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Dispersion behaviour of laser-synthesized nanometric SiC powders in aqueous medium with ammonium polyacrylate

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Abstract

The dispersion behaviour of laser-synthesized nanometric SiC powders in water using ammonium polyacrylate (molecular weight = 10,000) as dispersant was investigated. The influence of oxidation, presoaking time, ammonium polyacrylate (NH_4PA) concentration, and pH on suspension stability and coagulation rate of aggregates was determined. The stabilization mechanism is discussed. Excellent dispersion stability was obtained for oxidized (500 °C) powders containing 2.45 wt.% NH_4PA at pH 9.25 after a lengthy aging treatment.

Keywords: D. SiC; Dispersion; Nanopowder; Ammonium polyacrylate; Dispersant; Aqueous medium

1. Introduction

Advanced ceramics own excellent properties such as high-temperature stability, corrosion resistance and wear resistance compared to metals. However, the commercial application of monolithic ceramics has been hindered due to their brittleness and degradation of mechanical properties at elevated temperatures. In recent years, ceramic materials containing nanophases, namely nanoceramics and nanocomposites, have been receiving increasing attention owing to improvements in mechanical properties. For example, SiC nanoceramics exhibit superplasticity [1] and the mechanical properties of nanocomposites containing nanometric SiC were excellent compared to those of monolithic ceramics and ordinary ceramic composites [2]. In these materials, the size of the SiC plays an important role where smaller SiC shows greater strengthening effect at lower addition levels in nanocomposites. Laser synthesis is a unique route to produce nanosized, uniform, and spherical SiC powders of high purity [3]. However, the extremely large surface area makes the powders susceptible to agglomeration, which results in difficulty in achieving a homogeneous distribution of the nanophase, so pores remain in the sintered body. It is well known that these are disadvantageous to the mechanical properties of ceramics. Colloidal processing is a common route for the fabrication of ceramics, so studies on the aqueous dispersion behaviour of laser-synthesized SiC is necessary to lessen the degree of agglomeration.

Tartaj et al. [4] studied the electrokinetic behaviour of plasma-synthesized nanometric SiC in water in the absence of a dispersant, the stability of the suspension was improved by heating the powder at 650 °C for 30 min, which could replace the amorphous carbon layer on the powder surface with a SiO_2 layer and increase the magnitude of the ζ potential. Although dispersion can be improved by controlling the charge at the powder/liquid interface, more practicable dispersion results can be gained only with the introduction of an appropriate dispersant to the suspension. Polyelectrolytes can combine electrostabilization and steric stabilization mechanisms in the slurry, so better dispersion can be obtained with this kind of dispersant.

Polyacrylate salts have been proved effective dispersants for oxide ceramics, such as Al_2O_3, ZrO_2, etc. [5]. Recently, the application of this kind of dispersant in the processing of non-oxide ceramic powders, such as Si_3N_4 [6], was reported, where the polymer was adsorbed to the powder surface through hydrogen bonding through Si–OH bonds. Since the silanol is the major functional group also on SiC powder surfaces [7], polyacrylate salts

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are expected to improve the dispersion of nanometric SiC in an aqueous medium. However, nanometric powders will be expected to behave differently from submicron powders due to the large surface area.

In the present work, the dispersion behaviour of laser-synthesized nanometric SiC powders with ammonium polyacrylate as dispersant in water was studied.

2. Experimental procedure

The SiC powder used in the present study is a commercial product of the Institute of Metal Research, which was prepared by the laser-synthesis method using SiH_4 and C_2H_2 as reactants. The powders were used as-received or after being heat-treated in static air at 500, 550, and 600 °C for 1 h, which are entitled SC, SC500, SC550, and SC600, respectively. The C and O content in SiC powders were analysed by a CS-444 (LECO Corporation, USA) and a TC 436 (LECO) respectively, the Si content was analysed by molten $NaCO_3$ method. X-ray diffraction (XRD, D/max-rA, Rigaku Corporation, Tokyo, Japan) was employed to determine the crystalline phases using CuK_α radiation monochromatized by graphite; the particle size and morphology of the powders were examined by transmission electron microscopy (TEM, EM420, Philips, Netherlands).

