Journal of the European Ceramic Society **17** (1997) 1387–1392
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0955-2219/97/$17.00
PII: S0955-2219(97)00010-1

Processing of Aqueous α-Al_2O_3, α-SiO_2 and α-SiC Suspensions with Polyelectrolytes.

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(Received 13 June 1996; revised version received 2 December 1996; accepted 9 December 1996)

Abstract

The preparation of aqueous α-Al_2O_3, α-SiO_2 *and* α-*SiC suspensions with polyelectrolytes, i.e. the* NH_4^+ *salt of polymethacrylic acid (PMA-*NH_4^+*) and the acidic form of polyethylene imine (PEI-*H^+*), is investigated. It is based on the adsorption of these polyelectrolytes which in turn depends mainly on the nature of the polyelectrolyte, and the charge density that develops on the powder surface in water. The efficiency of these dispersants is primarily attributed to the electrostatic interaction between -*COO^- *groups of PMA-*NH_4^+ *and positive sites on the alumina surface at pH 8–9 as well as between –*NH_2^+*– groups of PEI-*H^+ *and negative sites of the silica surface or of the oxidized surface of silicon carbide in acidic media. Good dispersion and stability of dispersions are then obtained through electrostatic and steric stabilization. As an application, the preparation of an* Al_2O_3*–SiC aqueous mixed slurry was investigated as a preliminary step in the processing of* Al_2O_3*/SiC nanocomposites. © 1997 Elsevier Science Limited.*

1 Introduction

The stability of colloidal suspensions can be greatly improved by synthetic polymers. Such organic aids in ceramic processing are extensively used in non-aqueous media where 'electrostatic stabilization' is less successful because of the low dielectric constant of the medium.[1] In aqueous systems, it has been reported[2] that both steric and electrostatic mechanisms can contribute to the stability of suspensions.

Many factors such as the nature of the particle surface, of the adsorbed polymer (or of the polyelectrolyte) and of the solvent are known to affect suspension stability.[3] The adsorption of polymers onto powder surfaces is a rather complex process which is controlled by the competitive affinities of the deflocculant with the powder surface and with the solvent.[4] The interaction of functional groups of the polymer with cationic sites on the mineral surface can therefore play an important role in the adsorption process. According to the work of Aksay and co-workers on alumina,[2] a good dispersion is obtained when the polyelectrolyte develops charges, the sign of which is opposite to the natural charges on the powder surface at a given pH.

In this paper, we intend to provide a clearer understanding of powder dispersion with the aid of adsorbed polyelectrolytes, and to relate it to the chemistries of the particle surfaces and of the polymers. Aqueous oxide and non-oxide suspensions will be considered as a general example. Particular emphasis will be given to the dispersion of α-Al_2O_3 with NH_4^+ salt of polymethacrylic acid and to the dispersion of α-SiO_2 and α-SiC with polyethylene imine neutralized in acidic media. It is also an objective of this paper to describe a methodology of using polyelectrolytes for powder processing of a mixed (oxide–non oxide) aqueous suspension.

2 Experimental Procedure

2.1 Starting materials

The main features of the powders used in this study are summarized in Table 1. Two polyelectrolytes were used in this work. The first is an, NH_4^+ salt of polymethacrylic acid (PMA-NH_4^+, Table 2, Fig. 1) with an average molecular weight of 10 000 (Darvan C, Vanderbilt, GB). Detailed information concerning this polyelectrolyte and its adsorption behaviour on oxides has been published by Cesarano *et al.*[2] The second is a polyethylene imine (PEI, Aldrich, Fig. 2), a secondary polyamine with an average molecular weight of 50 000. Addition of a strong acid, such as nitric acid, HNO_3 to a solution of PEI neutralizes the

Table 1. Powders used in the present work

	Supplier	*Specific surface BET* (m^2g^{-1})	*Average grain size* (μm)
α-Alumina	P172SB-Pechiney, France	10	0·3
α-Alumina	AKP30-Sumitomo, Japan	7·5	0·3
α-Quartz	Sifraco Millisil C800, France	5	1·5
α-Silicon carbide	Lonza UF45, France	45	0·15

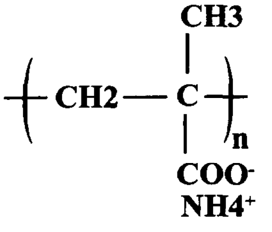
Table 2. Dispersants used in the present work

Polyelectrolyte	*Symbol*	*Average molecular weight*
NH_4^+ salt of polymethacrylic acid	PMA-NH_4^+	10 000
Polyethylene imine	PEI	50 000
Polyethylene imine neutralized by nitric acid to an extent of 50 %	PEI-0·5H^+	Ib.
Polyethylene imine neutralized by nitric acid to an extent of 70%	PEI-0·7H^+	Ib.

