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Slip Casting of SiC–SiAlON Composites

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Abstract

SiC–SiAlON composites were prepared by the reaction sintering of SiC, kaolin and silicon mixtures in a nitrogen atmosphere. To form complex shapes, slip casting was used, with water preferred as an economic dispersion medium. The methodology to obtain a highly concentrated, well-dispersed, slurry (73% by weight of dry matter) is described. Zeta potential and complementary redox potential measurements revealed the nature of the surface species as a function of pH and indicated compatible conditions for the three constituents (kaolin, SiC, Si). Sodium metasilicate was used as deflocculant and CMC as organic binder. © 1997 Elsevier Science Limited.

Résumé

Des composites SiC–SiAlON ont été préparés par frittage réaction sous azote de mélange de SiC, kaolin et silicium. Cet article décrit la méthodologie suivie pour obtenir des suspensions concentrées bien dispersées (73% en poids de matière sèche). Les mesures complémentaires de potentiel zêta et rédox ont permis de déterminer la nature des espèces superficielles selon le pH et de choisir des conditions de mélange compatibles pour les trois constituants (SiC, kaolin, Si). Le métasilicate de sodium a été utilisé comme défloculant et la CMC comme liant.

Introduction

SiC–SiAlON composites resist corrosion of molten metals like zinc, lead and aluminium. They are used as refractory components in the processing of such metals, for which complicated parts with thin walls are required. These parts can be fabricated by slip casting; however, for economic reasons, water and inexpensive raw materials are prerequisites. Therefore, in this work, the SiAlON phase was obtained by the reaction sintering of kaolin and silicon under nitrogen atmosphere.

To promote the reaction, the slurry containing kaolin and silicon powder but also coarser silicon carbide grains has to be as homogeneous as possible, and to fulfil slip casting, a high slurry concentration (more than 70% by weight of dry matter content) and a suitable rheology behaviour are needed.

This paper describes the combined dispersion of the three main constituents (kaolin, SiC, Si) in water.

Experimental

The raw materials used were a French kaolin (37 wt% Al_2O_3, 0·9 % alkali and alkaline earth), silicon powder (>98%, diameter <50 μm) and α-SiC (diameter <100 μm). Their proportions were 16·5, 38·5 and 45 wt%, respectively.

Rheological data were obtained by using a Haake (RV3) viscosimeter. Zeta potential was measured by electrophoresis of concentrated slurries (EMTA Micromeritics USA).

A special apparatus[1] recorded the polarisation curves of the suspension; it consisted of a reference electrode with saturated calomel, a large platinum counter-electrode (surface = 1 cm^2 and a work electrode of the same nature (surface = 0·006 cm^2. Polarisation curves were recorded with a scanning rate of 5 mV/s. To insure equilibrium conditions, measurements were carried out 24 h after the slurry preparation.

Results

Kaolin dispersion is well understood[2] and did not require any special attention.

The SiC grains, in view of their large dimensions, were considered as an inert material, whose suspension is mainly controlled by the behaviour of the other phases. Therefore, we first investigated the silicon deflocculation mechanism.