Distilled water was used as the dispersion medium. Ammonium polyacrylate (NH_4PA, Jinghong Chemical Co., China), with an average molecular weight of 10000, was used as dispersant. The pH values of the suspension were determined using a pH meter (RAS PHC-2, Shanghai Weiye); the pH level was adjusted with diluted AR-grade HCl and NaOH. First, the NH_4PA of the different amount (0–6 wt.% referred to the solids) was added to the distilled water, and then the powders were added. The effect of presoaking on the dispersion also was investigated, samples subjected to short-term (1 h) or long-term (1 month) soaking carry the suffix S or L, respectively, e.g. SC500S or SC500L. Following soaking, a 10-min ultrasonification (50 W) was used, followed by pH readjustment and another 10-min ultrasonification. This procedure was used to obtain a homogeneous suspension with a solid concentration of 1 mg/ml. The suspension was poured into a 10-ml graduated tube with a rubber seal for sedimentation testing. The suspension separated into three parts during the rest: the upper clear water, the remained suspension, and the lower sediment. The suspension volume was recorded at different intervals. A minute portion of the suspension was diluted with pH-adjusted water and the sizes and the zeta potentials of the aggregates in dilute suspensions were measured using a Zetasizer 3000 (Malvern Instruments, Malvern, UK).

3. Results

3.1. Characteristics of nanometric SiC powders

The chemical compositions of the as-synthesized SiC powder was as follows: Si: 70.5 wt.%; 27.6 wt.%; O: 2.3 wt.%. The oxygen contents of SC500, SC550, and SC600 were 3.1, 4.2, and 7.2 wt.%, respectively. Fig. 1 shows an XRD pattern of the as-synthesized nanopowders indicating that the powders were mainly β-SiC (3C-polytype), a slight intensity due to stacking faults [8] was observed. A TEM micrograph of this powder (Fig. 2) shows that the powders had an average particle size of about ~20 nm and were uniform in size and nearly spherical. However, the particles were agglomerated heavily.

3.2. Dispersion behaviour of as-synthesized SiC

In the sedimentation test of as-synthesized SiC with a 1h presoaking (SCS), floccules were observed in all samples, showing that water alone was insufficient to disperse the powder. Fig. 3 shows the effect of NH_4PA content on the life of the suspension at pH 9.25, which is the time required for the suspension to sediment completely. The as-synthesized SiC in water without any dispersant settled

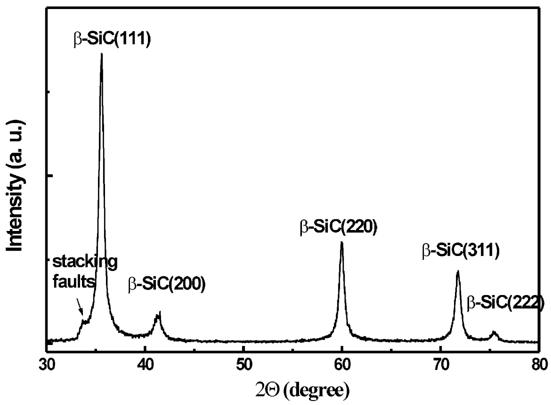

Fig. 1. XRD pattern of as-synthesized nanometric SiC powders.

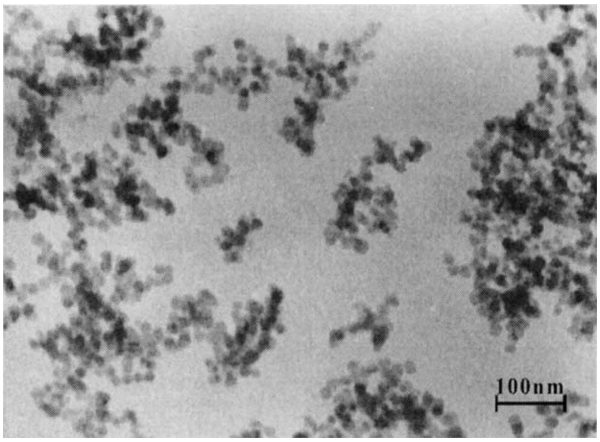

Fig. 2. TEM micrograph of SiC nanopowders.