–NH– basic groups and then confers a positive charge to the polymer skeleton according to the reaction:

$$[-CH_2-CH_2-NH-]_n \xrightarrow{H_3O^+} [-CH_2-CH_2-NH_2^+-]_n + H_2O \qquad (1)$$

The proportion of ionized groups depends on the amount of acid added. Secondary amines are known as weak bases. The pK_a of a secondary amine, –NH– ($pK_a \approx 10{\cdot}4$) is slightly larger than that of ammonia, NH_3 ($pK_a \approx 9{\cdot}2$). The pH of an aqueous solution containing 1 wt% PEI is about 11 (Fig. 3). This value is in fair agreement with that obtained through the classical equation $pH = 7 + pK_a/2 + (\log c)/2$, where c denotes the concentration of [–NH–] groups. According to Fig. 3, the variation of pH versus the quantity of HNO_3 added is rather slow. This phenomenon is attributed to electrostatic interactions which develop within the polymer chain between $-NH_2^+-$ groups, which in turn lead to an apparent increase in pK_a during neutralization of the basic groups. This effect is similar to that observed when polyacrylic acid is neutralized by a strong base such as sodium hydroxide.[5] The proportions of nitric acid which were added to the PEI solutions were, respectively, 50 and 70% with respect to the concentration of initial –NH– groups (Table 2). The polyelectrolytes thus obtained will be denoted below by PEI-0·5H^+ and PEI-0·7H^+. The contents of polyelectrolytes used as dispersants are expressed in wt% with respect to the ceramic powder.



$$-\!\left[CH2-\underset{\substack{|\\ COO^-\\ NH4^+}}{\overset{\substack{CH3\\ |}}{C}}\right]_n\!-$$

Fig. 1. Chemical structure of PMA-NH_4^+.

$$-\!\left[CH2-CH2-NH\right]_n\!-$$

Fig. 2. Chemical structure of PEI.

2.2 Characterizations

2.2.1 Grain size distribution

The degree of dispersion of a ceramic suspension was evaluated in terms of particle size distribution as revealed by an X-ray absorption/sedimentation technique (Sedigraph 5100, Micromeritics, France). Suspensions containing 20 wt% of ceramic powder were prepared with various amounts of PMA-NH_4^+ in the case of Al_2O_3 (Pl 72SB), and with various amounts of PEI-0·5H^+ or PEI-0·7H^+ in the case of SiO_2 and SiC powders.

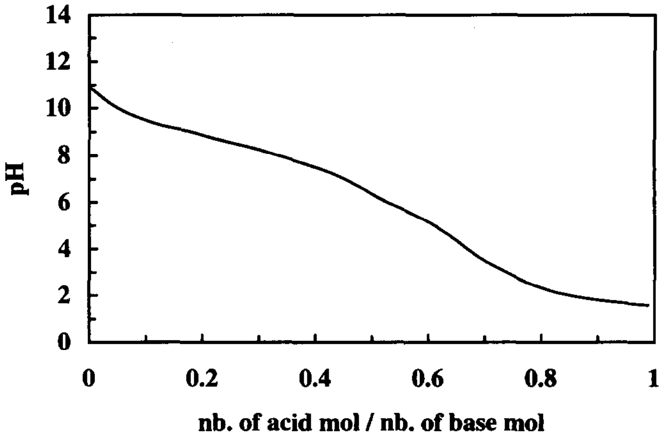


Fig. 3. Variation of pH of a PEI solution during neutralization with nitric acid.

