Journal of the European Ceramic Society 23 (2003) 379–385
www.elsevier.com/locate/jeurceramsoc

Surface modification of SiC powders by hydrolysed aluminium coating

K. Prabhakaran[1], J. James, C. Pavithran*

Regional Research Laboratory, Council of Scientific and Industrial Research (CSIR), Thiruvananthapuram, 695 019 Kerala, India

Received 12 February 2002; received in revised form 22 May 2002; accepted 1 June 2002

Abstract

SiC powders are surface modified to behave like alumina in aqueous suspensions by coating the powders with in situ generated hydrolyzed aluminium from dilute aqueous aluminum nitrate solutions in a pH range of 3–4.5 using hexa-methylene-tetramine as the base generator at ambient temperature. By examining the zeta potential and rheological properties of aqueous suspensions of the powder with different Al-coverage, it was observed that the coated powder begins to show alumina-like surface properties at an Al-coverage of 0.1 mg/m^2, in contrast to 0.5 mg/m^2 that was the minimum value reported earlier for observing the effect. This is explained by proposing a coating mechanism which proceeds through adsorption of a layer of cationic hydrolysed aluminum molecules, such as $[Al(OH)(H_2O)_5]^{2+}$ and $[Al_2(OH)_2(H_2O)_8]^{4+}$, during which the particles attain alumina-like surface charge properties. The modified powder retained alumina-like surface characteristics when stored under moist conditions and in acidic suspensions. The low value of Al-coverage and the resulting low increase ($<10\%$) of powder surface area are advantageous for preparation of concentrated SiC and SiC–Al_2O_3 composite suspensions in acidic aqueous medium with rheological properties similar to that of their counterparts containing alumina only.

Keywords: Coatings; Dispersion; SiC; Surface modification; Suspensions; Al_2O_3

1. Introduction

Colloidal processing of ceramics has gained importance mainly because of the possibility of fabricating high density compacts by using process such as slip-casting, filtration and/or plastic forming techniques from well dispersed suspensions. Aqueous ceramic suspensions are dispersed either by adjusting the slurry pH away from the pH_{iep} of the powder (electrostatic stabilization) or by using polyelectrolytes as dispersing agents (electrosteric stabilization). However, powder dispersion characteristics and the flow properties of the resulting suspensions are controlled by the powder surface charge which vary with the type of powder and even with their source. Due to this surface property variation it is often necessary to use a specific pH or a certain dispersing agent for each separate powder. Identification of a common pH or dispersing agent becomes difficult specially when different types of powders with wide difference in their surface properties are used for preparing composite powder suspensions.

Alumina coating of powders has been used to improve colloidal processing of various ceramics by controlling the particle surface charge.[1–9] The coating produces particles with uniform surface properties by suppressing the surface heterogeneity that originates from impurities or process conditions. For non-alumina ceramics such as SiC and Si_3N_4, the coating also produces alumina-like surface. These coated powders, by virtue of their alumina-like surface, show dispersion characteristics of alumina and they along with alumina form homogenous suspensions for fabrication of composites. In addition, the coating enhances the strength of their green compacts and improves the sintering behaviour.[10,11]

However, the coating is generally followed by an increase in the surface area or change in the surface morphology of particles.[2,4] Surface area of the coated powders increases with increase in the amount of

---

* Corresponding author. Fax: +91-471-491712.
E-mail address: pav@csrrltrd.ren.nic.in (C. Pavithran).

[1] Present address: Naval Materials Research Laboratory (DRDO), Mumbai 400 001, India.

0955-2219/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0955-2219(02)00172-3

adsorbed hydrolysed aluminium. This leads to an increase in the slip viscosity which become more predominant in concentrated slips. Concentrated (>50 vol.%) suspensions with low viscosities (<1 Pa s) are desired for fabrication of dense and near-net-shape green bodies by ceramic processes such as slip-casting and gelcasting.[12,13] Hence when coated powders are used for preparation of concentrated slurries it is desired that the coating thickness or the amount of adsorbed aluminium is minimized to achieve the desired level of modification.