promptly after the ultrasonification. The addition of dispersant improved the dispersion where 4.0 wt.% NH$_4$PA gave the highest suspension stability. Fig. 4 shows the size growth of agglomerates in NH$_4$PA solution. Firstly, the coagulation rate decreased with increasing NH$_4$PA reaching a minimum at a dispersant content of 4.0 wt.%; further addition of NH$_4$PA caused a slight increase of coagulation rate, these results are consistent with the sedimentation results. The electrophoresis results (Fig. 5) show that the isoelectric point (IEP) values varied from 2.0 to 3.1 for different dispersant concentrations, although the effect of dispersant on the IEP was not consistent. Above the IEP, the magnitude of the zeta potential values ($|\zeta|$) for a given NH$_4$PA concentration increased with pH. In the pH range of 8.5–11, $|\zeta|$ also increased with increasing NH$_4$PA concentration (see top right corner in Fig. 5).

3.3. *Dispersion behaviour of heat-treated SiC*

Excess oxygen in the starting powders will deteriorate the properties of non-oxide ceramics, so it was assumed that a suitable heat-treatment process would improve the dispersion without overoxidizing the powders. The zeta potential as function of pH for SiC nanopowders subjected to different oxidation treatments, SC, SC500, SC550, and SC600, is plotted in Fig. 6. The as-received powder SC had the lowest $|\zeta|$ among the samples in pH 8.5–10.5, while SC500 showed the highest $|\zeta|$. According to the chemical analysis results, the oxygen contents were 2.3, 3.1, 4.2, and 7.2 wt.% for SC, SC500, SC550, and SC600, respectively. Since high magnitude of ζ leads to high electrostatic repulsion between particles, this is the only stabilization mechanism in presence of dispersant. It was evident that heating the powders at 500 °C gained the best electrostatic stabilization in water and introduced relatively low oxygen levels ($\sim$1.0 wt.% SiC was oxidized), so the dispersion behaviour of SC500 was studied in detail.

Fig. 7 shows the influence of NH$_4$PA concentration on the suspension stability of SC500S. The suspension stability of SC500S was improved substantially compared with SCS (Fig. 3) for all NH$_4$PA concentrations. For the dispersant-free samples (Fig. 3 ■ and Fig. 7

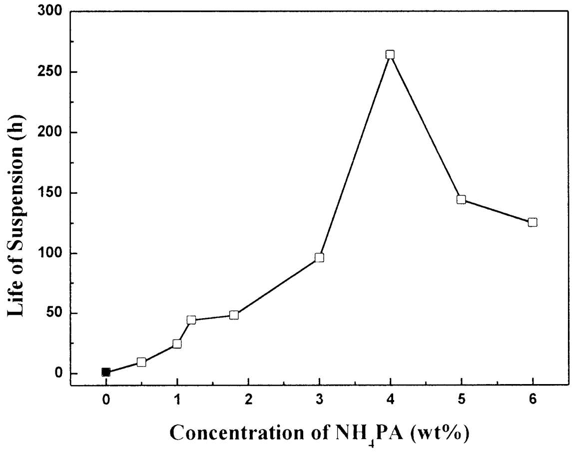

Fig. 3. Life of suspension for SCS at pH 9.25 as a function of NH$_4$PA concentration.

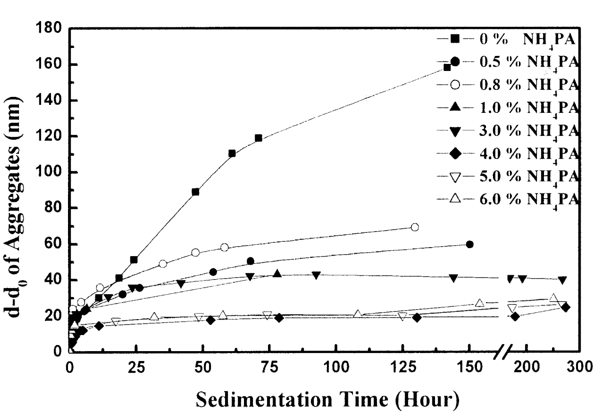

Fig. 4. Size increment of aggregates for SCS at pH 9.25 as a function of sedimentation time.

