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Sol–Gel Coating of Alumina Fibre Bundles

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Abstract

A procedure for coating alumina fibre bundles with fibrillar boehmite particles is described. Fibrillar boehmite particles, having a specific surface area of 150 m^2/g, were adsorbed onto the surface of the alumina fibres. The surface of the alumina fibres was first charge reversed by adsorption of a charge reversing agent. Polyvinylsulphate (PVS) proved to be an excellent charge reversing agent, whereas citric acid and Tiron (3,5-pyrocatecholdisulphonic acid disodium salt) were unable to reverse the surface charge of the alumina fibres. By using polyvinylsulphate (PVS), it was possible to adsorb an arbitrary number of layers of fibrillar boehmite particles. The coating of the alumina fibre bundles resulted in an increase in specific surface area from 0·09 m^2/g for the uncoated fibres, to 0·7 m^2/g for alumina fibres coated with four layers of fibrillar boehmite particles. The adsorbed boehmite particles were fixed onto the alumina fibre surface by calcination at 550°C for 120 min, during which the boehmite was transformed into γ-Al_2O_3. The coated alumina fibre bundles were characterized by krypton adsorption and scanning electron microscopy (SEM). © 1997 Elsevier Science Limited.

1 Introduction

Thin coatings of sol particles on ceramic surfaces find use in various applications. One example is catalysts, where the surfaces of either honeycomb monoliths or fibrous substrates are coated with a porous wash-coat of sol particles in order to increase the specific surface area.[1,2] A sufficiently high specific surface area of a catalyst facilitates the dispersion of the active materials, such as noble metals. High dispersion of the active material means that a large proportion of added noble metal is exposed to the reactants, e.g. a prerequisite for a total high catalytic activity. Another

example is ceramic membranes, consisting of porous substrates coated with sol particles to obtain nano-sized pores.[3] Such membranes can, for instance, be used for ultrafiltration, gas separation and as catalytic reactors. A third example are long fibre ceramic matrix composites, where the fibres are coated with appropriate sols to achieve an adequate bonding between the fibres and the matrix after sintering.[4] This will result in a desired non-catastrophic fracture behaviour of the composites. Also ceramic raw material powders can be coated with sols, which will act as a sintering additive or will affect the dispersion properties of the powder.[5]

Several techniques to deposit particle coatings onto substrates have been reported in the literature. These techniques are based on physical and/or electrostatic adsorption mechanisms followed by a stabilizing step in which the adsorbed particles are fixed onto the fibre surface. One example of the physical adsorption technique is wash-coating.[6] A substrate is simply immersed in a slurry and drawn up, after which the particles in the wet film form a layer on the substrate. This method is, for instance, commercially used to produce automotive catalysts consisting of sol-particle coated honeycomb monoliths. By using the same method to coat fibre bundles, the fibres will, unfortunately, cement together. One way to solve this problem is to pull fibre tows through a water-based sol with hexane floating on the top.[7] A thin hexane layer prevents the fibres from cementing together. As an alternative to physical deposition, a substrate can be coated with particles by electrostatic adsorption, where the surfaces of the substrates and particles are adjusted to obtain the appropriate functional groups and charges for adsorption. By using this method, uniform particle layers with controllable thicknesses on complex substrate geometries can be produced. In addition, it is possible to coat adjacent fibres in a bundle or a weave.

In order to adsorb positively charged particles of, e.g., boehmite, alumina, zirconia or titania, at