Alumina coating of ceramic powders can be accomplished by either the colloidal coating[6] or precipitate coating method.[2] In the colloidal method, the coating is formed by electrostatic adsorption of small alumina particles from sols or colloidal suspensions. The precipitate coating, on the other hand, is achieved by condensation of hydrolysed aluminium, generated in situ from an aluminium alkoxide or salt solution, on the particles. Whereas aluminium alkoxides are hydrolysed from their non-aqueous solutions by addition of controlled amount of water, aluminium salts are hydrolysed from aqueous solutions by using a base generator (urea or hexamethylene-tetramine) and employing a reaction temperature of 85 °C. Colloidal coating generally produce thick coatings (>10 nm) since they are derived from boehmite platelets or alumina sol clusters of size above 1 nm. On the other hand, thin coatings (<3 nm) were possible by the precipitation method wherein the coatings were formed from Al-solutions by in situ generation of hydrolysed aluminium and their condensation on the particle surface.

Liden et al.[2] have optimised surface modification of SiC and Si_3N_4 powders with hydrolysed aluminium coating from an alkoxide solution by controlling the hydrolysis and polymerization reactions of the alkoxide molecules. They report an Al-coverage minimum of about 0.5 mg/m^2 to give the powders alumina-like properties. They have also observed a surface area increase by about 20% for the coated powder. In this context there is a need for obtaining the desired properties at a lower Al-coverage. In this paper we report that alumina-like surfaces of SiC can be obtained at significantly low Al-coverage values by using dilute aluminium salt solutions and controlling the hydrolysis reactions in a narrow pH range. The implications are discussed.

2. Experimental procedures

Two SiC powders with different particle size and specific surface area were used. The "fine" powder with an average particle size of 0.2 μm and the BET surface area of 35 m^2/g was obtained from M/s Ibiden Co., Ogaki, Japan and the "coarse" powder with a particle size of 2 μm and the surface area of 4.1 m^2/g was obtained from M/s Grindwell-Norton, India. α-Alumina (AKP-15, Sumitomo Corporation, Japan) with a particle size of 0.63 μm and the surface area of 3.7 m^2/g was used for preparation of aqueous codispersions with SiC. Aluminium nitrate (E-merck India Ltd.) and Hexamethylene tetramine (HMTA) (Fluka, Switzerland) were of reagent grade.

SiC powders with various amounts of hydrolysed aluminium coating were obtained by the following procedure. Aqueous SiC slurries (about 30 vol.%) containing various amounts of aluminium nitrate and HMTA in 4:3 mole ratio and of pH about 3 were tumbled in a polyethylene bottle along with silicon carbide balls for about 12 h. The resulting mix was then aged at ambient temperature (~30 °C) for 36 h. The slurries were centrifugally separated, washed repeatedly with distilled water and dried in flowing air at ambient temperature. The powder thus dried retained a water content of about 5% by weight. The Al-solution concentration was varied such a way that the amount of Al available for coating was in the range of 0.1–0.5 mg/m^2 of the powder surface area. An aging time of 36 h was fixed after studying the Al-absorption Vs time behaviour for a typical Al-solution concentration for a duration up to 60 h.

The amount of aluminium absorbed on the powder was obtained by determining the amount of aluminium in the spent solution and knowing the amount of aluminum initially taken. Aluminium in the spent solution was estimated titrimetrically using Ethylenediamine-tetra-acetic acid (EDTA) following a standard procedure.[14]

The modified powders were characterized by dispersing them in aqueous medium and examining the rheological properties of the suspensions and zeta potential of the powder as function of pH. The rheological properties were studied using concentrated (30–40 vol.%) suspensions of the 'coarse' powder. The viscosity of the suspensions at shear rates of 4.65–93 s^{-1} was measured using RVT/HBT Synchro-lectic viscometer with SC4–21/13R small sample adapter of coaxial geometry (Brookfield Engineering, Stoughton MA). Zeta potential measurements using dilute (~10 vol.%) suspensions of the 'fine' powder were carried out in a zeta potential analyzer (Micromeritics, model 1202). The BET surface area of the as received and the coated powders were measured in surface area analyzer (Model Gemini III 2375, Micromeritics Instrument Corp., Norcross, GA) using nitrogen adsorption.