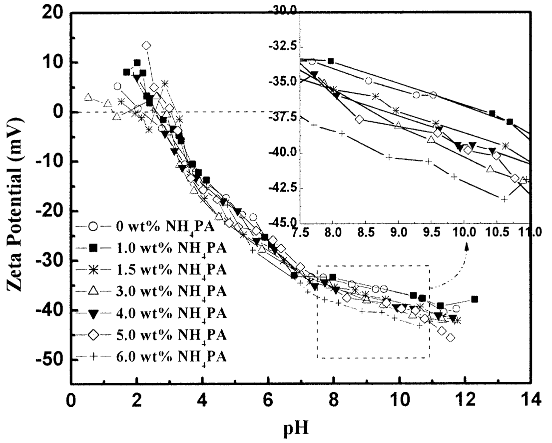

Fig. 5. Zeta potential of SCS as a function of NH$_4$PA concentration and pH.

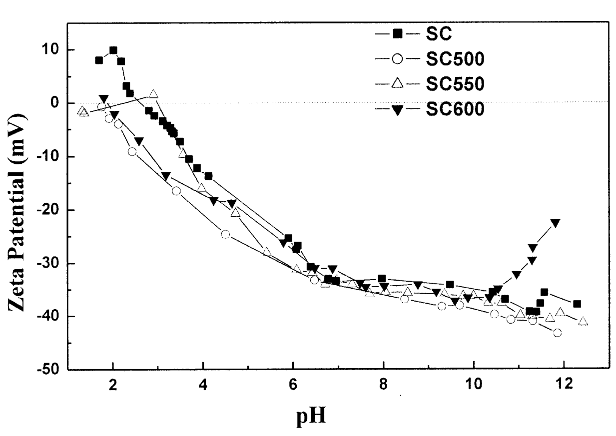

Fig. 6. Zeta potential as a function of pH and oxidation temperature.

□), the improvement clearly was due to the increase in $|\zeta|$ (Fig. 6 ■ and □ at pH 9.25) because electrostablization was the only stabilization mechnism in this case. The addition of NH$_4$PA further improved the dispersion. 2.0–3.0 wt.% NH$_4$PA gave fairly good stability, the optimal content being ~3.0 wt.%, at which level the suspension could be stored for more than 20 days with 80% suspension volume being preserved. This optimal amount was less than that for the as-received powders, which was 4.0 wt.% NH$_4$PA (see Fig. 3).

3.4. Dispersion behaviour of SC500L

In order to determine the influence of presoaking on the suspension stability, a set of samples of SC500 was soaked in the deflocculant solution for 1 month before ultrasonification. The sedimentation results at pH 9.25 (Fig. 8) indicated that the optimal NH$_4$PA concentration was 2.45 wt.%, which was a little lower than that of short-term aged samples SC500S. The aging treatment showed no improvement to the dispersion stability in the absence of NH$_4$PA (Fig. 7 □ and Fig. 8 ■). However, in the suspensions containing dispersant, the stability was enhanced due to the aging, especially for the suspension with the optimal amount of dispersant. This suspension could be stored for nearly 60 days with 80% suspension height being preserved.

The agglomeration of the aggregates for SC500L at pH9.25 as a function of sedimentation time is shown in Fig. 9. The suspension without NH$_4$PA had the highest agglomeration rate, and the minimal agglomeration rate was observed at 2.45 wt.% NH$_4$PA, which is quite consistent with the sedimentation results. Compared to the data for SCS (Fig. 4), SiC500L had relatively lower agglomeration rates, suggesting that the oxidation and aging treatments were beneficial to the dispersion.

3.5. Suspension stability and electrokinetic behaviour versus pH

Fig. 10 shows the effect of pH on the suspension stability for SC500L with 2.45 wt.% NH$_4$PA. The suspension had poor stability in acidic and alkalescent solutions, while high stability was observed at pH $>$ 8.15. The highest stability was observed for at pH 9.25, which is near that for Si_3N_4 [6].