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relatively low pH values on an alumina substrate it is necessary to lower the isoelectric point (i.e.p.) of the alumina substrate. The point of zero charge (p.z.c.) of alumina can be lowered by doping the alumina surface with small amounts of chloride ions.[8,9] By using this method, the p.z.c. of γ-Al$_2$O$_3$ can be lowered to about pH 5·5. However, this is not low enough for alumina to be able to adsorb colloidal particles of boehmite, zirconia or titania at pH values between 3·0 and 4·0 where these particles are strongly positively charged. A more efficient way to lower the i.e.p. of alumina is to adsorb organic molecules, which bear negative charges at low pH values. Substituted phenols, such as Tiron (3,5–pyrocatecholdisulphonic acid), and carboxylic acids, such as citric acid, have been used to lower the i.e.p. of α-Al$_2$O$_3$.[10-12] In these investigations, the i.e.p. of α-Al$_2$O$_3$ was lowered to pH 3·4 when using citric acid and to about pH 3·0 when using Tiron. Citric acid and other organic acids have been found to adsorb on the surface of α-Al$_2$O$_3$ according to a ligand exchange mechanism.[13] Since the alumina surface can be negatively charged at pH 4·0 by lowering its i.e.p., e.g. by using either Tiron or citric acid, it is plausible to assume that particles, which are positively charged at pH 4·0, can be adsorbed on such an alumina surface. Another method of lowering the i.e.p. of alumina is to adsorb an anionic polymer, which is able to maintain its negative charge at low pH values (i.e. the functional group of the repeating unit has a low pK_a). A commercially available anionic polymer having a functional group in the repeating unit with a low pK_a value is polyvinyl sulphate. The sulphonic acid group has a pK_a of about 0·0.[14]

The preparation of alumina fibre bundles, in which each filament is coated with fibrillar boehmite particles, is described in this paper. The stepwise procedure that is used to coat the alumina fibres is schematically illustrated in Fig. 1.

2 Experimental Procedure

2.1 Materials

Sol base: Basic aluminium chloride solution, Locron L, containing 23·4 wt% Al$_2$O$_3$ (Hoechst GmbH, Germany).

Charge reversing agents: Polyvinylsulphate potassium salt [-CH$_2$CH(OSO$_3$K)-]n, n=1500, (Sigma Chemical CO, USA, practical grade). Tiron [3,5-pyrocatecholdisulphonic acid disodium salt (monohydrate)] (pro analysi, Merck, Germany). Citric acid, (pro analysi, Merck, Germany).

Fibres: Alumina fibres, 10 μm in diameter, ALMAX, (Mitsui Mining Company, Ltd, Japan).

2.2 Methods

2.2.1 Preparation of fibrillar boehmite
Particles of fibrillar boehmite were prepared by autoclaving a basic aluminium chloride solution[15,16] (0·8 mol/dm^3 Al), at 160°C for 24 h. The sol particles were then gelled at pH 9·0 by adding 1·0 mol/dm^3 aqueous ammonia solution. The gel was filtered through a Büchner funnel and washed with distilled water until it was free of chlorine. The gel was freeze-dried and the boehmite particles were recovered. The specific surface area of the freeze-dried boehmite particles was measured, and then they were redispersed in dilute hydrochloric acid using an ultrasonic bath. The pH of the resulting boehmite sol was adjusted to pH 4·0 with nitric acid.

2.2.2 Investigation of electrokinetic properties of alumina fibres and boehmite particles
Alumina fibres (1g) were calcined at 600°C for 2 h to remove any organic residues. The specific surface area of calcined alumina fibres was measured. The fibres were then ground and redispersed in distilled water. A sample of the colloidal fraction of the ground fibres was then taken out and put in a 10 mmol/dm^3 solution of NaCl. The electrophoretic mobility of the alumina particles was then measured as a function of pH. A sample from a boehmite sol containing 1 wt% AlOOH was put in a 10 mmol/dm^3 solution of NaCl and the electrophoretic mobility was measured as a function of pH.

2.2.3 Investigation of the effect of different charge reversing agents on the i.e.p. of boehmite particles
In order to investigate the effect of adsorption of different charge reversing agents on the electrophoretic mobility of boehmite particles, a boehmite sol (1 wt% AlOOH) was slowly added under stirring to a solution containing 10 mmol/dm^3 NaCl and various amounts of one charge reversing agent. The amount of charge reversing agent was in the range 0·2–1·5 mg of charge reversing agent per square metre of boehmite. After addition of the boehmite sol to
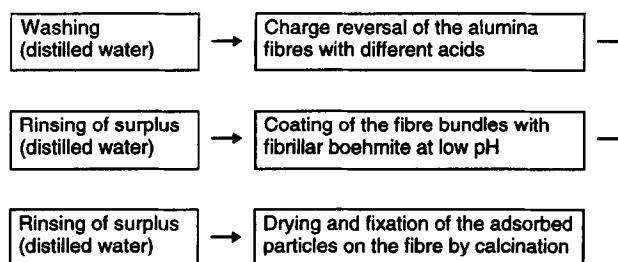