3. Results and discussion

In this investigation Al-solution concentration was kept below 0.5 mg/m^2 of the powder surface, the minimum amount of Al required for modification by the procedure adopted by Liden et al.[2] In addition, the coating experiments were performed at ambient temperature (~30 °C), as against 80 °C that has been employed by earlier investigators for coating from aluminium salt solutions, so that the HMTA hydrolysis producing ammonia and simultaneous hydrolysis of aluminium occurred in a slow and controlled manner.[15,16]

3.1. Al-adsorption vs reaction time

The progress of HMTA hydrolysis and SiC particle surface modification by adsorption of hydrolysed aluminium was monitored by measuring the slurry pH and viscosity at different intervals. Fig. 1 shows the variation of pH and viscosity with reaction period (including both tumbling and ageing time) of a 28 vol.% aqueous SiC slurry containing 0.2 mgAl/m^2 of the powder surface along with stoichiometric amount of HMTA. The slurry pH increases very slowly from 3.4 to 4.1 during a reaction period of 72h. The slurry viscosity simultaneously decreases from 0.8 to 0.25 Pa s. Estimation of aluminium content in the spent solution revealed that aluminium adsorption on the particles increased with reaction time leading to an Al-coverage of 0.1 mg/m^2 during a period of 48 h. Significant adsorption was not observed after 48 h, corresponding to the plateau region of the viscosity–time curve, possibly due to depletion of aluminium in the solution and sluggishness of HMTA hydrolysis at higher pH.[16]

3.2. Al-adsorption vs Al-solution concentration

Assuming that the hydrolysis reactions become sluggish after 48 h, the coating experiments were repeated for different Al-solution concentration (hereafter referred as Al-concentration) for a fixed duration of 48 h. Fig. 2 shows that Al-adsorption (hereafter referred as Al-coverage) increases from 0.05 to 0.33 mg/m^2 by varying the Al-concentration in the range 0.12–0.44 mg/m^2 of the powder surface. More or less identical Al-coverage values were obtained for both the ‘fine’ and ‘coarse’ powders using identical Al-concentrations with respect to the powder surface area. Desired Al-coverage could be obtained by judiciously fixing the Al-concentration and the reaction period as well as controlling the pH and temperature.

3.3. Rheological properties of suspensions vs Al-coverage

Al_2O_3 and SiC show wide difference in their dispersion characteristics in acidic aqueous medium due to large difference in their pH$_{iep}$. The suspension of SiC with pH$_{iep}$ of about 4 flocculates at pH 4 while Al_2O_3 with pH$_{iep}$ about 8 shows homogenous dispersion. Al-coating shifts the pH$_{iep}$ of SiC towards that of alumina. The extent of SiC surface modification by different levels of Al-coating can, therefore, be assessed by examining the rheological properties of their aqueous suspensions at pH 4.

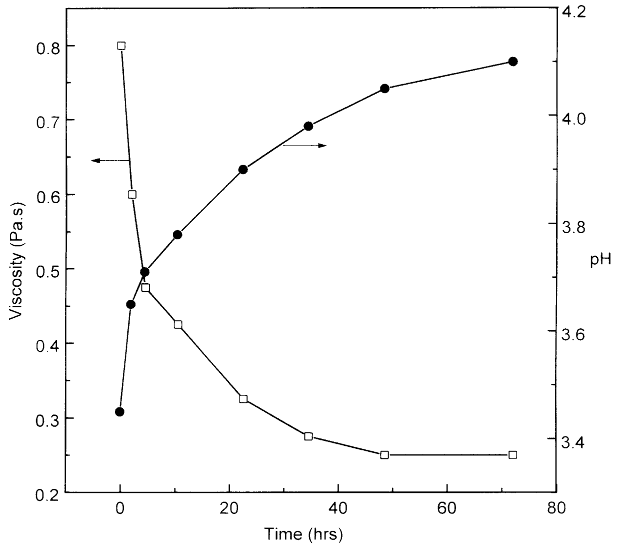

Fig. 1. Variation of pH and viscosity at 9.3 s^{-1} with room temperature ageing of an aqueous SiC slurry (28 vol.% solid) mixed with aluminium nitrate (0.22 mgAl/m^2 of the powder surface) and stoichiomeric amount of HMTA. The ageing time includes a tumbling period of 12 h.