The ζ potential as a function of pH of SC500L with different dispersant concentrations soaked for 1 month

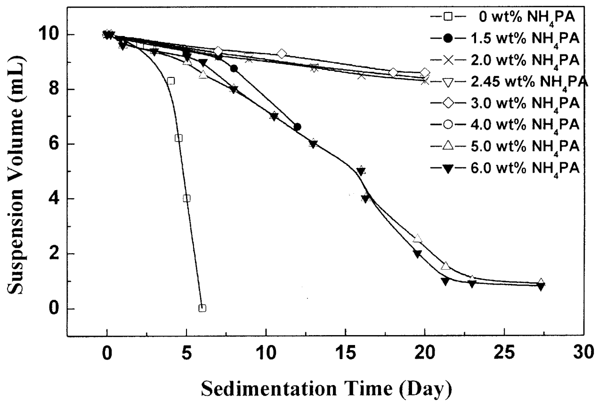

Fig. 7. Suspension stability of SC500S at pH 9.25 as a function of NH$_4$PA concentration.

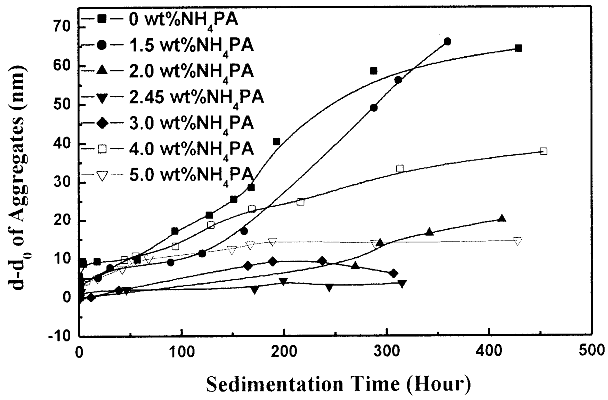

Fig. 9. Size increment of aggregates for SC500L at pH 9.25 versus sedimentation time.

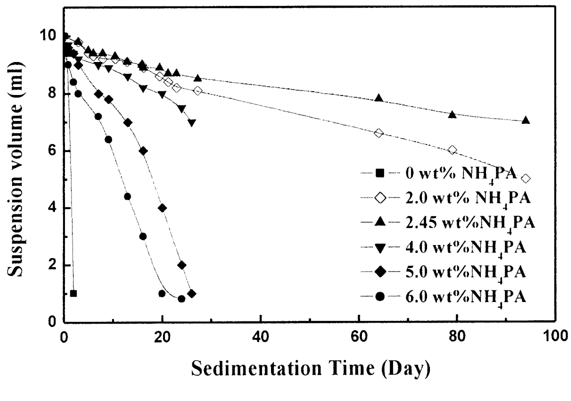

Fig. 8. Suspension stability of SC500L at pH 9.25 as a function of NH$_4$PA concentration.

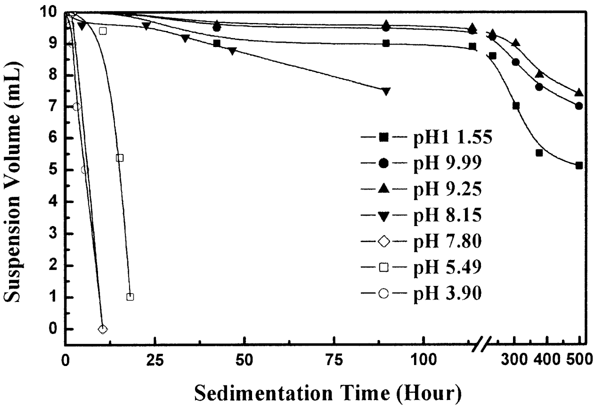

Fig. 10. Dependence of suspension stability on pH for SC500L.

is shown in Fig. 11. The trend of ζ versus pH is similar to that for SCS (Fig. 4). However, the $|\zeta|$ is higher than that of SCS at the same pH and NH_4PA concentration. In the pH range 8–11, the $|\zeta|$ increased with increasing of the dispersant level up to 6.0%. The dependence of the $|\zeta|$ on the pH in this range was relatively small compared to that in the acidic region.

4. Discussion

NH_4PA dissociates according to the reaction [5]:

$$-[-RCOONH_4-]-_n = -[-RCOO^- -]-_n + n\,NH_4^+$$

The dissociation begins at pH > 3.5, with the fraction (α) dissociated increasing with increasing pH, approaching unity at pH values ⩾8.5. The dissociated $RCOO^-$ groups have a negative charge, which will lead to a configurational transformation of NH_4PA from a relatively small coil at low pH to a fully extended molecule at high pH owing to the electrostatic repulsion between nearby chains. The expansion factor can be of the order of 10–100 according to the molecular weight of the polymer. This will influence greatly the suspension properties.