The samples were ultrasonicated for 3 min at 300 W prior to the measurement of the particle size distribution. The variation of the mean grain size of alumina versus the amount of PMA-NH_4^+ is plotted in Fig. 4. The same variation is depicted in Figs 5 and 6, respectively, for SiO_2 and SiC powders dispersed with different amounts of PEI-based polyelectrolytes.

2.2.2 Adsorption isotherms

The adsorption of PMA-NH_4^+ on alumina was evaluated by a gravimetric technique. Suspensions containing 20 wt% Al_2O_3 were prepared with various amounts of PMA-NH_4^+ at pH ≈ 8–9. The samples were then allowed to reach equilibrium on a gentle mechanical shaker for 72 h, and then centrifuged at 2000 r.p.m. for 60 min. A given fraction of the supernatant was dried in an oven at 50°C for 3 days, then at 120°C for 1 h. This temperature was selected to avoid a significant weight loss of the polymer by thermal degradation. The residue was then heated at 600°C for 5 h. The weight difference before and after calcination makes it possible to estimate the quantity of non-adsorbed polyelectrolyte in the supernatant. Then the adsorbed amount on the alumina surface can be calculated. The adsorption isotherm of PMA-NH_4^+ on P172SB alumina is shown in Fig. 7. It is similar to those reported in the literature.[2] The quantity of PMA-NH_4^+ adsorbed onto the surface of alumina amounts to 0·35 mgm^{-2} at pH ≈ 8–9 on the plateau, in agreement with the value reported in Ref. 2.

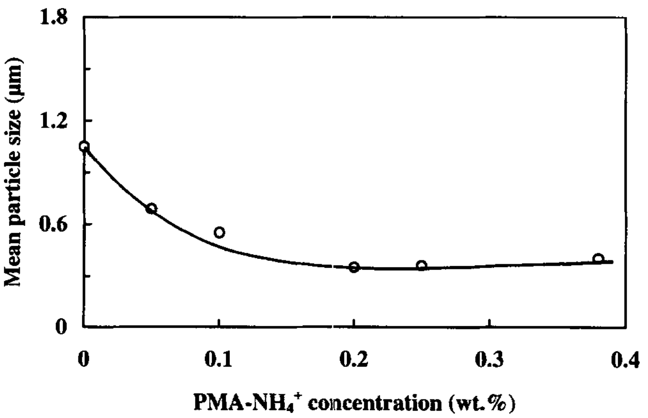


Fig. 4. Variation of mean particle size of α-Al_2O_3 (P172SB) versus quantity of PMA-NH_4^+ added.

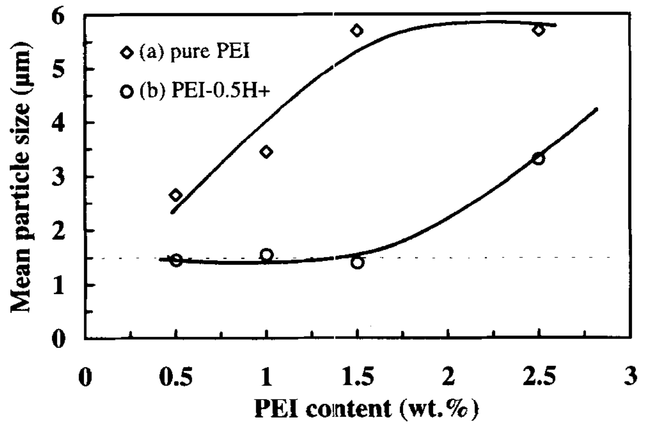
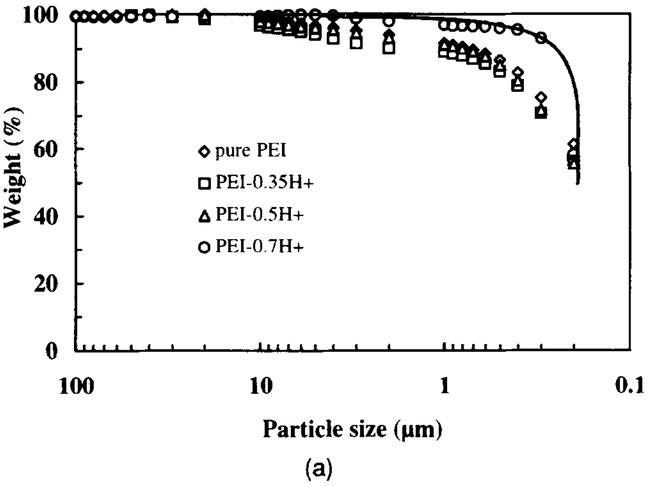


Fig. 5. Variation of mean particle size of silica powder versus quantity of (a) pure PEI and (b) PEI-0·5H$^+$ added.