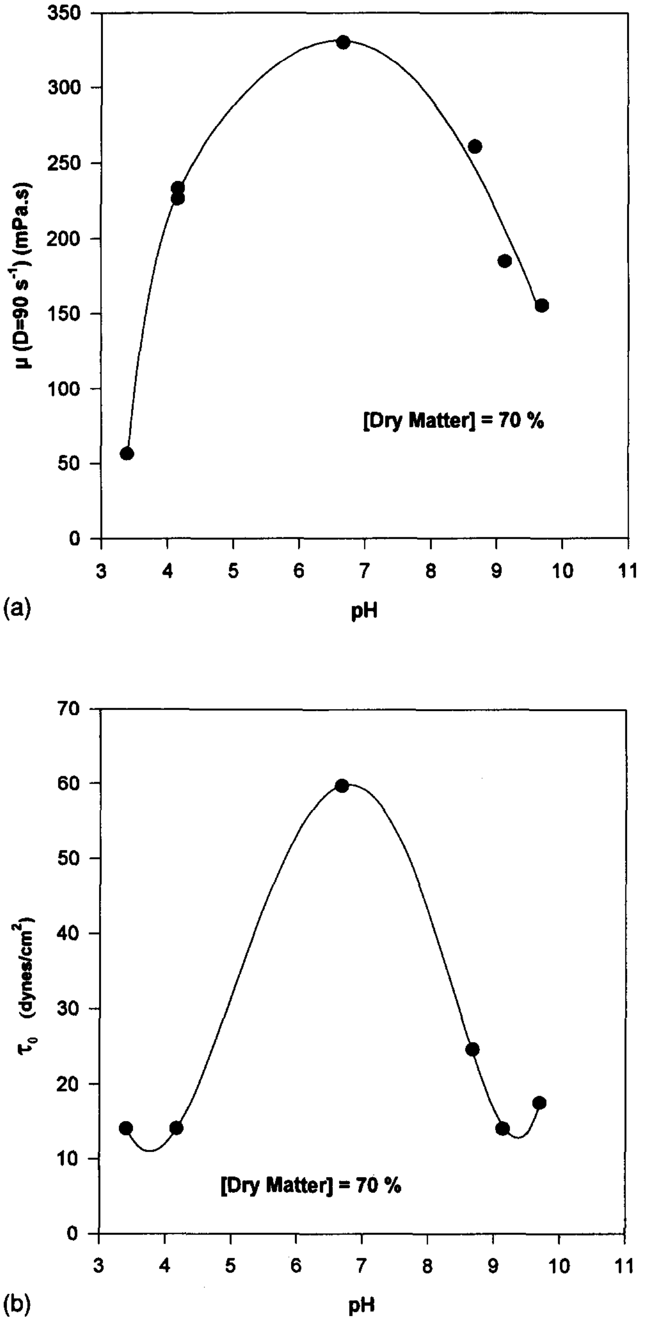

Fig. 1. (a) Viscosity as a function of pH for silicon; (b) Yield value as a function of pH for silicon.

Silicon deflocculation

Figure 1 shows the evolution of the rheological characteristics as a function of pH for silicon suspensions after 24 h ageing. Viscosity and yield stress reach a maximum value at pH 6·7.

The apparent viscosity (μ_B) is governed by the sliding forces between the particles when they are free of their 'house of cards' configuration[3] whereas the yield stress (τ_0) is proportional to the stress necessary to destroy this particle configuration. The point at pH 6·7 corresponds to a fundamental structure change related to the particle surface charge.

The zeta potential evolution versus pH is shown in Fig. 2; the zeta potential is negative for the pH span covered, but two distinct zones are to be explained: below pH 8·5, a straight portion is observed whose extrapolation up to the zero point of charge corresponds to that of SiO_2 at pH 2·3. This suggests that the silicon particles are covered by an oxidised layer.

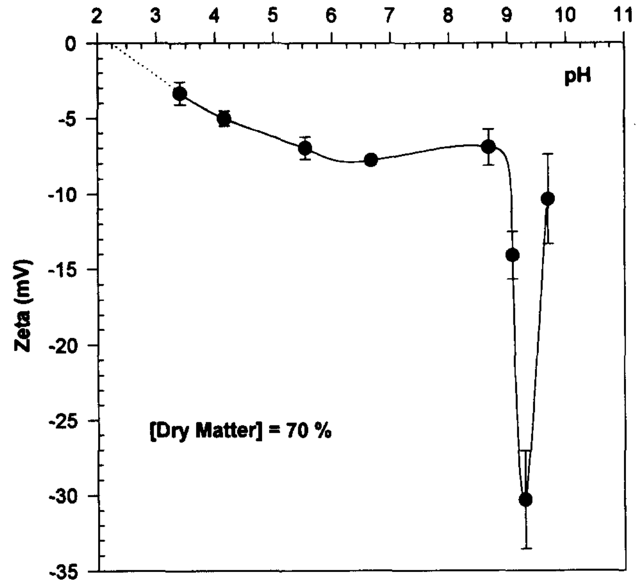

Fig. 2. Zeta potential as a function of pH for silicon.

Above pH 8·5, the ζ curve shows a minimum at pH 9·35. Due to the ionic force increase resulting from further NH_4OH addition, the ζ potential value decreases for higher pH.

In order to explain the absence of correspondence between the rheological properties and the zeta measurements, the redox potential of a silicon slip was determined as a function of pH value just after the water–silicon contact as well as after 24 h ageing. Figure 3 shows that, as pH increases, the redox potential decreases to become negative. After 24 h, the redox potential sign change is at pH = 6·7 and the curve exhibits a minimum around pH = 9·4.

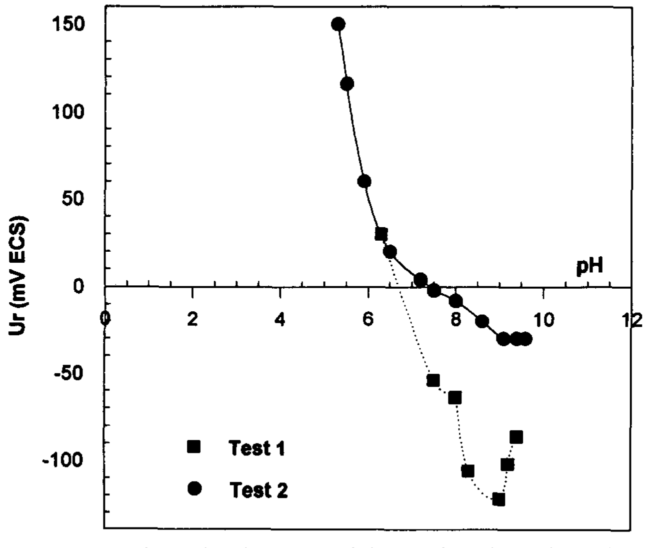

Fig. 3. Evolution of redox potential as a function of pH for silicon. Test 1: fresh suspension; Test 2: 24 h ageing.

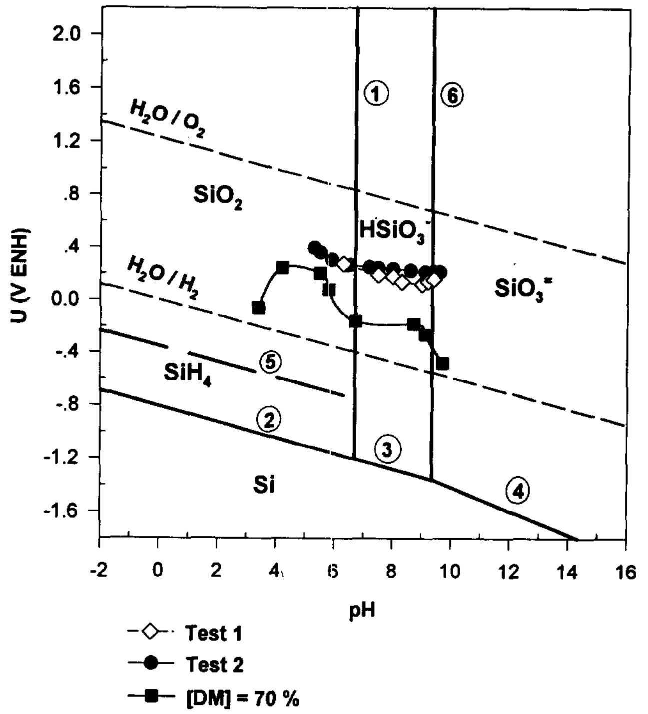

Fig. 4. Redox potential U–pH equilibrium diagram for silicon in aqueous solution at 25°C.

These curves were converted into a potential–pH diagram for silicon with the following hypotheses:

- the silica layer on the silicon surface is hydrated,
- the silicate concentration in the solution is very low,
- the silicon activity equals one.

The first hypothesis defines the equilibrium constants, whereas the other two are useful to calculate the concentrations. Moreover, to quantify the second hypothesis, a silicate ion concentration near to 10^{-6} M was chosen. In this case, the activity coefficient can be taken equal to one.

The U–pH diagram (4) shown in Fig. 4 has been built up, as follows:

$$SiO_2 + H_2O \rightleftharpoons HSiO_3^- + H^+ \qquad (1)$$
$$\mathrm{pH} = 11{\cdot}84 + \log[HSiO_3] \quad (\mathrm{p}K = 11{\cdot}84)$$

$$Si + 2H_2O \rightleftharpoons SiO_2 + 4H^+ + 4e^- \qquad (2)$$
$$U = -0{\cdot}807 - 0{\cdot}059\,\mathrm{pH} \quad (U_0 = -0{\cdot}807\ \mathrm{V})$$

$$Si + 3H_2O \rightleftharpoons HSiO_3^- + 5H^+ + 4e^- \qquad (3)$$
$$U = -0{\cdot}708 - 0{\cdot}0738\,\mathrm{pH} \quad (U_0 = -0{\cdot}632\ \mathrm{V})$$

$$Si + 3H_2O \rightleftharpoons SiO_3^= + 6H^+ + 4e^- \qquad (4)$$
$$U = -0{\cdot}531 - 0{\cdot}0885\,\mathrm{pH} \quad (U_0 = -0{\cdot}455\ \mathrm{V})$$

$$SiH_4 + 2H_2O \rightleftharpoons SiO_2 + 8H^+ + 8e^- \qquad (5)$$
$$U = -0{\cdot}353 - 0.059\,\mathrm{pH} \quad (U_0 = -0{\cdot}353\ \mathrm{V})$$

$$HSiO_3^- \rightarrow SiO_3^= + H^+ \qquad (6)$$

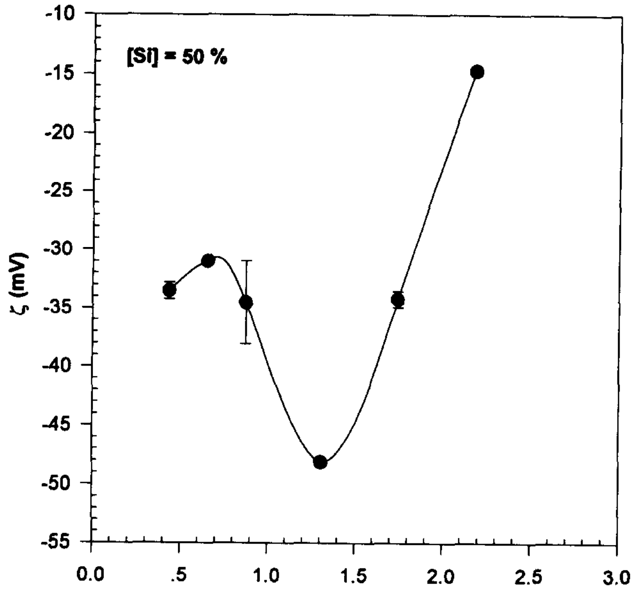

Fig. 5. Zeta potential as a function of metasilicate content for silicon.

$$\mathrm{pH} = 12 + \log\frac{[SiO_3^=]}{[HSiO_3^-]} \quad (\mathrm{pk} = 12)$$

Equation 6 leads to a pH value which is difficult to determine, because the $[SiO_3^=]$ concentration is unknown, but lower than that of $[HSiO_3^-]$. As the concentration ratio between both anions changes from 10^{-3} to 1, the pH varies from 9 to 12.

In Fig. 4, a ratio of 10^{-2} was chosen. Therefore, the silicon system in suspension is governed by:

$$SiO_3^= \underset{12>\mathrm{pH}>9}{\overset{+H^+}{\Leftrightarrow}} HSiO_3^- \underset{\mathrm{pH}=6{\cdot}7}{\overset{+H^+}{\Leftrightarrow}} SiO_2 + H_2O$$

So, the ζ potential curve for $\mathrm{pH} < 6{\cdot}7$ is similar to the one for hydrated silica (SiO^- species on surface). Above pH 6·7, the ζ potential increases owing first to monovalent charges ($HSiO_3^-$) and secondly to divalent species ($SiO_3^=$), which explains the shape change of the curve at $\mathrm{pH} \cong 9$.

The maximum of the rheological characteristics is thus here not explained as usual by the zero point of charge effect, but by a change of the surface ionic species: SiO_2 is more and more preponderant at pH lower than 6·7 and $HSiO_3^-$ at pH higher than 6·7 up to 9.

So, in order to disperse the silicon slurry, sodium metasilicate was chosen, for two reasons:

- First, as just explained above, this silicate has the same structure as the silicon particle surface, which could facilitate its adsorption on the particle surface.
- Secondly, it is a classical deflocculation agent for kaolin, which is the second raw material of the mixture.

Figure 5 shows the evolution of the zeta potential as a function of Na_2SiO_3 addition, where a

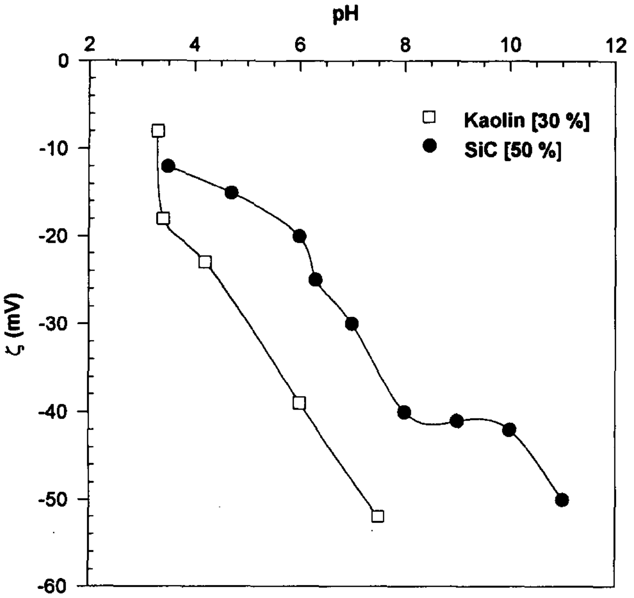

Fig. 6. Zeta potential as a function of pH for kaolin and silicon carbide.

maximum value is reached for about 1·3‰ of Na_2SiO_3. For higher concentrations, the slurry becomes rapidly flocculated (for instance with 5‰ addition).

Kaolin and SiC dispersion

The zeta potentials of kaolin and SiC powders were measured as a function of pH. As shown in Fig. 6, both curves exhibit negative values which become higher than 30 mV for pH > 7. Owing to such high values, the use of a deflocculation agent is not necessary.

The zero point of charge for both the kaolin and SiC systems, estimated by extrapolation of the experimental curves, is obtained at pH close to 3, that is close to that of pure silica. But for the SiC system, the curve may be divided into three zones taking into account that the oxidation of SiC produces SiO_2 at the surface but also CO_2 which dissolves into the suspension. The pKa of the system $HCO_3^-/CO_3^=$ gives:[5]

$$\frac{[H^+][HCO_3^-]}{[CO_2]} = 10^{-6.35} \text{ and } \frac{[H^+][CO_3^=]}{[HCO_3^-]} = 10^{-10.3}$$

As a consequence, below pH 6·35, the neutral species CO_2 is dominant and the negative charge is only due to the silanol groups (ZPC at pH < 3).

For pH > 6·35, the dicarbonate form should be more and more predominant as pH increases, which should induce a change of the potential evolution.

Close to pH 10·3, the $CO_3^=$ anion concentration increases with, as a consequence, a rapid increase of the ζ potential.

Mixture procedure

When the mixture is prepared according to the procedure described above, the coarse SiC grains do not stay in suspension, so a binder (CMC—carboxymethylcellulose) is added. Optimisation of its concentration is also the result of rheological and electrical measurements.

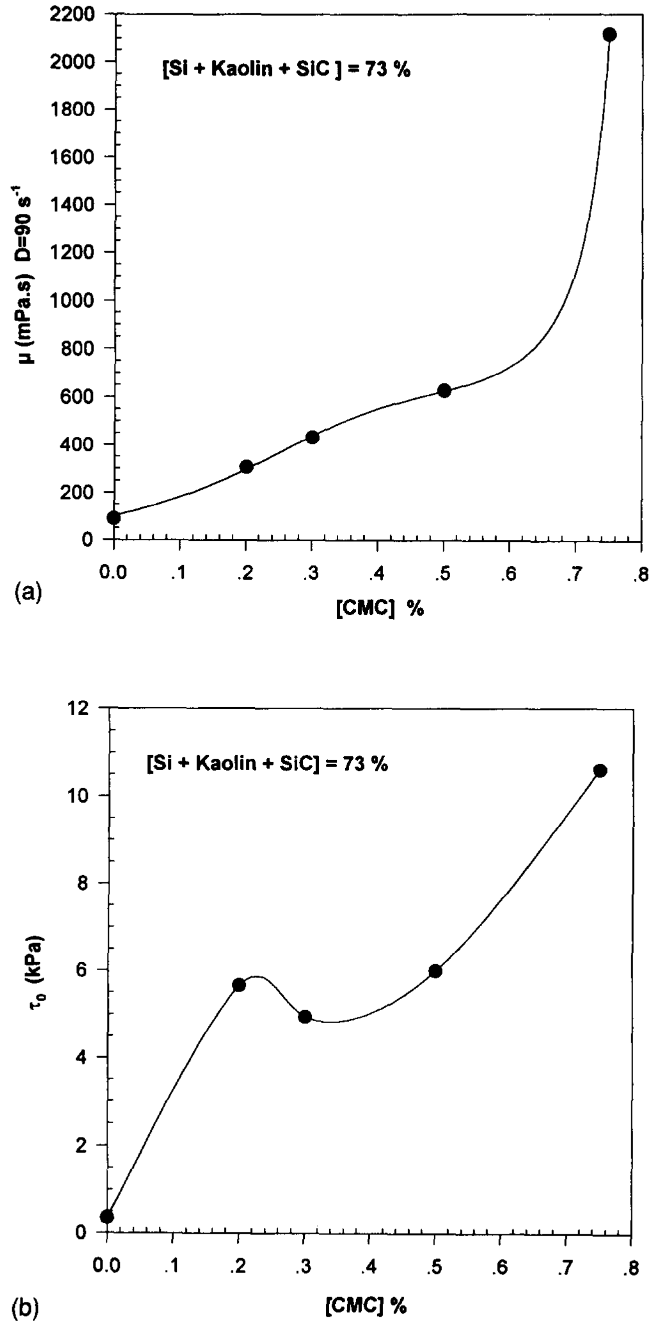

Fig. 7. (a) Apparent viscosity as a function of CMC addition for the mixture of the three constituents; (b) Yield value as a function of CMC addition for the mixture of the three constituents.

Figure 7 shows that the apparent viscosity increases linearly up to 0·5% CMC addition. For higher concentration, a fast increase of the curve is obtained. The yield value (τ_0) increases regularly up to 0·2% and then remains more or less constant between 0·2 and 0·5% addition.

The effect of CMC addition on the anodic polarisation curves is shown in Fig. 8. For these measurements, a platinum microelectrode was used. In this figure, the current plateau observed

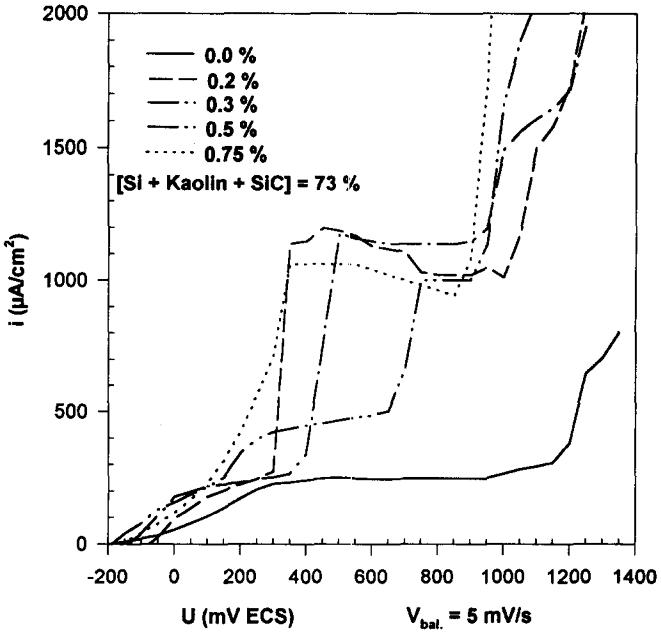

Fig. 8. Anodic curves as a function of CMC addition for the final mixture.

before the water electrolysis is due to the oxidation of the organic constituents adsorbed on the particle surface. A maximum effect is reached for 0·2% of CMC addition. A higher amount leads to a sharp increase of the viscosity. This 0·2% value was chosen because it leads to an apparent viscosity compatible with the slip casting technique.

Finally, the adopted preparation procedure was first to mix the silicon powder with 1·3‰ sodium metasilicate and, after completion of metasilicate adsorption, kaolin and then SiC grains were added together with 0·2% CMC. The ready-to-use suspension exhibits the following characteristics:

- dry matter content = 73%
- pH = 8·4
- apparent viscosity (at 90 s^{-1}): 200 mPa s.

Conclusions

This study describes a preparation procedure for the aqueous slip casting of a mixed oxide–non oxide system. Zeta potential and redox potential measurements have indicated the nature of the surface species as a function of pH and suggested compatible processing conditions for the three inorganic constituents (kaolin, SiC, Si).

The use of sodium metasilicate as deflocculant has been investigated and carboxymethylcellulose can be chosen as the organic binder.

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