At pH values above the isoelectric point, the zeta potentials of SiC have negative values (Fig. 5), so there will be electrostatic repulsion between the dispersant and the powder surface. However, adsorption still can take place between the silanol groups (Si–OH) at the SiC surface and the carboxylate groups on the polyacrylate chain through hydrogen bonding, as in the case of Si_3N_4 [6], this molecular adsorption is not of the "high-affinity type" [5], some adsorbed chains can be desorbed form the powder surface. Finally, an equilibrium between of adsorption and desorption is reached, the adsorption amount in the end depends on the amount of Si–OH site on the powder surface, the NH_4PA concentration in the solution, pH etc. The adsorption of ionised NH_4PA will make the powders more negatively charged. The competition between the molecular adsorption and the electrostatic repulsion will determine the contribution of NH_4PA to the dispersion. So the dispersion of SiC powders in NH_4PA solution depends on the following factors: the magnitude of the zeta potential of the clean powder (without dispersant), the increment of the zeta potential due to adsorption of ionised dispersant, and the steric effect of the absorbed polymer.

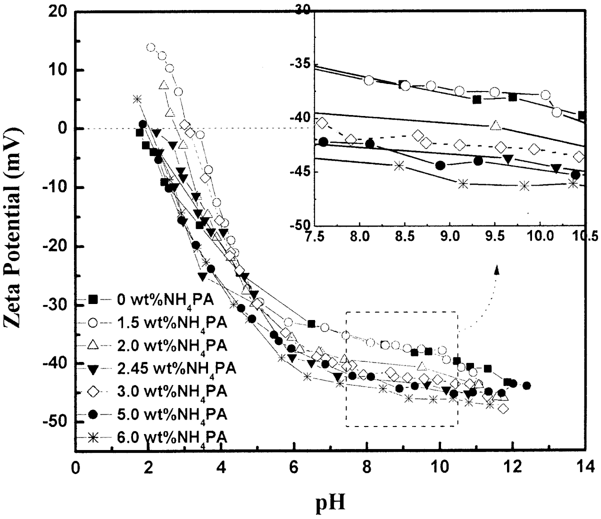

Fig. 11. Zeta potential of SC500L as a function of NH_4PA concentration and pH.

The as-received SiC powders have a poor dispersibility in water without dispersant, and only limited improvement is obtained by the addition of NH_4PA (Figs. 3 and 4). This is related to the surface characteristics of the powders. Although the powders are rich in silicon according to the chemical analysis results above (Si/C molar ratio = 1.06 assuming that oxygen exists in the form of SiO_2), the excess Si exists in the core of the particle and a very thin layer of free carbon has been observed on powder surfaces [9]. Carbon cannot be wet well by water [10,11], and it has been shown that polyacrylate shows much less effect on carbon compared to oxides or insoluble salts. Approximately 100 times as much polyacrylate must be added to gain the equivalent amount of dispersion due to the poor adsorption between the polymer and carbon surface [11]. Thus, the thin carbon layer worsens the dispersion of as-synthesized nanometric SiC. The preoxidation treatment of the SiC powders at 500 °C can eliminate the carbon layer [12] and form a thin SiO_2 amorphous surface layer [4] according to the increase of oxygen content. This raises the $|\zeta|$ of the powders (Fig. 6) which is due to the increase of surface silanol sites as in the case of Si_3N_4 [5], and so the adsorption of NH_4PA on the powder surfaces will be enhanced. So the suspension stability of SC500S was greatly improved compared to as-synthesized SiC. Further, the optimal dispersant concentration also decreased from 4.0 to 3.0 wt.%.

The ζ potential of the powder with adsorbed NH_4PA is composed of two parts: the potential of the clean powder itself, ζ_p, and that from the negative adsorbed polymer, ζ_{PA}. $|\zeta_{PA}|$ is proportional to the amount of absorbed NH_4PA at a given pH. The adsorption of NH_4PA on SC increased with increasing NH_4PA concentration up to 6.0 wt.% in the suspension (Fig. 5), which can be explained by the equilibrium between the adsorption and desorption. However, the best dispersion effect was obtained not at 6.0 wt.% but at 4.0 wt.% dispersant concentration, which may be due to excessive NH_4PA in the solution, resulting in bridging between particles.