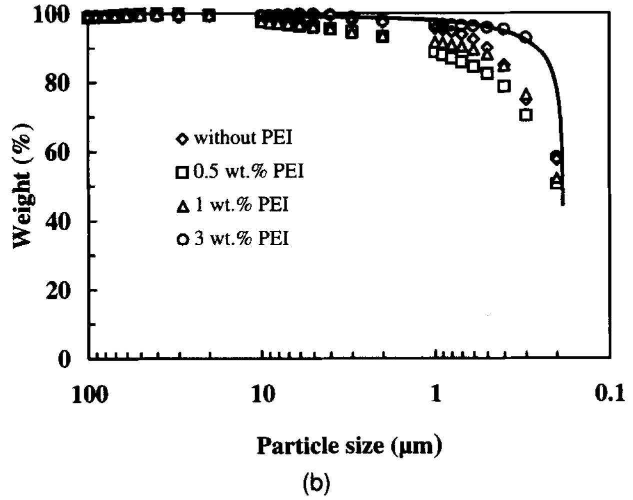


Fig. 6. Distribution of SiC particle size with different proportions (a) of ionization of 3 wt% PEI content and (b) of PEI-0·7H$^+$.

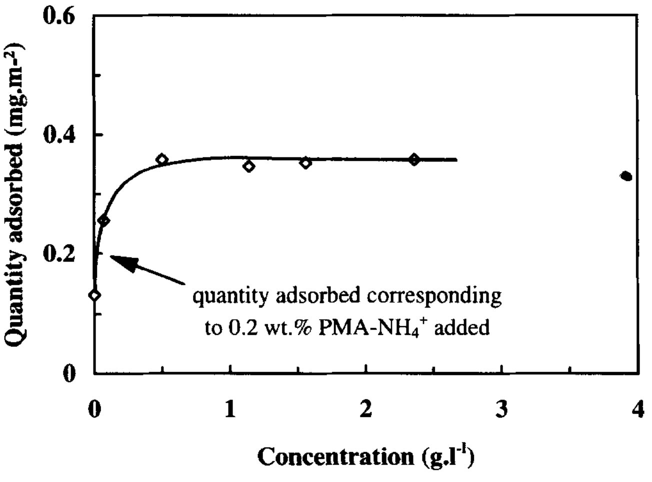


Fig. 7. Adsorption isotherm of PMA-NH_4^+ on P172SB alumina surface. The pH of the suspension is approximately 8·5.

2.3 Zeta-potential experiments

Zeta potential values of the alumina particle charges in the suspensions were measured using an Electrokinetic Sonic Amplitude (ESA) measurement apparatus (Model ESA 8000 Matec).

This technique is based upon the acoustic wave that is generated by the respective motion of the electric double-layer ions and of the charged particles submitted to a high–frequency alternating electric field (1 MHz). This motion generates a sound wave at the same frequency as the electric field, with an amplitude proportional to the electrostatic potential at the shear plane where the zeta potential is defined, the particle concentration and the amplitude of the applied electric field. The ultrasonic signal is detected and converted to a voltage (ESA) by a piezoelectric transducer. In the case of our suspensions, the ESA data are directly proportional to the zeta potential; the curves of variations of the electrokinetic properties in terms of pH and/or dispersant amounts will be presented with ESA values as the *y*-axis.

For each powder, two aqueous slurries were prepared containing a 3·5 vol. % solid loading. In one of these two slurries deflocculant was added: 0·2 wt% of PMA-NH_4^+ for alumina (AKP30), 0·5 wt% of PEI-0·5H^+ for silica and 3 wt% of PEI-0·7H^+ for the SiC powder. The ionic strength of each slurry was adjusted with 0·01 M NaCl. After ultrasonication for 3 min at 600 W, in order to break agglomerates, a period of 24 h was allowed to achieve chemical equilibrium between the powder surface and the deflocculant in the suspension. For the three powders, ESA measurements were carried out with and without deflocculant. During these experiments the pH was adjusted with 1 M HCl and 1 M NaOH. To maintain dispersion during the measurement itself, a magnetic stirrer is placed under the sample.