Fig. 1. Procedure for coating alumina fibre bundles with fibrillar boehmite particles.

the solution containing a charge reversing agent, the dispersion was stirred for 30 min and then adjusted to pH 4·0 before measuring the electrophoretic mobility. The charge reversing agents used were Tiron, citric acid and polyvinylsulphate.

2.2.4 Coating alumina fibre bundles using different charge reversing agents

Figure 2 schematically shows the set-up of the equipment for the coating of alumina fibre bundles with boehmite sol particles. One fibre bundle at a time was fixed inside the container according to the figure, after which the container was filled up with distilled water through the feeder (to the left). During the whole process, the fibre bundles were immersed in the water solution, in order to keep all single fibres apart from each other. The volume of the container including the supply tube was approximately 11 ml. A water solution, 20 ml, containing 500 p.p.m. of a charge reversing agent (the pH was adjusted to pH 4 for all three solutions) was slowly added to reverse the charge of the fibre surfaces. After 10 min of surface modification, the surplus of the charge reversing agent was carefully washed off with 100 ml of distilled water. Subsequently, 15 ml of a dilute boehmite sol, 1 wt% AlOOH, was slowly added. After 10 min of treatment, unadsorbed sol particles were washed off with 100 ml of distilled water. The fibre bundle was drawn up from the container. As a reference material, the surface modification step was omitted for one of the fibre bundles. All fibre bundles were dried in room atmosphere and calcined at 550°C for 120 min to fix the sol particles on the fibre surfaces. Finally the surface was analysed by using SEM to examine the effect of
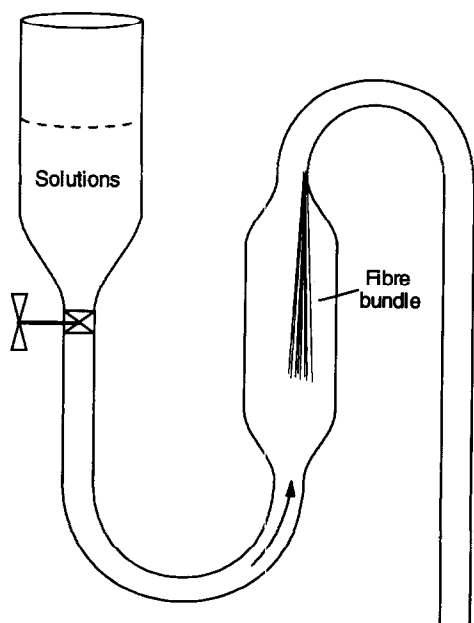
the different charge reversing agents on the coating efficiency.

2.2.5 Material characterization

Measurements of electrophoretic mobility were carried out using a Zetasizer II c (Malvern Inc.). The surface of the coated fibres was studied using scanning electron microscopy (SEM, Jeol JSM-5300). Specific surface areas of the materials prepared were determined by nitrogen adsorption or krypton adsorption according to the BET method on a Digisorb 2600 instrument (Micromeritics). When the specific surface area of a sample was low (less than 5 m^2/g), krypton adsorption was used.

3 Results and Discussion

3.1 Effect of different charge reversing agents on the electrophoretic mobility

Figure 3 shows the electrophoretic mobility of ground alumina fibres and fibrillar boehmite particles as a function of pH. It is seen that both the alumina particles and the boehmite particles have a high positive electrophoretic mobility at pH 4·0. The i.e.p for the alumina fibres is at about pH 9·0, whereas that of the boehmite particles is at about pH 8·3. The i.e.p. values for α-Al$_2$O$_3$ and boehmite reported in literature are about pH 9·1 and pH 8·8, respectively.[17] The difference observed in i.e.p. for boehmite can be explained by the presence of chloride ions remaining from the preparation.