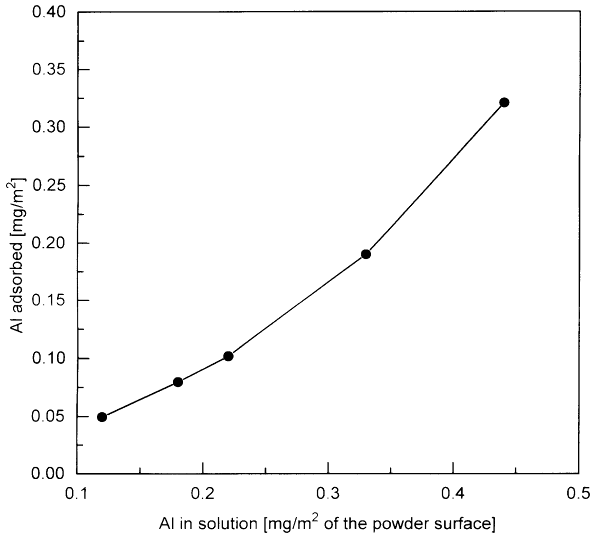

Fig. 2. Effect of Al-solution concentration on Al-adsorption on SiC particles during a reaction period of 48 h.

Fig. 3 shows the effect of different Al-coverage of the particles and shear rate on the viscosity of SiC aqueous suspensions at pH 4. As expected, the suspension of the unmodified powder was highly unstable at pH 4 and showed high viscosity and shear thinning flow behaviour due to flocculation. Powder surface modification with hydrolysed aluminium coating brings down the suspension viscosity and modifies the flow behaviour. It can be seen that the slurry viscosity at 9.3 s^{-1} decreases with increase in Al-coverage up to 0.1 mg/m^2. Significant

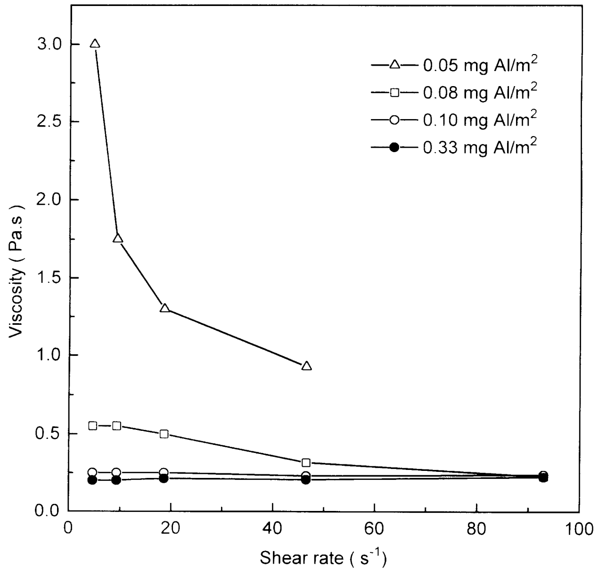

Fig. 3. Effect of different Al-coverage of particles and shear rate on the viscosity of aqueous SiC slurries at pH 4.

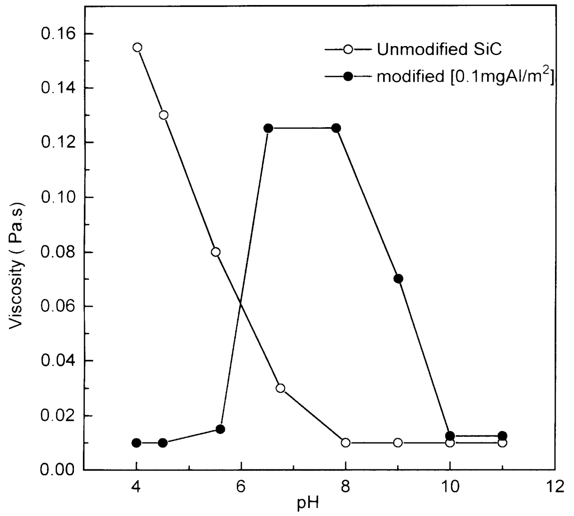

Fig. 4. Viscosity at 9.3 s^{-1} vs pH plots for the aqueous slurries of surface modified (0.1 $mgAl/m^2$) and unmodified SiC powders.

variation of the viscosity does not occur by increasing the Al-coverage above 0.1 mg/m^2. In addition, the flow behaviour of the suspension shows a gradual transition from pseudo-plastic for the flocculated systems containing powders with Al-coverage <0.1 mg/m^2 to newtonian for dispersed systems containing powders with Al-coverage $\geqslant 0.1$ mg/m^2.

3.4. Viscosity and zeta potential vs pH

Fig. 4 shows the viscosity of the suspension of the modified powder with Al-coverage of 0.1 mg/m^2 in comparison to that of the unmodified powder suspension at pH between 4 and 11. The unmodified powder suspension shows dispersion and viscosity minimum at pH above 8. The modified powder suspension, on the other hand, shows dispersion in acidic medium at pH 4 as well as in alkaline medium at pH above 10 as for alumina suspension.