3 Results and Discussion

3.1 Dispersion of α-alumina

The zero point of charge (zpc) of the alumina used is approximately 8·7 (Fig. 8, curve a). The adsorption isotherm of PMA-NH_4^+ on α-Al_2O_3 (Fig. 7) clearly exhibits the characteristics of a high-affinity adsorption at pH ≈ 8–9. At the values of pH near and below the zpc of alumina, the density of positive charges on the surface of an alumina particle is large enough to allow electrostatic interactions with $-COO^-$ groups of the polyelectrolyte chain. Consequently the α-Al_2O_3-zpc shifts from pH 8·7 down to 5·3 as observed in curve b of Fig. 8.

Previous studies [2, 6] showed that the PMA-NH_4^+ was efficient for dispersion and stabilization of the alumina suspensions both by electrostatic repulsion and steric stabilization. In this preliminary study the adsorption of PEI on alumina was not considered.

3.2 Dispersion of α-quartz

The zpc for α-SiO_2 is approximately 2 (Fig. 9 (a)) in agreement with the value generally reported in the literature.[7] Then at a neutral or moderately acidic pH, the surface charge of silica is negative, in opposition to that of alumina which is positive under the same conditions. Then a positively charged polyelectrolyte is necessary to obtain a strong adsorption on the silica surface. This is the reason why polyethylene imine, ionized by addition of a strong acid (nitric acid), was chosen. The $-NH_2^+-$ groups will be then able to link with the negative sites of the surface. The global surface charge then becomes positive after addition of 0·5 wt% PEI-0·5H^+ (Fig. 9 (b)).

The mean particle size in the suspension is always larger than 2·5 μm when pure PEI is used

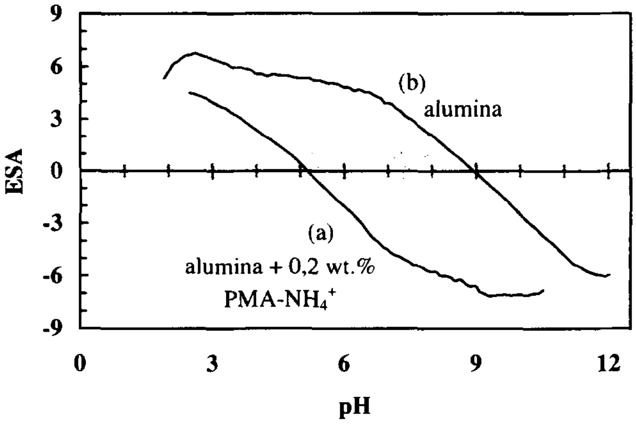


Fig. 8. ESA response versus pH for α-Al_2O_3 (Sumitomo AKP30) powder with (curve a) and without (curve b) PMA-NH_4^+ as a dispersant.

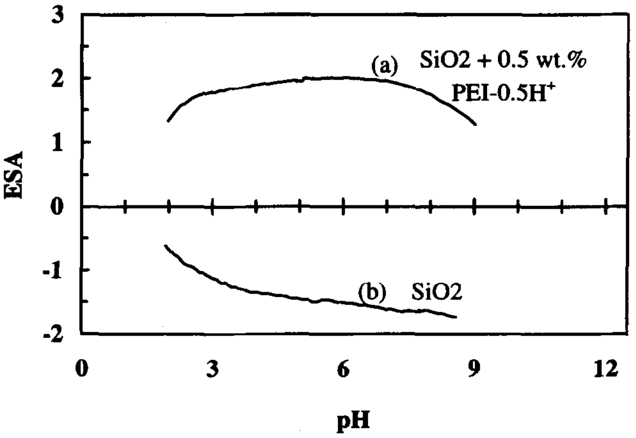


Fig. 9. ESA response versus pH for α-SiO_2 powder with (curve a) and without (curve b) PEI-0·5H^+ as a dispersant.

