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Direct coagulation casting of silicon nitride suspension via a dispersant reaction method

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Abstract

A direct coagulation casting method for silicon nitride suspension via dispersant reaction was reported. Tetramethylammonium hydroxide (TMAOH) was used as dispersant to prepare silicon nitride suspension with high solid loading and low viscosity. Influences of TMAOH and pH value on the dispersion of silicon nitride powder were investigated. Glycerol diacetate (GDA) was used to coagulate the silicon nitride suspension. Influences of the concentration of glycerol diacetate on the viscosity and pH value of the suspension were investigated. It was indicated that high viscosity sufficient to coagulate the suspension was achieved by adding 1.0–2.0 vol% glycerol diacetate at 40–70 °C. The coagulation mechanism was proposed that the silicon nitride suspension was destabilized by dispersant reacting with acetic acid which was hydrolyzed from glycerol diacetate at elevated temperature. Coagulated samples could be demolded without deformation by treating 50 vol% silicon nitride suspensions with 0.2 wt% tetramethylammonium hydroxide and 1.0–2.0 vol% glycerol diacetate at different temperatures. Dense silicon nitride ceramics with relative density above 98.8% had been prepared by this method using glycerol diacetate as coagulating agent sintered by different methods.

Keywords: C. Mechanical properties; D. Si_3N_4; DCC; Dispersant reaction; Glycerol diacetate

1. Introduction

Direct coagulation casting (DCC) is based on the idea of that a high solid loading suspension is destabilized by a time-delayed internal reaction using a catalyst [1]. The suspension is coagulated by either shifting pH to the isoelectric point (IEP) of the suspending powder or increasing the ionic strength to a certain amount. During the coagulation of suspension, pH or ionic strength is changed by time-delayed reactions or enzyme-catalyzed to lead viscoelastic green bodies with high mechanical strength to be demolded [2,3]. DCC has been applied to prepare alumina, silicon carbide as well as silicon nitride [4–9]. Hruschka et al. prepared homogeneous and stable silicon nitride suspension with ≤ 60 vol% silicon nitride powders by the addition of $Al(OH)_3$ and citric acid diammonium salt which was easily solidified by DCC [7]. Jung et al. showed that the silicon nitride suspension could be coagulated by using aluminum acetate as coagulating agent. Internal coagulation is mainly due to Al^{3+} ions release [8]. Liu et al. showed that the silicon nitride suspension could be coagulated by using urea–urease system. The coagulation rate increased sharply with the increase of reaction temperature [9]. The reports above investigate the coagulation process of silicon nitride and the properties of the green bodies have been characterized. Yet, the properties of the ceramics have been rarely reported.

In colloidal forming process, ceramic powders are required precise controlling of homogeneity, rheology, and dispersion within acceptable criteria [10,11]. The difficulty of preparation of silicon nitride suspension is to achieve a well-stabilized and dispersibility suspension with low viscosity. Cerovic et al. pointed out that the dispersion behavior of ceramic suspension was dictated by the interfacial chemistry of solid

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and suspending media [12]. The point of zero charge, isoelectric point and the surface charge of particles are important to guide these interfacial properties. Previous research indicated that the silicon nitride powders had an isoelectric point at pH of 6.3 [13]. The adsorption, electrostatic interactions and rheological properties of colloidal processing of silicon nitride with poly (acrylic acid) had been investigated by Hacklel [14]. Recently, the research of dispersion mechanism of aqueous silicon nitride suspensions at high solid loading had been reported by Liang et al. [15]. Both electrostatic and steric forces were present, and needed, for efficient stabilization at high solid loading. These studies emphasize the general rules of dispersion, which are important for suspension preparations and industrial applications.

In the previous researches of our group, glycerol diacetate was used as a pH regulator to assist the decomposition of citric salts to coagulate concentrated alumina suspensions [16,17]. The aim of this paper is to investigate the influence of glycerol diacetate on the silicon nitride suspension which was prepared using TMAOH as dispersant. The influence of glycerol diacetate on the pH and rheological properties of silicon nitride suspension was investigated. The suspension could be coagulated after adding of glycerol diacetate at elevated temperatures. A direct coagulation casting method for silicon nitride suspension was proposed by controlling the dispersant reaction with temperature increasing. The properties of coagulated samples and sintered ceramics were characterized.

