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Effect of concentration and molecular weight of polyethylenimine on zeta potential, isoelectric point of nanocrystalline silicon carbide in aqueous and ethanol medium

Prasenjit Barick[a,*], Bhaskar Prasad Saha[a], Rahul Mitra[b], Shrikant V. Joshi[a]

[a]Centre for Non-Oxide Ceramics, International Advanced Research Centre for Powder Metallurgy and New Materials, Balapur Post, Hyderabad 500005, India
[b]Department of Metallurgical and Materials Engineering, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal 721302, India

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Abstract

The effect of dispersant concentration and its molecular weight on zeta potential of nanocrystalline silicon carbide in an aqueous medium was investigated. An increase in the concentration of the dispersant, such as polyethylenimine (PEI), in slurry prepared from nanosized silicon carbide, was found to augment the iso-electric point and zeta potential. However, the zeta potential was observed to decline as the pH of the slurry shifts towards the basic region. This aforementioned behavior is attributed to the enhanced mutual repulsion between the polymer chains of the dispersant adsorbed on the surfaces of SiC particles and those approaching the surfaces. The higher ionization potential of polymers in the acidic region compared to the basic region increases the adsorption. The relationship between zeta potential and pH is however, noted to remain virtually unchanged with molecular weight of PEI. Further, it is observed that zeta potential of SiC decreases with the increase in solid content of the slurry. Rheology study reveals that the ethanol based slurry has a lower viscosity than the water based slurry, making ethanol the preferred dispersing medium for colloidal processing of nanometric SiC powder.

Keywords: Isoelectric point; Molecular weight; PEI; Silicon carbide; Zeta potential

1. Introduction

In colloidal processing, the realization of stable, low viscous slurry with high solid content depends upon how discretely and uniformly the particles are dispersed in the slurry, which is often obtained with the addition of a suitable dispersant [1,2]. In order to achieve the above, it is important to investigate the zeta potential of a system, because the stability of a powder suspension critically depends on it. A zeta potential value of high magnitude (either positively charged or negatively charged) is always desirable. There are several potential dispersants available, such as polyethylenimine (PEI), ammonium polyacrylate (NH_4PA), ammonium polycarboxylate (APC), etc. to stabilize SiC ceramics [3–6]. Among the above, PEI is known to be an effective dispersant for stabilization of nanometric SiC powder [3]. Consequently, PEI was chosen as the dispersant to investigate the present study.

Previously, it has been reported that the presence of an amorphous carbon layer on the surface of SiC nanoparticles can reduce the stability of an aqueous suspension due to the non-Derjaguin and Landau, Verwey and Overbeek (DLVO) hydrophobic force [7]. In another study, Singh et al. [6] dispersed 30 nm SiC powder in an aqueous medium using APC as a dispersant, and observed that the isoelectric point of SiC changes from 4.9 to 3.6. It was also observed that the net charge on SiC particles becomes more negative as the polymer chains of the dispersant are adsorbed on the particulate surface. Another study has reported that the initial degree of ionization (α_i) of PEI has a significant effect on the dispersion of SiC nanoparticles in the aqueous medium [8]. Coupe et al. [9] have reported that addition of PEI to an ethanolic suspension of nanometric SiC shifts the isoelectric point towards a higher pH value, i.e. pH ≈ 10–11.

*Corresponding author. Tel.: +91 40 24452441; fax: +91 40 24442699.
E-mail address: prasenjit@arci.res.in (P. Barick).

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Furthermore, in a study, Hou et al. [3] have shown that stability of the slurry increases with increase in PEI concentration upto a value of 2.5 wt%. The isoelectric point of nanometer-sized silicon carbide particles (40–50 nm) dispersed in ethanol medium increases from 9.5 to 12.3 with addition of PEI [3]. It has also been reported that PEI, in the presence of citric acid, could effectively enhance the stability of SiC slurry due to the formation of a complex compound between PEI and citric acid [10]. Sun et al. [11] have shown that adsorption of PEI molecules on SiC particles occurs via a surface silica layer by electrostatic interaction between the negatively charged SiC surface and the positively charged polymer molecules in acidic and neutral pH range. In the basic pH range, the adsorption of PEI molecules on the SiC surface takes place through hydrogen bonding of non-electrostatic nature [11].

As is evident from the above discussion, although several issues concerning the zeta potential of nanoscale silicon carbide powder have been addressed earlier, yet a systematic study of the influence of dispersant concentration and molecular weight (MW) on zeta potential behavior of nanometric SiC does not exist.