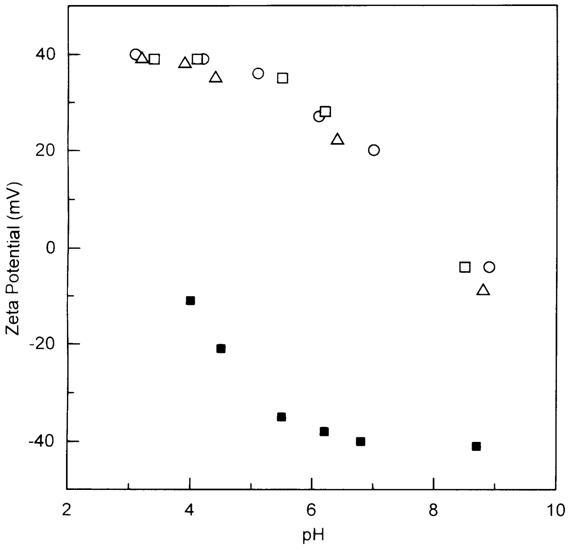

Fig. 5. Zeta potential vs pH plot for SiC (■), Al_2O_3 (○) and SiC surface modified with 0.1 $mgAl/m^2$ (△) and 0.33 $mgAl/m^2$ (□).

Fig. 5 shows the change in zeta potential with pH of the modified SiC powders, 0.1 and 0.33 $mgAl/m^2$, in comparison with the unmodified SiC and a typical commercial α-Al_2O_3. Whereas the unmodified powder shows its characteristic negative potential in this pH range, the modified powders show positive potential in acidic suspensions and negative potential in basic suspensions, characteristic of alumina. Furthermore, the zeta potential vs pH plot of the modified powders closely follow that of a typical α-alumina. It may also be interesting to note that the potential values of the modified powder do not vary significantly by increasing the Al-coverage from 0.1 to 0.33 mg/m^2.

3.5. Surface area of the coated powders

Significant change in the surface area from that of the uncoated powder was not observed for the coated powder with Al-coverage of 0.1 mg/m^2. However, increase in the surface area became significant ($>10\%$) for Al-coverage values 0.2 mg/m^2 and above. This is in agreement with the observations by Liden et al.[2] who has reported a surface area increase by 10–40% for powders with Al-coverage in the range 0.2–0.7mg/m^2.

3.6. Stability of the coating

Though thin coating is desired when surface area increase is concerned, stability of the coating under different environment decides the use of these coated powders in ceramic processing. Aging of the aqueous suspensions of the modified powder (0.1 mgAl/m^2) showed that the coating was fairly stable in acidic medium but highly unstable in alkaline medium. The coated powder that recovered from an alkaline suspension showed dispersion characteristics of the unmodified SiC upon redispersing in acidic medium, possibly due to exposure of the native SiC surface by dissolution of the coatings in the alkaline medium. On the other hand, the acidic suspension of the coated powder showed settling tendency only after 20 days.

Similarly, the powder retained alumina-like dispersion characteristics only when stored under moist conditions. While the moist powder (water content ~5%) readily dispersed in water, the suspension of the powder that was dried at 110 °C showed high viscosity and low stability, possibly due to thermally activated condensation of hydrolysed aluminium through de-hydroxylation which would reduce the active sites for protonation and bring down the particle surface charge.

Fig. 6 shows the photograph of the modified (0.1 mgAl/m^2) and unmodified powder suspensions at pH 4 and 7. The modified powder suspension, as for alumina suspension, is stable at pH 4 and unstable at pH 7, and vice versa for the unmodified powder. Fig. 7 shows the viscosity and flow properties of concentrated (>50 vol.%) aqueous SiC–Al_2O_3 composite powder suspensions at pH 4. As expected, addition of small amount of the unmodified SiC powder in alumina suspension drastically increase the slurry viscosity due to heterocoagulation. On the other hand, incorporation of the modified powder, as high as 25 vol.%, does not bring any significant change in the slurry viscosity and flow behaviour from its counterpart containing alumina only.