(Fig. (5a)). This value deviates from the value given by the manufacturer of the powder ($\approx 1{\cdot}5$ μm). One concludes that α-SiO_2 cannot be dispersed by pure PEI. Under such conditions, the pH of the suspension is close to 9, the polymer is only weakly charged, and then a very limited efficiency is expected. A better dispersion of α-SiO_2 can be achieved by using the polyelectrolyte PEI-0·5H^+ in which 50% of the –NH– groups are ionized as $-NH_2^+-$ (Fig. 5 (b)). The mean particle size reaches a value close to that given by the manufacturer, for an amount of polymer added lower than 2·5 wt%. The positive charges of the polyelectrolyte allow adsorption on the negatively charged silica surface (Fig. 9), and lead to powder dispersion, probably through a mechanism similar to that occurring when the alumina slurry is stabilized with PMA-NH_4^+. The increase in the mean particle size observed when the amount of dispersant becomes larger than 2·5 wt% can be attributed to a reagglomeration of α-SiO_2 particles due to interactions between the adsorbed polymeric chains or to the compression of the double electrical layers when the ionic strength of the solution increases.

3.3 Dispersion of α-silicon carbide

The X-ray diffraction pattern of the SiC UF45 powder indicates the presence of a weak peak which corresponds to crystalline SiO_2 (probably cristobalite). On the other hand, the zpc of this SiC powder is approximately 2, close to that of SiO_2 (Fig. 10). According to the chemical analysis, this SiC powder contains 3 wt% of oxygen, probably in the form of SiO_2. This suggests that SiC particles are covered by a silica layer. Consequently, if the dispersion of SiC powder is similar to that of silica, ionized PEI could prove an efficient dispersant. The quantity of polyelectrolyte adsorbed onto oxide surfaces reported in the literature is generally of the order of 0·5 mg m^{-2}.[2] In the case of alumina, the data plotted in Fig. 7 suggest an amount of 0·35 mg m^{-2} on the plateau. Due to a surface area of 45 m^2 g^{-1} for the SiC powder, 2·25 wt% of polyelectrolyte at least should be necessary to disperse this powder if a quantity of 0·5 mg m^{-2} adsorbed was considered. Then, several experiments were performed in order to determine the influence of the neutralization ratio. Dispersion becomes better when the proportion of ionized $-NH_2^+-$ groups increases (Fig. 6 (a)). A good dispersion of the SiC powder is observed after adding 3 wt% of PEI-0·7H^+ at pH 3 (Fig. 6(b)). The mean particle size is close to 0·15 μm. The mechanism for stabilization is probably similar to that involved for silica. The adsorption of the ionized polymer leads to charge reversal of the SiC surface (Fig. 10(b)), as previously observed for silica.

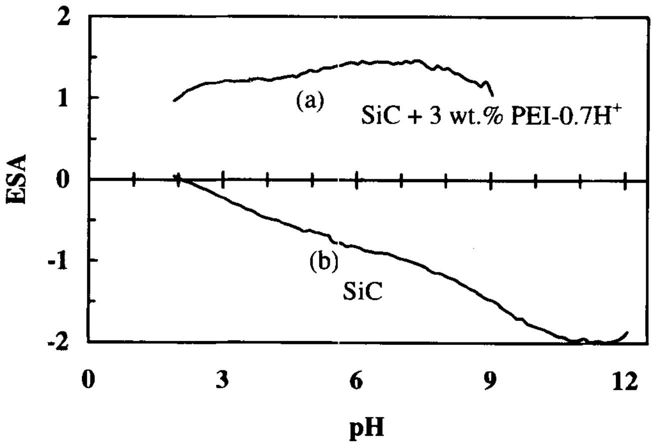


Fig. 10. ESA response versus pH for α-SiC powder with (curve a) and without (curve b) PEI-07H^+ as a dispersant.