Fibrillar boehmite particles have a high specific surface area, 150 m^2/g, compared with the ground alumina fibres, 4.7 m^2/g. In order to make as accurate measurements as possible of the effect of different charge reversing agents on electrophoretic mobility, fibrillar boehmite was chosen as adsorbent for the charge reversing agent due to the high specific surface area of the fibrillar boehmite particles. This choice can be motivated
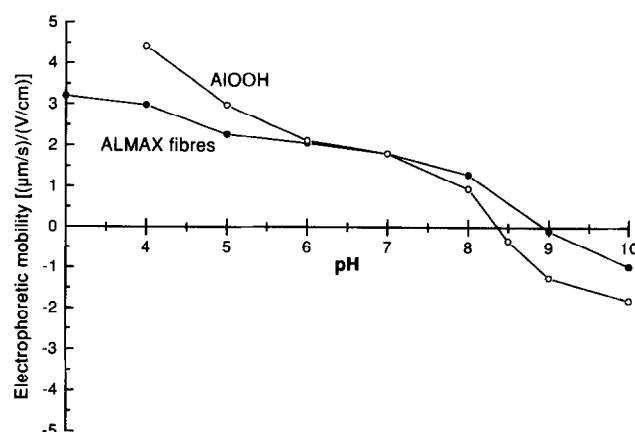
Fig. 2. Illustration of equipment set-up for coating alumina fibre bundles with fibrillar boehmite particles.

Fig. 3. Electrophoretic mobility of ground ALMAX alumina fibres (●) and fibrillar boehmite particles (○) as a function of pH.

by the fact that both α-Al$_2$O$_3$ and boehmite have a high positive electrophoretic mobility at the pH used (pH 4·0) when adsorbing the charge reversing agents.

The effect of the three charge reversing agents on the electrophoretic mobility of fibrillar boehmite as a function of the amount of charge reversing agent added per square metre boehmite is shown in Fig. 4. The figure clearly demonstrates that polyvinylsulphate is the only charge reversing agent that is capable of reversing the sign of the electrophoretic mobility of the boehmite particles. Addition of about 1 mg polyvinylsulphate per square metre boehmite is sufficient to provide the boehmite particles with a high negative electrophoretic mobility.The sign of the mobility is reversed when approximately 0·43 mg polyvinylsulphate per square metre boehmite is added. When adding less polyvinylsulphate than 0·4 mg per square metre boehmite, the system flocculated making measurements of electrophoretic mobility impossible. However, when using Tiron or citric acid as charge reversing agent, no reversal of the sign of the electrophoretic mobility was observed when adding up to 2 mg charge reversing agent per square metre boehmite. These results were somewhat unexpected since both citric acid and Tiron were reported to lower the i.e.p. of alumina below pH 4·0.[10-12] One possible explanation for this result may be that a considerably higher amount of charge reversing agent was used per square metre alumina (about 20 mg per square meter alumina) and that the concentration of the alumina slurry was much higher than the concentration of the boehmite sol used in this investigation.

3.2 Effect of different charge reversing agents on the coating efficiency

Figure 5(a) shows a SEM micrograph of an uncoated alumina fibre. The surface is rough which indicates that the alumina fibres are porous.
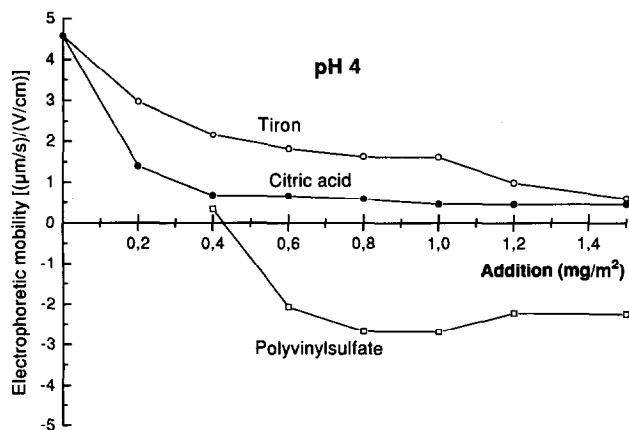
Fig. 4. Electrophoretic mobility of fibrillar boehmite particles in solutions of different amounts of three charge reversing agents at pH 4: Tiron ($\bigcirc$), citric acid ($\bullet$) and polyvinylsulphate ($\square$).