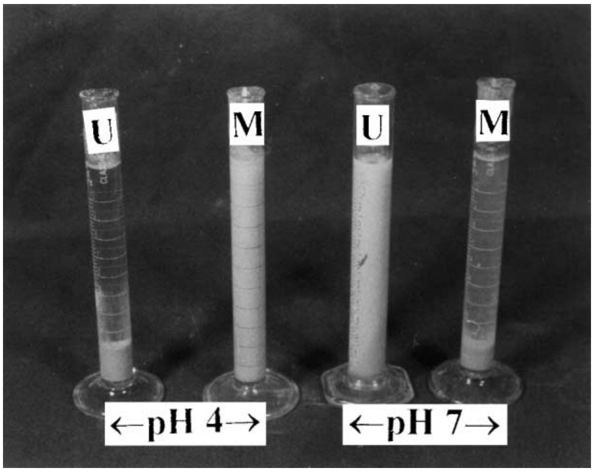

Fig. 6. Photograph of aqueous dispersions of unmodified (U) and surface modified (M) SiC powders at pH 4 and 7 showing alumina-like dispersion behaviour of the powder by modification with 0.1 mgAl/m^2.

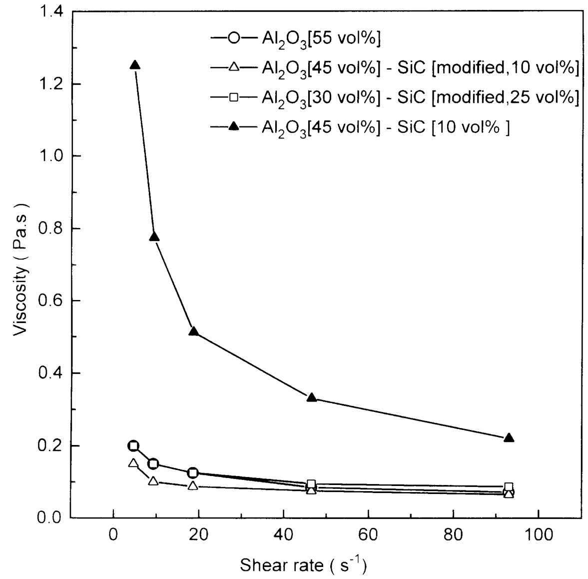

Fig. 7. Viscosity and flow behaviour of aqueous SiC–Al_2O_3 composite suspensions at pH 4. Modified SiC surface contains 0.1 mgAl/m^2.

3.7. Surface modification mechanism

From the above discussed experimental results it is obvious that SiC powders coated with hydrolysed aluminium by the present procedure begin to show alumina-like surface characteristics at an Al-coverage as low as 0.1 mg/m^2 in contrast to 0.5 mg/m^2 reported by earlier investigators. Assuming that a uniform surface layer is formed, 0.1 mgAl/m^2 is equivalent to about 2 Al per nm^2 which suggests a layer of molecular size.

Wood et al.[17] have reviewed the hydrolysis of aluminium salts in aqueous medium using HMTA or urea as the base generator. Aluminium in aqueous solutions exists as the monomer $[Al(H_2O)_6]^{3+}$ below pH 3.5. Homogenous hydrolysis initially generates small cationic hydrolysed molecules. With continued base generation, these molecules grow in size by intermolecular condensation to produce $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ known as Al_{13} ion. These reactions take place below pH 4.5. Bulk of the aluminium exists as $[Al(OH)_3]^0$ between pH 4.5 and 11. Above this pH $[Al(OH)_4]^-$ ions are formed. Thus the hydrolysis reactions in the present investigation being controlled below pH 4.5 favours SiC particle surface modification with coatings of Al_{13} ion or its precursor molecules.

It is well known that the surface of SiC contains a SiO_2 film due to oxidation. In a humid environment the oxide surface hydrolyses to form negatively charged surface groups, $\equiv Si(OH)^-$. Yang et al.[18] in their study on dispersion of SiC powder in Al_{13} solution proposes the following chemical reactions between the negatively charged surface sites of SiC particles and the positively charged Al_{13} ions leading to particle surface modification through reversal of the surface charge sign: $\equiv Si(OH)^- + [AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+} \rightarrow \equiv Si\text{–}O\text{–}Al\text{–}AlO_4Al_{11}(OH)_{23}(H_2O)_{12}^{6+} + H_2O$.