In the present study, a thorough investigation was carried out on the effect of PEI concentration and its MW on the zeta potential as well as the isoelectric point of nanosized SiC dispersed in an aqueous medium. The influence of varying PEI concentration on the above properties was also ascertained in case of nanosized SiC powders dispersed in ethanol medium. The effect of powder content of the slurry on zeta potential of nanosized SiC was also studied. Finally, viscosity measurement was also carried out to see the effect of dispersibility of nanosized SiC powder in two different media viz. water and ethanol.

2. Experimental procedures

2.1. Materials

Commercially available β-SiC powder (purity ≈ 99%, free Silicon < 0.25%, free carbon < 0.75%) comprising nanosized particles was obtained from Inframat Advanced Materials, USA. A 50% aqueous solution of MW 50,000–100,000 PEI was obtained from ICN Biochemical Inc., USA, while 50% aqueous solutions of MW 2000 and 25,000 were obtained from Sigma-Aldrich, USA. Quantity of PEI is expressed as the dry weight percentage basis (dwb%) of SiC powder.

2.2. SiC slurry preparation for zeta potential measurement

A 0.01 vol% nanosized SiC containing slurry was used for zeta potential measurements. The density of β-SiC (3.21 g/cm^3) was used for calculating the powder quantity. The procedure adopted for slurry preparation had the following steps: (i) measured quantity of 0.1 wt% PEI stock solution was mixed with distilled water; (ii) dry SiC powder of required quantity was slowly added to the premixed solution by stirring; and (iii) the slurries were then ultrasonicated for 30 min to break the agglomerates using a single stage ultrasonic cleaner (Micro Clean-109, Oscar Ultrasonics, India). After ultrasonication, the slurries were continuously stirred before analysis. Aqueous solutions of 0.05 M HCl and 0.1 M NaOH were used for titration of SiC slurries. However, for titration of ethanol dispersed slurry, concentration of HCl and NaOH was maintained as 0.01 M.

Initially, the PEI (MW 50,000–100,000) in different amounts such as 0, 0.08, 0.16, 0.40, 2 and 4 wt% was added to each suspension. The PEI with different MWs, such as 2000 and 25,000, was also used at two specific concentrations of 0.40 and 4 wt% respectively, keeping the conditions of mixing identical to those adopted in case of other SiC slurry specimens to assess the influence of MW on zeta potential. In order to measure the zeta potential at varying SiC powder concentrations, appropriate amount of NaCl was added to the slurry in order to adjust the ionic strength of the medium. In this case, SiC slurries were prepared without PEI dispersant.

2.3. SiC slurry preparation for viscosity measurement

SiC slurry with 5 vol% solid content in water and ethanol medium was prepared keeping all the parameters such as dispersant content, time for mixing, RPM of pot jar mill and ambient condition identical. First, the required amount of SiC powder was dispersed in the liquid medium, and ultrasonicated for 30 min in the presence of 1.5 wt% PEI (MW 25,000). Subsequently, the slurry was prepared using a pot jar mill with WC balls as the milling media. The milling duration was 24 h prior to viscosity measurement.

2.4. Zeta potential measurement

The zeta potential measurements were performed on the 0.01 vol% β-SiC powder slurry with the desired amount of PEI and without PEI, using a Zeta potential measuring instrument (Zetasizer, Nano-Z, Malvern Instruments Limited, UK). No background electrolyte solution, e.g. KCl or NaCl, was used. The zeta potential was measured as a function of pH during the titration of slurries. All 0.01 vol% SiC slurries showed an initial pH of ≈ 7.3. The pH adjustments were carried out from the initial pH point of slurry with the help of an auto-titration system (MPT-2 autotitrator, Malvern Instruments Limited, UK).

2.5. Viscosity measurement

Viscosity of the SiC slurries was measured at 25 °C using cup and bob geometry, with the help of a rotational viscometer fitted with a spindle, which is driven by a frictionless air bearing (Bohlin Gemini 2, Malvern Instruments Limited, UK). The viscosity was measured at controlled shear rate mode within the range of 1–100 s^{-1}.

3. Results and discussion

3.1. Characterization of SiC powder

The XRD peaks (Fig. 1) from the SiC powder have confirmed the presence of only β-SiC with cubic (zinc blende) crystal structure. Examination of this powder using transmission electron