Figure 5(b) and (c) show, alumina fibres which have been treated with citric acid and Tiron, respectively, followed by adsorption of fibrillar boehmite particles. The figures clearly show that almost no boehmite particles have been adsorbed onto the surface of the alumina fibres. Figure 5(b) shows that only a few boehmite fibrils are discernible on the fibre surface, whereas Fig. 5(c) shows that the alumina fibre surface is completely free from adsorbed boehmite particles.

However, Fig. 5(d) shows that fibrillar boehmite particles can be adsorbed on the surface of alumina fibres when using polyvinylsulphate as the charge reversing agent. As seen in Fig.5(d), the fibre surface is completely coated with a layer of fibrillar boehmite particles.

3.3 Effect of coating on specific surface area

The specific surface area of the uncoated alumina fibres was 0·09 m^2/g using Kr as adsorbing gas. The low surface area indicates that the pores seen in the SEM image of the uncoated alumina fibres Fig. 5(a) are macro pores according to the IUPAC definition.[18] Table 1 shows the Kr-BET surface areas of uncoated alumina fibres and alumina fibres coated with boehmite particles using different charge reversing agents. When citric acid or Tiron was used as the charge reversing agent, no significant increase in specific surface area was observed. The SEM images (Fig. 5(b) and (c)) of these samples support this result. However, when polyvinylsulphate was used as the charge reversing agent, the specific surface area was increased significantly. By coating the fibres in more than one step, it was possible to increase the specific surface area further. The fibre samples were calcined at 550°C for 2 h between each coating in order to fix the fibrillar particles onto the fibre surface. During the calcination, the boehmite was transformed into γ-Al$_2$O$_3$.[19] After coating the fibres with four layers of particles, the specific surface area of the material was increased to 0.7 m^2/g, which is about eight times the specific surface area of the uncoated fibres.