The presoaking treatment showed little effect on the dispersion stability of SC500 in absence of deflocculant

(Fig. 7 □ and Fig. 8 ■), which is consistent with the results of Tartaj et al. [4]. However, in the presence of NH_4PA, the dispersion stability was improved when the aging time was prolonged from 1 h to 1 month. This is a result of the slow process of surface oxidation, hydrolysis, and increase in Si-OH during aging [10], which improved the adsorption of NH_4PA due to the increase of adsorption site on the powder surface and the dispersion was enhanced. The optimal dispersant concentration also was further decreased to 2.45%.

The ζ_{PA} of SCS and SC500L at their optimal dispersant concentrations (4.0 and 2.45 wt.%, respectively) was calculated from Figs. 5 and 9 and plotted in Fig. 12. It is clear that SC500L adsorbs more NH_4PA than SC at all pH values, even though SC contained more NH_4PA in the suspension, which indicates that the oxidation and presoaking was beneficial to the adsorption. The $|\zeta_{PA}|$ increased while the pH was raised because polyacrylate began to dissociate and reached its maximum near pH = 4.8. When the pH was raised further up to ~pH 10, the electrostatic repulsion between the ionised polymer and the negative powder surface increased, weakening the adsorption and decreasing the $|\zeta_{PA}|$. Since the polymer was less negatively charged at lower pH, the adsorbed NH_4PA decreased with increasing pH value. When the pH value was near 9.25, although the dispersant adsorption on particle surface was less than that at lower pH values, the magnitude of the ζ potential of the clean powder ($|\zeta_p|$) was high, so the total ζ potential was more negative than that at lower pH (Fig. 11). On the other hand, the adsorbed polyacrylate could fully extend, so both electrostatic and steric stabilization reach their maxima, so giving the highest suspension stability (Fig. 10).

The total zeta potential varied inconsequentially at pH = 8.0–11.55 (Fig. 11), but the suspension stability varies significantly, especially when the pH value was raised from 8.15 to 9.25. This indicates that the steric stabilization of adsorbed NH_4PA is the dominating stabilization mechanism in this pH range.

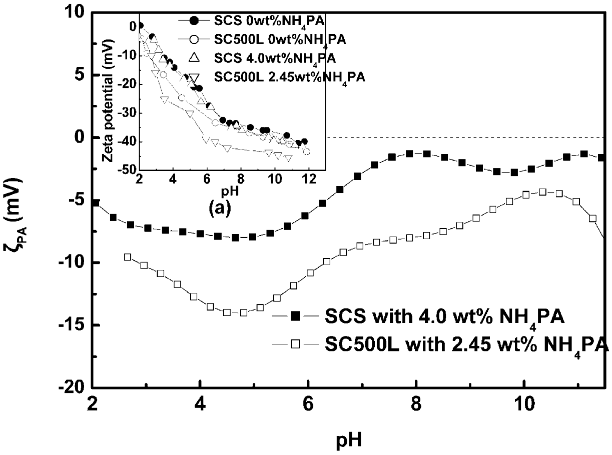

Fig. 12. ζ_{PA} as a function of pH.

5. Conclusions

The dispersion behaviour of laser-synthesized nanometric SiC in water using ammonium polyacrylate as deflocculant was investigated systematically. The as-synthesized powders showed bad dispersion stability in water without any dispersant because the dispersion was determined only by the surface charge. The dispersant adsorbed poorly on the powder surface and could offer only a limited contribution to the dispersion. Oxidation of the powders at 500 °C in air eliminated the thin nonwetting carbon layer and improved the adsorption between NH_4PA and the powders, substantially enhancing the suspension stability. A lengthy aging time in water further increased the dispersion stability in the presence of NH_4PA. For the oxidized powders, the dispersion was governed by steric stabilization. The powders oxidized at 500 °C and presoaked in water for 1 month showed excellent dispersion stability with 2.45 wt.% NH_4PA concentration at pH = 9.25.

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