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Spray-freeze-dried nanosized silicon carbide containing granules: Properties, compaction behaviour and sintering

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ABSTRACT

Spherical granules comprising silicon carbide nanoparticles have been produced with the help of spray-freeze-drying (SFD) technique. The effect of solid loading of slurries on rheological properties, flowability and morphology of the resulting SFD granules has been studied. Further, a systematic study has been performed to investigate the effect of applied pressures and granule density on the relative densities and microstructures of the green compacts. A marginal increase in viscosity is noted as the solid content of slurries increases from 5 to 15 vol% with significant increase in viscosity being observed in case of 18 vol% slurry. The granules prepared from SiC slurries are spherical in shape with their mean size, density, gravimetric flow rate, and yield strength increasing with the increase in solid content. The mechanical properties of sintered SiC produced from SFD granules are found relatively superior to that made from commercially available spray-dried (SD) granules.

1. Introduction

Silicon carbide (SiC) is an attractive non-oxide ceramic material, because of its unique combination of low density (3.21 g/cm^3) and outstanding mechanical properties including hardness (HV ~ 24.5–28.2 GPa), flexural strength (440–500 MPa), elastic modulus (440–475 GPa), as well as impressive thermal conductivity (~41 W/m °C) and oxidation resistance [1,2]. These properties make SiC a potential candidate for numerous applications such as protective armor material, aluminium electrolysis cell, engine components, as well as nuclear fuel coating for next generation fusion reactors [1–7]. Nevertheless, the strategic and high performance applications require the properties of SiC, which are directly influenced by the characteristics of green compacts, to be continuously upgraded; this consequently makes use of homogeneous, spherical granules instead of raw powder highly desirable.

Powders comprising irregularly shaped nanoparticles exhibit (i) a strong tendency to agglomerate because of higher surface area and strong Van-der Waal's forces of attraction, (ii) poor flowability, (iii) very low bulk density and a high amount of dust, which can cause technological and health problems [8]. In contrast, the granules with spherical shape show good flowability as well as proper die filling during compaction leading to relatively high and uniform bulk density across the compacts. It is also pertinent to note that granule strength must be low enough to ensure complete rupturing of granules during compaction, while ensuring that the granules are mechanically stable for sustaining transportation and handling [8]. Complete destruction of granules during compaction is essential to avoid formation of fragments in green compacts, as they contribute to inhomogeneity in density and formation of isolated pores that act as crack releasing defects in the sintered components [8].

In general, ceramic granules comprising primary particles (nanometer or sub-micrometer sized) are produced by SFD or SD technique [9–12]. The SFD technique has gained considerable recent interest as the granules obtained by this method ensure homogeneity in composition and complete crushing upon compaction, and yield uniform distribution of other minor ingredients in green as well as in sintered compacts compared to that in the SD technique [8,11]. Consequently, the SFD technique is deemed as promising to produce free flowable spherical granules containing ceramic nanoparticles [8,11]. In the past, SFD technique has been used to produce granules of SiC comprising sub-micrometer sized particles dispersed in an aqueous slurry containing liquid phase sintering additives such as yttrium oxide (Y_2O_3) and aluminium oxide (Al_2O_3) for SiC [11]. The SFD technique has also been used to produce granules of many other ceramic powders like nano-zirconia, alumina, silicon nitride and di-electric

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material like barium strontium titanate [13–16]. However, to the best of the authors' knowledge, SFD of nano-sized SiC powder dispersed in an aqueous slurry consisting of a suitable water soluble carbon (C) deriving agent as a sintering activator to produce ready-to-press (RTP) granules, has not been reported previously.

In this context, the present work has been carried out with the objective to develop RTP granules comprising SiC nanoparticles using SFD technique adopting an inexpensive aqueous processing route as an intermediate step. In the SFD technique, the attributes of the nano-SiC powder slurry play a significant role in controlling the properties of granules. Thus, an investigation has been carried out to ascertain the influence of solid loading on: (i) rheological behaviour of the nano-SiC slurry, and (ii) granule properties. Further, investigations have been performed on the effect of applied pressure and granule density on the compaction behaviour of green compacts. Finally, properties such as density, hardness, indentation fracture toughness (IFT), and Young's modulus of sintered SiC made from SFD granules have been compared to those of self-sintered SiC (SSiC) made from commercially available RTP grade SiC granules.

2. Experimental procedure

2.1. Raw materials

Commercially available SiC powder (Inframat Advanced Materials, USA) having particle size in nanometric range ($D_{50} \approx 40$ nm) and ~99% purity, was used for this study. Sucrose (S.D. Fine Chemicals, India) with net C content of 24.8 wt% was used as the source of carbon acting as a sintering activator [17,18]. Sucrose, being highly soluble in water and with reasonably high carbon yield (~24.8 wt%) upon pyrolization, was preferred from among a large number of C-yielding additives [19–21]. Boron carbide (B_4C) ($D_{50} \approx 0.7$ μm), another sintering aid [18], was obtained from Electro Abrasives Corporation, NY, USA. Polyethylene imine (PEI) of molecular weight (MW) 25000 i.e. PEI-25000 (Sigma Aldrich, USA) was used to disperse the SiC powder [22,23]. Commercially available spray-dried RTP grade, SiC spherical granules (Sika Densitech 15) was obtained from Saint-Gobain, Norway.