4 Discussion

Polyelectrolytes can flocculate colloidal systems of opposite surface charge. They adsorb readily and patchwise on surfaces of opposite charge according to the 'electrostatic patch' model.[20] Figure 6 shows schematically how boehmite particles are adsorbed on an alumina surface, which has been charge reversed by polyvinylsulphate. A minimum in colloidal stability is generally observed when a certain amount of a polyelectrolyte is added to a
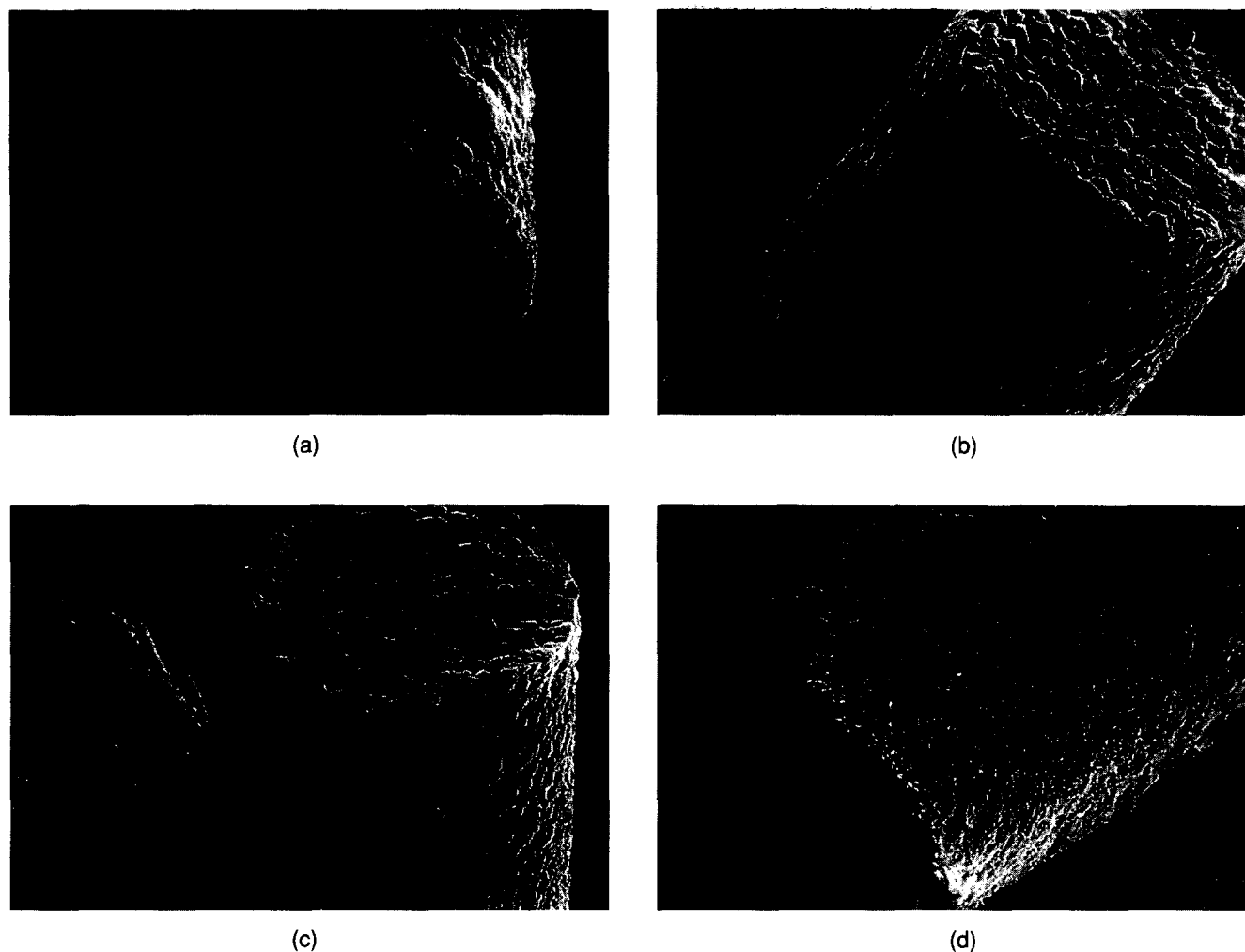
(a)

(b)

(c)

(d)

Fig. 5. SEM micrographs showing surface of ALMAX alumina fibres (ϕ = 10 μm) with different charge reversing agents and coated once with fibrillar boehmite: no agent (reference) (a), citric acid (b), Tiron (c) and PVS (d). The white arrows in Fig. 5(b) mark a few fibrillar particles adsorbed on the fibre surface.

colloidal system that has an opposite surface charge.[21] Using higher concentrations results in charge reversal and stabilization of the colloidal system. The results in this investigation suggest that about 0·4 mg polyvinylsulphate per square metre boehmite is required to achieve optimal flocculation, whereas more than 1 mg polyvinyl-sulphate per square metre boehmite causes charge reversal, and hence stabilization, of the particles. The anionic polymer chains interact strongly with the alumina surface and are not as sensitive to dilution as single molecules. Single molecules,

such as citric acid and Tiron, adsorbed on the surface of alumina, are likely to desorb from the surface when the system is diluted (i.e. rinsed with distilled water) owing to entropy effects. This may be an explanation as to why the boehmite particles were not adsorbed on the alumina fibre surface. Polyvinylsulphate is not as sensitive to dilution as

Table 1. Effect of coating on specific surface area

Charge reversing agent	No. of coatings	Kr-BET(m^2/g)
---	0	0.09
—	1	0.09
Citric acid	1	0.10
Tiron	1	0.09
PVS	1	0.20
PVS	2	0.40
PVS	4	0.70