The density of such active sites on SiC particle is about 2 per nm.[19] Al_{13} ion has a size of about 1 nm.[17] Hence, assuming that each Al_{13} ion reacts with two sites on the particle, only 17% of the total available sites get occupied at an Al-coverage of 0.1 mg/m^2. Furthermore, assuming that the reacted Al_{13} ions carry five positive charges per molecule, the coating provides only very low surface charge of about 13 μc/cm^2 to the particles while a surface charge of 30–35 μc/cm^2 is required for producing alumina-like surface.[20] On the other hand, saturation of the active surface sites as well as desired surface charge density with equivalent amount of Al can be obtained using precursor molecules of Al_{13} ion, particularly by the monomeric $[Al(OH)(H_2O)_5]^{2+}$ and dimeric $[Al_2(OH)_2(H_2O)_8]^{4+}$ species, which carry higher charge per aluminium atom when compared to Al_{13} ion. Liden et al.[2] have studied the change in electro-kinetic behaviour of SiC particles in dilute (10^{-5} M) $AlCl_3$ aqueous solutions with increase in pH from 2 to 11. They have observed a gradual change in the electrokinetic behaviour along with reversal of the particle surface charge sign from negative to positive on increasing the pH to 6.5. This has been attributed to adsorption of monomeric hydrolysed aluminium molecules. The present results support this view.

Liden et al.[2] also propose a multiple-step reaction for the growth of hydrolysed aluminium coating on SiC from an alkoxide solution. They suggest that the reaction starts with chemical adsorption of a monolayer of the alkoxide molecule. The layer build up by addition of further alkoxide molecules on the monolayer along with adsorption of small aggregates of hydrolysed alkoxide molecules that are formed in the solution. These reactions take place simultaneously so that a continuous layer is formed only at an Al-coverage of about 0.5 mg/m^2. A multiple-step reaction may be operative in the present system also, but in a more controlled manner under the present experimental conditions of low Al-solution concentration (<0.5 mgAl/m^2 of the powder surface), very slow hydrolysis and high substrate particle concentration. The results of the present study can be explained by the following layer build up mechanism. The Al-hydrolysis starts with small increment of the pH above 3.5 producing small amount of Al_{13} pecursor molecules. These molecules are simultaneously absorbed on the particle surface through electrostatic interactions. As the pH increases further, more hydrolysed aluminium molecules are produced and simultaneously absorbed on the particles. This process continues till the powder surface sites get saturated with these molecules during which the particle also attain maximum positive charge density. As discussed earlier, an Al-coverage of 0.1 mg/m^2 is sufficient to produce this result and the above reactions may be taking place at a pH below 4 as can be inferred from Fig. 1. Upon continued supply of aluminium and increase in pH, the layer grows by intermolecular condensation reactions, enriching the layer with condensed species such as Al_{13} ions. Since the condensation reactions lead to a decrease in the charge carrying capacity per aluminium atom, increase of Al-coverage above 0.1 mg/m^2 does not bring any significant change in the zeta potential of the powder and rheological properties of the suspensions.

4. Conclusions

In this paper the results of surface modification of SiC powders by hydrolysed aluminium coating from dilute aqueous aluminium nitrate solutions using hexamethylene tetramine as the base generator and conducting the hydrolysis at ambient temperature in a pH range of 3–4.5 are presented. The coated powder begins to show alumina-like dispersion characteristics at an Al-coverage of 0.1 mg/m^2 and significant change of zeta potential value of the modified powder and rheological properties of the suspension was not observed by increasing the Al-coverage by more than three times. The above observations can be explained by a multistep reaction for development of the coating. The coating build up through formation of a layer of cationic hydrolysed aluminium molecules such as $[Al(OH)(H_2O)_5]^{2+}$ and $[Al_2(OH)_2(H_2O)_8]^{4+}$ during which the particles attain alumina-like surface charge properties. With continued addition of aluminum, the layer grows by intermolecular condensation reactions. Significant change in the particle surface charge does not occur since condensation reactions lead to a decrease in the charge carrying capacity per aluminium atom. The modified (0.1 mgAl/m^2) powder retained alumina-like surface characteristics when stored under moist conditions and in acidic suspensions. The low value of Al-coverage and the resulting low increase of powder surface area are advantageous for preparation of concentrated SiC and SiC–Al_2O_3 composite suspensions in acidic aqueous medium with rheological properties similar to that of their counterparts containing alumina only.

Acknowledgements

K.P. gratefully acknowledges CSIR for providing Senior Research Fellowship during the tenure of this work.