2. Experimental

2.1. Materials

Commercially available silicon nitride powder (Vesta Ceramics AB, Sweden) with an average particle diameter of 0.8 μm and specific surface area of 9.39 m^2/g was used. CT3000SG alumina powder (average particle diameter: 0.33 μm, surface area: 8.08 m^2/g, Almatis, Ludwigshafen, Germany) and yttrium oxide powder (99.95%, average particle diameter: 0.39 μm, specific surface area: 0.3 m^2/g, Shanghai Junyu Ceramic-molded Product Co., Ltd., China) were used as sintering additives. Tetramethylammonium hydroxide (TMAOH) aqueous solution with concentration of 10 wt% was used to disperse the suspension. Glycerol diacetate (GDA) was used as a coagulation agent. Both were purchased from Hengye Zhongyuan Chemical Co., Ltd., Beijing, China. Analytical purity ammonia was used to tailor the pH value of the suspension. Deionized water was used in all preparation processes.

2.2. Preparation of silicon nitride suspension

In DCC process, high solid loading and low viscosity suspension were desirable. Silicon nitride suspensions with different solid loadings were prepared by tumbling the silicon nitride powder, sintering additives, water, dispersant, ammonia, and grinding media in polyethylene container for 24 h. TMAOH was used as dispersant with 0.1–1.0 wt% based on silicon nitride powder. Sintering additives were 2 wt% Al_2O_3 and 5 wt% Y_2O_3 based on silicon nitride powder. Agate balls with diameter of 5–10 mm were used as grinding media. The mass ratio between grinding media and silicon nitride powder was 1:2. Ammonia was used to adjust the pH value of the suspension to ca. 10.5–11.

2.3. Coagulation and sintering

The suspension was maintained at 25 °C for 5 h and degassed under vacuum condition for 15–20 min. Various amounts of glycerol diacetate were added to the suspension and mixed thoroughly by continuing the tumbling process for another 20 min to increase the homogeneity of the suspension. Then, the suspension was cast into a plastic mold. To prevent the evaporation of water during the coagulation process, a seal was used. The samples were placed in a water bath with a heating rate of 5 °C/min and treated at different temperatures for a period of time and then demolded. The green bodies were dried at 80 °C for 24 h. For the pressureless sintering process, the dried samples were sintered at 1850 °C for 2 h at a heating rate of 5 °C/min, under nitrogen atmosphere (0.1 MPa). For the hot pressing sintering process, the samples were put into a graphite mold with a diameter of 50 mm and sintered at 1800 °C for 2 h under 20 MPa uniaxial pressure at a heating rate of 5 °C/min, under nitrogen atmosphere (0.1 MPa).

2.4. Characterization

The pH value of silicon nitride suspension was measured by pH meter (LE438, Mettler, Toledo, Switzerland) in the temperature range of 25–70 °C. The rheological properties of the suspension were measured using a rheometer (KINEXUS PRO, Malvern Instruments, Worcestershire, UK) attached with C25 R0634 SS spindle and PC25 C0138 AL cylinder. In viscosity measurement, the shear rates were in the range of 0.1–1000 s^{-1}. Zeta potential was measured by a Zeta Potential Analyzer (CD–7020, Colloidal Dynamics Co., Ltd., Ponte Vedra Beach, FL, USA) via the electroacoustic measurement technique with a stirring speed set at 300 r/min. In zeta potential measurement, 10 vol% silicon nitride suspension was prepared. 1 mol/l HCl and NaOH were used to adjust the pH value. The density of the green bodies was determined on the cut and fine-ground rectangular bars by measuring the dimensions and weight. The density of the sintered samples was measured using the water displacement technique. To investigate the degree of oxidation of the silicon nitride powder after being in the suspension for different periods of time, a wave length-dispersive sequential X-ray spectrometer (XRF–1800, Shimadzu, Tokyo, Japan) with a Rhodium target was used to analyze the chemical composition of silicon nitride powder. Silicon nitride suspension with TMAOH and coagulated silicon nitride green body by glycerol diacetate was dried in stove at 80 °C and milled. For wet compressive strength measurements, cylindrical bodies with 25.5 mm in diameter and a height between 25 and 30 mm were cast. After