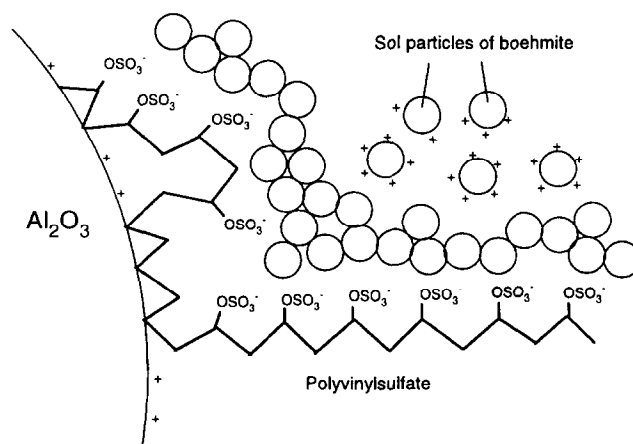The N_2-BET of fibrillar boehmite is 150 m^2/g.

Fig. 6. Schematic illustration of coating a PVS treated alumina surface with fibrillar boehmite particles.

citric acid or Tiron. It interacts more strongly with the alumina surface and the gain in entropy at desorption from the surface into the solution is small compared with the corresponding gain in entropy for citric acid and Tiron. However, both Tiron and citric acid can be used as deflocculants.[10,12] This can be explained by the fact that high concentrations of the dispersed material were used and that higher amounts of deflocculants per square metre of the dispersed material, in comparison with this study, were used. In concentrated systems, desorption of adsorbed deflocculants because of entropy effects is less likely.

4.1 Possible applications

Alumina fibres coated with a porous wash-coat of γ-Al$_2$O$_3$ may be used in various applications. If the material is to be used as a catalyst, the specific surface area of the material has to be at least an order of magnitude higher, perhaps even 20 times, than that accomplished in this investigation. This may be achieved by using smaller fibres (2–5 μm in diameter) and by adsorbing thicker particle layers. The thickness of the layers may be increased by increasing the boehmite sol concentration or by increasing the length of the polymer chain of the polyvinylsulphate.

This paper describes a method of depositing boehmite sol particles on an alumina surface by electrostatic adsorption. However, the same principle may be employed for other sols, such as zirconia, and this would be suitable for other applications. Different kinds of coatings on fibres are today developed to create an appropriate interface bond between the fibre and the matrix in long-fibre reinforced ceramic matrix composites (CMCs).[4] One example of such a material, for high temperature structural applications, is alumina-fibre/mullite-matrix composites.[22] By applying a thin coating of, for instance, zirconia particles on each fibre, the fibre/matrix strength will be lowered.[23] This favours desired fibre pull-out in the composite, which results in a tough material with a graceful crack behaviour. By utilizing the technique described in this paper and exchanging the boehmite sol for a zirconia sol, it may be possible to coat the fibres with thin, uniform layers of zirconia particles.

5 Conclusions

A stepwise procedure for coating alumina fibre bundles with an arbitrary number of layers of fibrillar boehmite has been developed. In the first step, the surface charge of the alumina fibres is reversed by adsorption of polyvinylsulphate. Posi-

tively charged particles of fibrillar boehmite are then electrostatically adsorbed on the negatively charged alumina fibres. Polyvinylsulphate proved to be an excellent agent for reversing the surface charge of the alumina fibres, whereas attempts to use citric acid and Tiron for the same purpose failed. When polyvinylsulphate is used, each alumina fibre in the bundle is completely covered with a layer of fibrillar boehmite particles. However, when citric acid or Tiron is used as the charge reversing agent, no fibrillar boehmite particles are adsorbed on the surface of the alumina fibres.

The adsorbed fibrillar boehmite particles are fixed onto the alumina fibre surface by calcination in air at 550°C for 120 min, during which the boehmite is transformed into γ-Al$_2$O$_3$. Using the procedure developed, we have shown that it is possible to increase the specific surface area by a factor of eight, from 0·09 m^2/g for the uncoated alumina fibres to 0·7 m^2/g for alumina fibres coated with four layers of particles. The coated alumina fibres are of potential interest for use in catalysts and for reinforcing ceramic composites.

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