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Slip casting of sialon for pressureless sintering

H. TSUDO, N. SASHIDA, T. YAMAKAWA, N. MIYATA
Central Research Laboratory, Nihon Cement Co. Ltd, 1-2-23, Kiyosumi, Koto-ku, Tokyo 135 Japan
E-mail: tudo_hiroyu@lab.nihon-cement.co.jp

The properties of aqueous slips of sialon were studied. Ammonium polyacrylate was used as a deflocculant. It was shown that the apparent viscosity for slips with solid content 40 vol % was low and the slip resulting from this is almost Newtonian. This slip proved sufficiently fluid for casting. However, the apparent viscosity for slips with solid content 45 vol % increased significantly. The slips resulting from this exhibited dilatant flow and were difficult to cast. The viscosity, fluidity, and pH of the slips were studied and tiles were cast and fired in nitrogen at 1740 °C for 3 h to a bulk density of 3.20 g cm^{-3}.

1. Introduction

Silicon nitride and sialon are materials with high strength and reasonable fracture toughness at high temperature. They have potential for usage as high temperature structural materials. The method of forming silicon nitride or sialon raw material powder is very important for producing parts to be used at high temperature. Injection moulding, slip casting, and extrusion are typical methods of forming ceramic powders, and an appropriate method is used according to the shape and number of products.

Slip casting of silicon nitride powders has been studied previously by Russian workers [1, 2]. Samsonov and Dobrovolskii [1] prepared slips by mixing silicon nitride with an aqueous solution of polyvinyl alcohol. Slip casting of silicon nitride with sintering aids has been studied by Rabinovich *et al.* [3]. They prepared slips by mixing silicon nitride with spinel; the solid-to-liquid ratio was 2:3 and the pH of the slip was 10.2. The density of the sintered body was 3.1 g cm^{-3}. Jack [4] refers to slip casting a mixture of silicon nitride and alumina which formed sialon after firing for 1 h at 1700 °C. However, there is no mention of sialon powder as the starting material.

The strength and fracture toughness of sialon products depend on the particle size of the sialon raw material powders. Hakoshima *et al.* [5] found that the use of fine sialon powders for the pressureless sintering of parts improved the mechanical properties. But fine powders generally exhibit a poor packing capability, and difficulties with the forming techniques often produce residual defects in the final microstructures.

The present work deals with the properties of aqueous slips of sialon with sintering aids. The most important step of this technique is the deflocculation of the slip. If the solid content of the slip is too high, the slip becomes thixotropic [6]. Especially high thixotropy can be obtained and becomes very awkward to work with the slip, with constant manual shaking of the slip being necessary to prevent it from solidifying. The optimum amount of deflocculant of the slip varies with the properties of the powder used.

A methodology for the study of deflocculation is presented in this work. It is based on potentiometric analysis, viscosity measurements and sedimentation. The green density of the cast is also measured.

2. Experimental procedure

Sialon powder, $z = 0.5$ ($Si_{5.5}Al_{0.5}O_{0.5}N_{7.5}$) with average particle size 0.5 μm and Brunauer–Erumett–Teller (BET) specific surface area 15 m^2 g^{-1} (supplied by Nihon Cement, Tokyo, Japan) was used throughout the work. Y_2O_3 powder (supplied by Nissho Iwai, Tokyo, Japan) was used as the sintering aid. The particle size distribution of the sialon powder was measured by Sedigraph (Micromeritics Instrument Corporation, Norcross, GA). BET specific surface area of the sialon powder was also measured by ASAP 2400 (Micromeritics Instrument Corporation, Norcross, GA).

Ammonium polyacrylate (D-735, Chukyo Yushi, