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Effect of Ageing Time on Pressure Slip Casting of Silicon Carbide Bodies

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Abstract

Binary silicon carbide powder mixtures, with the particle size distribution designed to optimize the particle packing density, were dispersed in aqueous medium in the absence and in the presence of different amounts of a deflocculant. The influence of ageing time on the rheological behaviour of finer powder slurries and on relative green density and rate of wall build-up was studied for pressure slip casting bodies prepared from binary suspensions. Good correlations between rheological characteristics of the suspensions and the structure and properties of the formed bodies were observed. © 1996 Elsevier Science Limited.

1 Introduction

Silicon carbide has been one of the most promising high-performance ceramic materials for the last decade. The structure and properties of ceramic components depend directly on the density, uniformity of microstructure and rheological properties of the green compacts from which they are formed. These properties can be improved by using colloidal consolidation techniques.[1] In previous works[2–5] we have shown that the rheological behaviour of silicon carbide suspensions and the properties of green bodies are strongly dependent on suspension stability set either by pH adjustment[2] or by adding a suitable amount of a deflocculant, and particle size distribution.[3,4]

The use of bimodal particle size distributions allowed us to maximize the green density of slip-cast bodies.[3,4] However, the resultant increase in fluidity of the slips due to liquid liberation, initially filling the interstitial pore space within coarse particles that has been replaced by the finer one, promotes particle segregation. This phenomena can be prevented by several methods.[5] One of them is to increase the consolidation rate by the use of an external pressure.[5,6]

During our first studies on slip casting of silicon carbide, the suspensions were always poured into plaster moulds immediately after preparation to avoid ageing effects. These effects seem to be difficult to anticipate from the results reported in the literature.[7–10] Weaver and Feke[7] refer to a number of studies where an increase in strength of interparticle physical bonds with time was observed, and proposed a model for the time variation of the electrical repulsion force due to double-layer relaxation. According to this model, two relaxation mechanisms — redistribution of charge within the Stern layer and interchange of charge between the Stern and the diffuse parts of the double-layer — can individually or jointly lead to repulsion decay. On the other hand, Aksay *et al.*[8] using suspensions of alumina and zirconia observed significant shifts in particle size distribution curves towards submicrometre size range on ageing. These shifts were comparable to those obtained by ball milling. Agrawal[9] studied the flocculation kinetics of alumina particles in dilute suspensions and reported a rapid growth in the size of flocs at pH values near the isoelectric point, whereas at pH away from the isoelectric point there was little or no growth. Wijnen *et al.*[10] suggested that ageing of aqueous silica aggregates is a process of migration of active, dissolved silica species, like monomeric silicic acid, from the more soluble and less dense peripheric places to the less soluble and denser parts within the aggregates. The rate at which the ageing process occurred was strongly dependent on the pH value of the solution.

The aim of this work was to evaluate the influence of ageing time on the rheological behaviour and pressure slip casting performance of silicon carbide suspensions in the absence and in the presence of a deflocculant.

2 Experimental

2.1 Materials and reagents

The starting materials were two commercially available SiC powders, NF0 and 1200P (Elektroschmelzw Kempten), with mean diameters of 1·2 and 13 μm, respectively. The deflocculant used was an ammonium salt of a low-molecular-weight polycarbonate acid (Targon 1128, Benkiser-Knapsack GmbH).

2.2 Techniques

The suspensions were prepared by first adding the powders to distilled water or to solutions having different concentrations (0·05 and 0·15 wt%) of Targon 1128, and hand stirring, followed by simultaneous stirring and ultrasonication for 10 min. The solids content of the suspensions was limited to about 0·01 wt% in electrophoretic measurements, and to 62·5 wt% in rheological and slip casting experiments, because of their high viscosity at and near the isoelectric point. The ageing process was carried out at room temperature in closed vessels.

The electrophoretic mobility was measured at room temperature using a microscope-type electrophoresis equipment (Mark II, Rank Brothers, Cambridge, UK) with a planar silica glass cell and blacked platinum electrodes. The ionic strength of the liquid medium was adjusted to 0·001 M NaCl just before the measurements.

The rheological properties of suspensions of the finer powder were evaluated with a cone–plate viscometer used before.[2] The pressure slip casting experiments were performed in a home-built apparatus described elsewhere.[11] The green density was measured in a mercury balance.[12]

The pore size and pore size distributions of the green bodies were determined with a porosimeter (PoreSizer 9320, Micromeritics). The high pressure part of each experiment was run in the automatic mode with a equilibration time of 10 s at each point.

3 Results and Discussion

3.1 Electrophoresis

The electrophoretic mobility (EPM) of the finer powder particles was measured to determine how the interface potential changes with pH of suspensions aged for different times. Typical results for the suspension without deflocculant are shown in Fig. 1. To aid clarity, only the curves for the freshly prepared suspension and suspensions aged for 5 and 30 days are presented. It can be observed that the isoelectric point of the fresh sample, at about pH 2·25, is gradually moved to lower pH values as the ageing time increases, and that the absolute electrophoretic mobility values always increase over the entire pH range studied. For the unaged sample, similar electrophoretic behaviour was reported and referred to in our previous works.[2,3] The surface of silicon carbide particles is usually covered by a thin film of silica.[5] This film can stem from the powder preparation step or from further reaction between surface silicon atoms and water molecules. The amorphous nature of this film[13] should favour surface hydroxylation. Exposure of these surfaces to water during the ageing process would be expected to cause silanol (≡Si–OH) formation at the most reactive (strained) defects.[14] Acid/base reactions occurring at interface particle/solution result in surface charge development:

$$\equiv SiOH_2^+ \xleftarrow{H^+} \equiv SiOH \xrightarrow{OH^-} \equiv SiO^- + H_2O \quad (1)$$

Silica is an acidic oxide, so that the second reaction on the right-hand side of eqn (1) is dominant over a substantial range of pH values. However, the bulk solid is not in thermodynamic equilibrium with the rest of the system and slow reactions between the two phases contribute to the observed ageing effects. The negative surface charge increases with ageing time and promotes an increase in repulsive electrostatic interparticle potentials.

The presence of Targon 1128 as a dispersing agent had a negligible influence on the EPM values measured in the acid region, while in the basic region EPM was improved. In the acid region the polycarbonate groups adsorbed at particle surfaces should exist in the undissociated form. A different situation is expected to occur in the basic pH region[3] where the negative charge developed in polyelectrolyte groups is added to the surface charge particles. This contribution should account for the observed results.

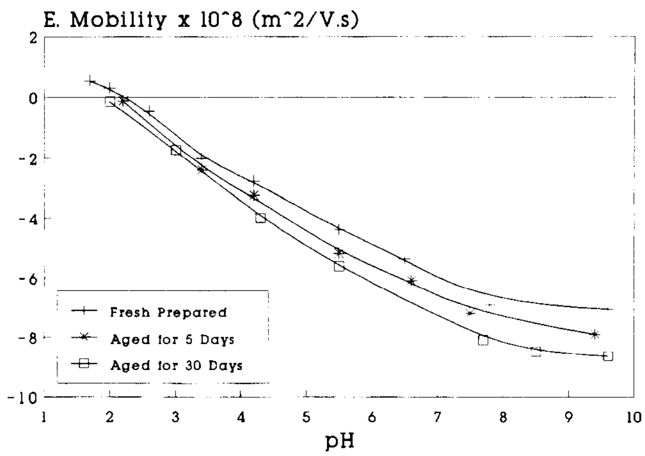

Fig. 1. Effect of ageing time on electrophoretic mobility.

3.2 Rheology

The Bingham yield stress and plastic viscosity of suspensions are plotted in Figs 2 and 3, respectively, as a function of ageing period. It can be seen that the rheological parameters always decrease as the ageing time increases, with the most significant changes occurring in the first days and in absence of deflocculant. The noticeable initial differences between the three curves plotted in Figs 2 and 3 tend to disappear as the ageing time increases. These differences can mainly be attributed to an electrosteric effect of the polyelectrolyte chains adsorbed at particle surfaces. As the ageing time proceeds, the uncovered surface reacts with the liquid phase. As a consequence, the amount of surface silanol groups formed increases and the electrostatic stabilization mechanism becomes predominant. It seems that some surface active sites were blocked by the adsorption of the electrolyte and were not available to react with water. This possibility could explain the lower extensions of the ageing time effect observed when Targon 1128 is present. With the improvement of suspension stability the collision efficiency of the particles is reduced[15] and, consequently, the size of particle aggregates and the slurry viscosity will decrease. These results are in agreement with the DLVO theory of colloid stability[16,17] which is able to predict the stability of colloids in polar liquids by considering the balance between electrical double-layer repulsions and van der Waals' attractions.

Noticeable reductions in apparent viscosity were also reported by Pivinskii and co-workers[18,19] and by Nordstrom and Karlsson[20] after ageing suspensions of zircon,[18] alumina[19] and hydroxyapatite.[20]

3.3 Pressure slip casting

All pressure slip casting experiments were run under a constant applied pressure of 588 kPa, for 2 min. The green density and wall thickness of the formed bodies are presented in Figs 4 and 5, respectively. Their observation leads to the following conclusions:

(1) the density of the samples increases over the whole ageing period, whereas the wall thickness shows the reverse trend;
(2) the most significant changes occurred in the first 10 days observed with the rheological parameters;

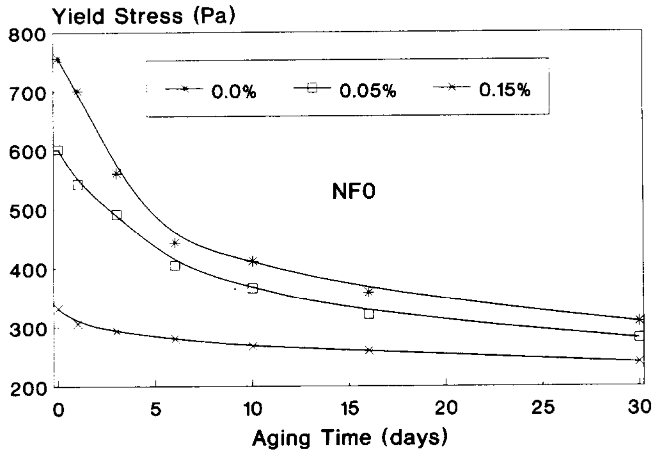

Fig. 2. Effect of ageing time on yield stress.

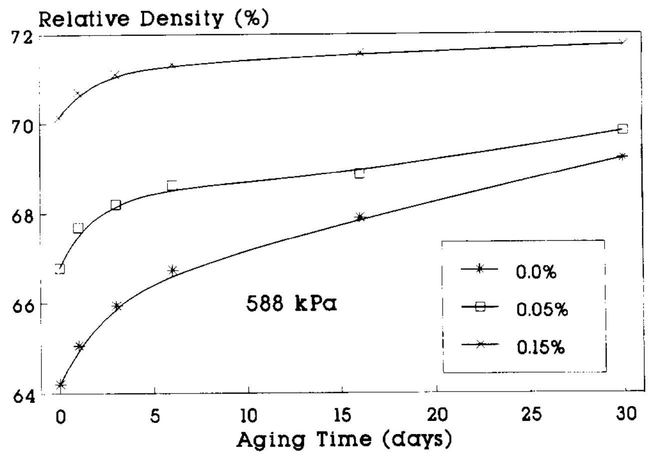

Fig. 4. Effect of ageing time on green packing density.

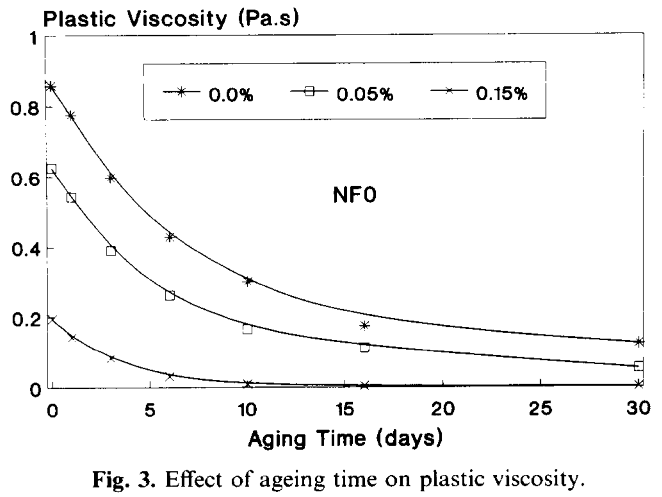

Fig. 3. Effect of ageing time on plastic viscosity.

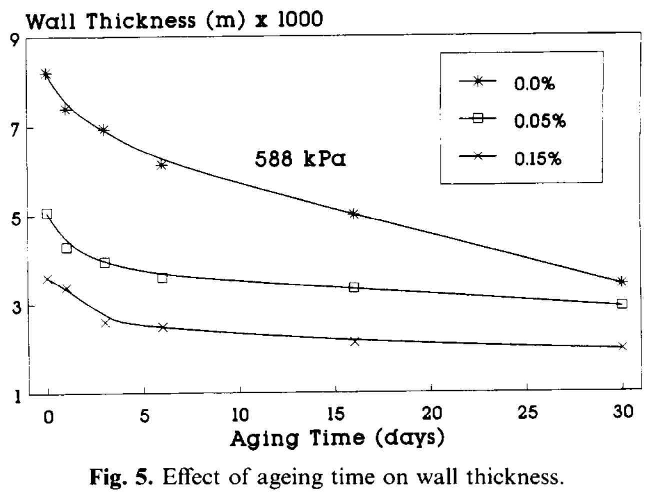

Fig. 5. Effect of ageing time on wall thickness.

(3) the differences in green density and rate of wall build-up between bodies obtained from different suspensions decrease as the ageing time increases;
(4) the curves suggest that the ageing process is not yet completed at the end of the 30th day and the above differences could be further reduced.

Figures 6 and 7 show the pore size distributions of the green bodies prepared from suspensions without and with 0·15% Targon 1128, respectively, unaged and aged for 5 and 30 days. It can be observed that:

(1) cakes obtained from fresh suspensions exhibit larger pore sizes and broader pore size distributions;
(2) the ageing process continually shifts the pore size distributions towards finer pores, the greater changes being observed in the absence of deflocculant;
(3) it is possible to get almost the same pore structure by ageing the bare suspension for one month compared with a deflocculated and unaged one.

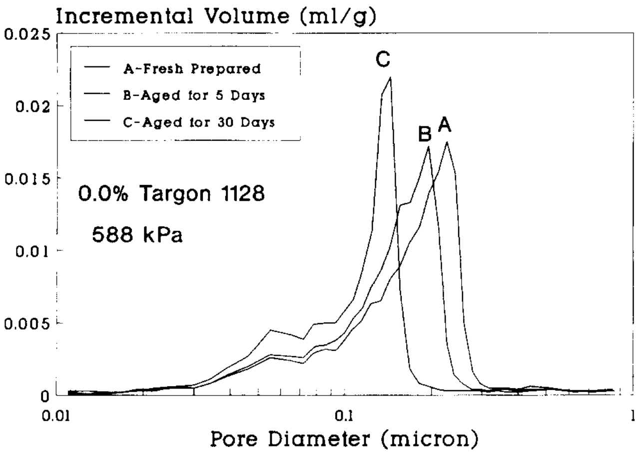

Fig. 6. Effect of ageing time on pore size distribution of green bodies formed in the absence of deflocculant.

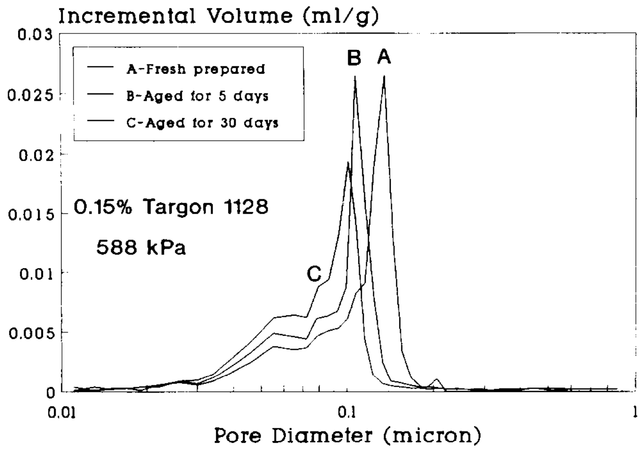

Fig. 7. Effect of ageing time on pore size distribution of green bodies formed in the presence of 0·15 wt% deflocculant.

These results are very consistent and show that the ageing time strongly increases the suspension stability against aggregation and modifies the structure of particles in suspension, leading to a decrease in the number of flocs and an increase in its density. Particles become gradually more separated and, on deposition, they are able to form denser and less permeable green structures. The close correlation between the rheological properties of the suspensions and the properties of the green bodies indicates that the structure of particles in suspension is transmitted to the solid wall being formed near the surface of the mould, as suggested before,[21] and a denser and less porous body should result as observed.

4 Conclusions

From the above data and discussion it is possible to draw the following conclusions:

(1) Ageing time significantly improves the colloidal stability of aqueous silicon carbide slips and the green properties of casts made from them.
(2) The principal changes in slip and cast properties occur within the first days.
(3) The effect of ageing time is more extensive in the absence of deflocculant.

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