDS, Solid State NMR, AES, SEM, and Hg-porosimetry.

2. Method

Elemental silicon (Si) grains (20–75 μm from Elkem) and electrode graphite grains (0–40 μm, Richard Anton) were mixed with a carbon-matrix enhancer (CS76 from Zschimmer & Schwartz), that contributes after pyrolysis with 2.5 wt.% and approximately 10 wt.% of the carbon (C) content so that the weight ratio between C and Si after pyrolysis is 2.33/1. A 4 wt.% extrusion promoter (methyl cellulose ether, Methocel K15 M from Dow), deionised water, and 4.8 wt.% elemental Al in the form of polymer coated Al

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http://dx.doi.org/10.1016/j.jeurceramsoc.2016.02.054
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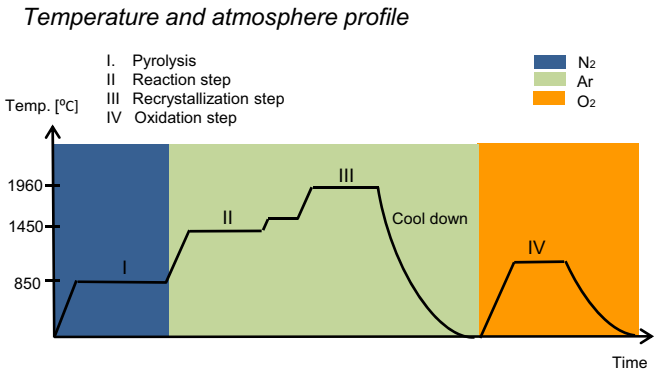

Fig. 1. Schematic representation of the temperature and atmosphere profile for the four step heat treatment.

pigment flakes (GRIMM Metallpulver) were added to the mixture. The 4.8 wt.% Al flakes correspond to 5 at.% (atomic percent) elemental Al as determined after pyrolysis. In addition to this, 0.5 at.% Cu powder (0–50 μm, GRIMM Metallpulver) was added to the initial mixture. This wet mixture was extruded into honeycomb monoliths at 60–70 bar pressure, and dried in a 0.9 m/s dry air flow for 5 h. Subsequently these extruded and dried monolith samples were subjected to a four step heat treatment (I → II → III → IV) as depicted in Fig. 1:

I Pyrolysis under 16.5 L/min flowing nitrogen (N_2) of 99.8% purity at 850 °C for 1 h in a tube furnace.
II The samples were placed in a graphite crucible in a high temperature furnace (70 L). The reaction step, in which Si and C reacted in order to form 3C-SiC (and some 2H-SiC), proceeded at 1450 °C for 2 h, and subsequently at 1650 °C for another 1 h under argon (Ar) (99%) with a flow rate of 4 L/min.
III The Ar atmosphere was renewed before the recrystallization step without cooling. In the recrystallization step, the samples were heated from 1650 °C to 1950 °C and held there for 2 h; whereupon the 3C-SiC and 2H-SiC polytypes were converted to 4H-SiC. Moreover, this recrystallization process also opens the pores of the microstructure. The samples were then cooled, whilst still under Ar, by switching off the furnace.
IV Oxidation of the monolith in air to 1100 °C for 5 h in an electrical furnace. Cooling was achieved by switching off the furnace.

In order to investigate the physical and chemical effects of Cu as partner additive, samples were prepared without Cu added to the initial mixture for comparison. These Cu-free samples were also processed under the same conditions as described above, and the characteristics of this product and process are reported by us elsewhere [8].

The samples were analysed by PXRD (powder X-ray diffraction) on a Panalytic X-ray diffractometer, using Cu-*Kα* radiation, for phase analysis and crystal structure determination. For elemental analysis: EDS (energy dispersive spectroscopy) and EDS-mapping were performed on a Bruker EDS with a 20 kV, 20 μA electron beam; and AES (Auger electron spectroscopy) including sputter removal of surface layers was obtained in an ultra-high vacuum system with a cylindrical mirror electron analyser from PHI. The samples were further analysed by SEM (scanning electron microscopy) and BS (back scatter) electron microscopy with a Leo and a Hitachi SEM, at 20 kV and 600 pA probe conditions, in order to determine their microstructures. A Hg-porosimeter from Thermo Fisher was used for determining the porosity and pore sizes of the monoliths.

3. Results

3.1. Pyrolysis

During this step, the N_2 has reacted with Al to form 3C-AlN and 2H-AlN, as described in our previous work [8].

3.2. Reaction step

During the reaction step at 1450 °C for 2 h under Ar and, subsequently, at 1650 °C for 1 h under Ar, the Si has reacted with C to form both 3C-SiC and 2H-SiC, and the microstructure has a low accessible porosity and small pore diameters.

3.3. Recrystallization step

The recrystallization step at 1950 °C under Ar has resulted in an opening of the pores, as the 3C-SiC and 2H-SiC polytypes convert to 4H-SiC through recrystallization into interlocked crystals.

In the monoliths with no added Cu, the SiC crystals are *euhedral* and tend to grow abnormally. The Al-Si liquid phase and an Al-rich supersaturated vapour phase drives the crystal growth process through Al containing intermediates. The resulting microstructure consists of interlocked crystals which are hexagonal and platy in shape with two flat faces and sloped edges, see Fig. 2 (left). This very distinctive crystal morphology is attributed to vapour-solid growth and is linked to a high surface diffusivity of the constituents. When Cu was added in trace amounts (0.5 at.%) to the initial reaction mixture, the microstructure, after the recrystallization step, comprises *anhedral* crystals which are highly interconnected and have a smaller size and narrower grain size distribution, see Fig. 2 (right). After the recrystallization step, the Cu is present as minor agglom-

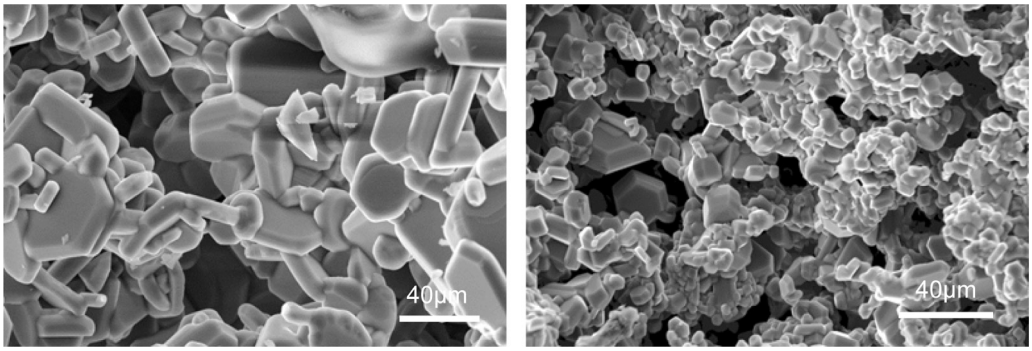

Fig. 2. The microstructure when Al is the sole additive (left), and with trace amounts of Cu as partner additive (right), reveal distinctively different features. The individual crystals are anhedral and more interconnected with smaller grains and a narrower grain size distribution in the latter.

Please cite this article in press as: J. Hvam, et al., The effect of trace amounts of copper on the microstructure, stability and oxidation of macroporous silicon carbide, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.02.054