3.4 Application to the processing of Al_2O_3/SiC nanocomposites

The main stage in processing of Al_2O_3/SiC composites is the dispersion of the second phase in the alumina matrix. The most convenient way to achieve the desired level of homogeneity is the preparation of a stable, mixed suspension of Al_2O_3 and SiC powders.[8] Generally, organic solvents are used for this purpose.[9, 10] In the present work, we have investigated a new way to stabilize an aqueous mixed slurry. An acidic medium (pH $\approx$ 3) was found to give excellent results for the preparation of an alumina slurry. At the same pH, a good dispersion of SiC powder using PEI-0·7H^+ was also observed, as reported in the previous section. In turn, a mixture of these two slurries leads to a stable and homogenous suspension. In order to check the homogeneity of the dispersion of SiC particles in an Al_2O_3 matrix, Al_2O_3/SiC (5 wt%) composites were fabricated. The mixed suspension was spray dried, and the resulting powder was first burned out at 500°C for 4 h in air, then hot pressed in flowing argon at 1800°C for 2 h under a pressure of 30 MPa. Samples were prepared for observation by transmission electron microscopy (TEM) using grinding, dimpling and ion beam thinning. The TEM observation of the Al_2O_3/SiC composite reveals a good homogeneity of the dispersion of SiC particles in the alumina matrix (Fig. 11). The second-phase particles are located either within the alumina grains or at the grain boundaries. The mean particle size of SiC after hot pressing is approximately 0·15 μm, in agreement with the value obtained earlier. Spray drying then proves to be a good technique to maintain the quality of the dispersion homogeneity during the aqueous processing of such nanocomposites.

Fig. 11. TEM micrograph of Al_2O_3(AKP30)/SiC (5 wt%) composite hot pressed at 1800°C.

4 Conclusions

Adsorption of polyelectrolytes on the oxide surfaces strongly depends on the respective charges of the polyelectrolyte and of the ceramic surface. A good adsorption results from interactions between the ionized groups developed on the polymers and active sites at the oxide surface. A new polyelectrolyte has been developed (ionized PEI) in order to disperse acidic SiO_2 powder. The same polyelectrolyte was used for dispersion of SiC powder in an aqueous medium provided that SiC particles are covered with an oxidized layer. Finally a homogenous and stable Al_2O_3–SiC mixed slurry has been successfully processed to prepare nanocomposites.

References

1. Lyklema, J., Principles of the stability of lyophobic colloidal dispersions in non-aqueous media. *Adv. Colloid Interface Sci.*, 1968, **2**, 65.
2. Cesarano, J., Aksay, I. A. and Bleier, A., Stability of aqueous α-Al_2O_3 suspensions with poly(methacrylic acid) polyelectrolyte. *J. Am. Ceram. Soc.*, 1988, **71**(4), 250.
3. Hirtzel, C. S. and Rajagopalan, R., Invited review stability of colloidal dispersions. *Chem. Eng. Comm.*, 1985, **33**, 301.
4. Fowkes, F. M. and Mostafa, M. A., Acid–base interaction in polymer adsorption. *Ind. Eng. Chem. Prod. Res. Dev.*, 1978, **17**, 3.
5. Arnold, R. and Overbeek, J. Th. G., The dissociation and specific viscosity of polymethacrylic acid. *Recueil des Travaux Chimiques des pays Bas.*, 1950, **69**, 192.
6. Wen-Cheng J. Wei, Su Jen Lu and Bu-Kon Yu, Characterization of submicron alumina dispersions with poly(methacrylic acid) polyelectrolyte. *J. Am. Ceram. Soc.*, 1995, **15**, 155–164.
7. Reed, J. S., *Introduction to the Principles of Ceramic Processing*. John Wiley and Sons, New York, 1988, p. 134.
8. Stearns, L. C., Zhao, J. and Harmer, M. P., Processing and microstructure development in Al_2O_3–SiC 'nanocomposites'. *J. Eur. Ceram. Soc.*, 1992, **10**, 473.
9. Okuyama, M., Garvey, G. J., Ring, T. A. and Haggerty, J. S., Dispersion of silicon carbide powders in nonaqueous solvents. *J. Am. Ceram. Soc.*, 1989, **72**(10), 1918.
10. Jang, H. M., Rhine, W. E. and Bowen, H. K., Densification of alumina–silicon carbide powder composites: I. Effects of a polymer coating on silicon carbide particles. *J. Am. Ceram. Soc.*, 1989, **72**(6), 948.