References

1. Bostedt, E., Persson, M. and Carlsson, R., Colloidal processing through surface modification. In *Euro. Ceram., Vol. I, Processing of Ceramics*, ed. G. de With, R. A. Terpstra and R. Metselaar. Elsevier, London, 1989, pp. 140–144.
2. Liden, E., Bergstrom, L., Person, M. and Carlson, R., Surface modification and dispersion of silicon nitride and silicon carbide powders. *J. Eur. Ceram. Soc.*, 1991, **7**, 361–368.

3. Jang, H. M., Moon, J. H. and Jang, C. W., Homogeneous fabrication of Al_2O_3–ZrO_2–SiC whisker composites by surface induced coatings. *J. Am. Ceram. Soc.*, 1992, **75**(12), 3369–3376.
4. Luther, E. P., Lange, F. F. and Pearson, D. S., Alumina surface modification of silicon nitride for colloidal processing. *J. Am. Ceram. Soc.*, 1995, **78**(8), 2009–2014.
5. Shih, W. H., Pwu, L. L. and Tseng, A. A., Boehmite coating as consolidation and sintering aids in aqueous silicon nitride processing. *J. Am. Ceram. Soc.*, 1995, **78**(5), 1252–1260.
6. Shih, W. H., Kisailus, D. and Shih, W. Y., Rheology and consolidation of colloidal alumina-coated silicon nitride suspensions. *J. Am. Ceram. Soc.*, 1996, **79**(5), 1155–1162.
7. Tang, Q., Xie, Z., Yang, J. and Huang, Y., Coating of silicon nitride and its colloidal behaviour. *J. Mater. Sci. Lett.*, 1998, **17**(14), 1239–1241.
8. Yang, C. Y. and Shih, W. H., Effects of acid on the coating of boehmite onto silicon carbide particles in aqueous suspensions. *J. Am. Ceram. Soc.*, 1999, **82**(2), 436–440.
9. Prabhakaran, K. and Pavithran, C., Gelcasting of alumina using urea-formaldehyde I—preparation of concentrated aqueous slurries by particle treatment with hydrolysed aluminium. *Ceram. Int.*, 2000, **26**(1), 63–66.
10. Wang, C. M., Mechanical properties of green compacts with coated powders. *Ceram. Int.*, 1996, **22**(2), 113–117.
11. Wang, C. M. and Riley, F. L., Alumina coating of silicon nitride powders. *J. Eur. Ceram. Soc.*, 1992, **10**, 83–93.
12. Aksay, I. A., Molecular and colloidal engineering of ceramics. *Ceram. Int.*, 1991, **17**(5), 267–274.
13. Omatete, O. O., Janney, M. A. and Strehlow, R. A., Gelcasting—a new ceramic forming process. *Am. Ceram. Soc. Bull.*, 1991, **70**(10), 1641–1649.
14. Vogel's Text Book of Quantitative Chemical Analysis, 5th edn. Jeffery, G. H., Bassett, J., Mendham, J. and Denney, L. C. (revisors). Longman Scientific & Technical, Longman Group UK Ltd., 1989, p. 324.
15. Dreyfors, J. M., Jones, S. B. and Sayed, Y., Hexamethylene tetrammine—a review. *Am. Ind. Hyg. Assoc. J.*, 1989, **50**(11), 579–585.
16. Chem, P. and Chem, I., Reactive cerium(IV) oxide powders by homogeneous precipitation method. *J. Am. Ceram. Soc.*, 1993, **76**(6), 1577–1583.
17. Wood, T. E., Siedle, A. R., Hill, J. R., Skarjune, R. P. and Goodbrake, C. J., Hydrolysis of aluminium—Are all gels created equal? In *Better Ceramics Through Chemistry IV*, ed. B. J. J. Zelinski, C. J. Brinker, D. E. Clark and D. R. Ulrich. MRS Symposium Proceedings, Vol. 180. Materials Research Society, Pittsburg, PA, 1990, pp. 97–116.
18. Yang, Q. and Troczynski, T., Dispersion of alumina and silicon carbide powders in alumina sol. *J. Am. Ceram. Soc.*, 1999, **82**(7), 1928–1930.
19. Whitman, P. K. and Feke, D. L., Comparison of surface charge behaviour of commercial silicon nitride and silicon carbide powders. *J. Am. Ceram. Soc.*, 1998, **71**(12), 1086–1093.
20. Prabhakaran, K., Ananthakumar, S. and Pavithran, C., Effect of hydrolysed aluminium treatment on rheological characteristics of α-alumina slurries. *J. Mater. Sci.*, 2001, **36**, 4827–4831.