2.2. Slurry preparation, freeze granulation

Aqueous based SiC slurries along with 12.08 wt% sucrose (produced 3 wt% carbon upon pyrolization) and 1 wt% B_4C were prepared under ambient conditions by mixing in a horizontal roller mill. The reagent PEI-25000, was used for making the slurry, due to its dual role as a dispersant and as an effective binder [24]. The slurry was ultrasonically agitated for ~30 min using a probe ultrasonicator (Model: Vibrosonics, Sonic, USA) to break the agglomerates and then allowed to be mixed further for 72 h. The homogeneous slurry thus produced was atomized into droplets, which were then fed into a freeze granulator chamber (Model: LS-2, Powder Pro, Sweden) containing liquid nitrogen to make frozen granules. Subsequently, the frozen granules were dried using a freeze-drier (Model: LYO GT 2, SRK System Technik Gmbh, Germany). The freeze drying process was allowed to continue till no increase in pressure inside the drying chamber was observed (after switching-off the vacuum pump) to ensure complete drying of granules. A schematic model of granule formation using the SFD technique is depicted in Fig. 1. The fraction of as-produced granules, which passed through 60BSS sieve (~250 μm) was utilized for further series of experiments.

2.3. Compaction of SFD granules and sintering

The compaction curves of the granules were generated to investigate the apparent yield pressure (P_y) or yield strength of granule assembly [25]. Generally, P_y is a critical point at which the granules start to deform and significant increase in density is observed beyond this point [25]. For such an investigation, ~0.5 g of each type of granule was compacted in a 10 mm diameter cylindrical steel die up to a maximum pressure of 150 MPa using a universal testing machine (UTM, INSTRON-4483, UK) maintaining a cross-head speed of 1 mm/min. The instantaneous load and cross-head displacement of the UTM during compaction was continuously recorded with the help of the attached computer system. The log-pressure versus relative density (R.D.) of green compacts, i.e. the compaction curve was obtained from the load versus cross-head displacement data and the final dimensions of the compacts [25,26]. The P_y was determined from the intersecting point of two straight lines fitted for the lower-pressure and higher-pressure regions of the compaction diagram [25]. The results reported herein are based on the average values obtained from three trials.

The granules were also compacted under further higher pressures using a uniaxial-hydraulic press. Green pellets having dimensions of 10 mm diameter and 2.5–3 mm height were used for evaluation of the green density obtained at such higher applied pressures. Pressureless sintering of the green compacts made from spray-freeze-dried (SFD-18(0.6 bar)) and spray-dried (SD) granules was carried out at 2100 °C and 2150 °C, respectively, with a dwell-time of 1 h in argon atmosphere using a high temperature sintering furnace (Model: 1605, AVS Inc., USA). In addition to this, spark plasma sintering of SFD-18(0.6 bar) granules was carried out at 1800 °C with dwell time of 10 min under 60 MPa pressure by keeping the samples inside a 30 mm internal diameter graphite die using spark plasma sintering apparatus attached with 25 Ton hydraulic press (Model: SPS 25-10, GT Advanced Technologies, USA). A summary of process parameters employed for granule preparation as well as their subsequent compaction is provided in Table 1.

2.4. Characterization techniques

The as-received SiC powder was examined using a transmission electron microscope (TEM, Technai G^2, The Netherlands). The rheological behaviour of SiC slurries was evaluated at 25 °C under controlled shear rate within the shear rate range of 1–500 s^{-1} using cup-and-cone geometry with the help of a rotational viscometer (Bohlin Gemini 2, Malvern Instruments Limited, UK). The surface tension of the slurries with different solid contents were measured according to Wilhelmy plate method using force tensiometer (Model: K100, KRÜSS GmbH, Hamburg, Germany). The crystalline phases present in the as-received SiC powder, granules and sintered samples were identified by X-ray diffraction (XRD) analysis with the help of a powder X-ray diffractometer (Brucker, AXS, Germany) using Cu-Kα radiation. The particle-size distribution in slurries was estimated using laser diffraction technique (Zetasizer nanoseries, Model: Nano S, Malvern Instruments Limited, UK). The relative density (R.D.) of each green compact was determined from the measured weight and the volume calculated from dimensions of samples. The bulk density of the sintered samples was determined in double purified water using Archimedes' principle assuming the theoretical density of SiC to be 3.21 g/cm^3 [1,2]. The sintered samples for the SEM characterization were prepared following standard ceramographic procedure, and finally by polishing with 1 μm diamond particle slurry. Subsequently, the pressureless or self-sintered samples were thermally etched at 1500 °C for 2 h under vacuum and SPS-ed samples were etched using mixture of molten potassium salts (KOH +KNO_3) before observation under SEM. The morphology of SFD granules and microstructures of the sintered samples were examined using secondary electron (SE) imaging in a scanning electron microscope (SEM, Model: S-3400N, HITACHI, Japan) operated at 20 kV. The mean sizes of SFD and commercial SD granules were determined in dry condition using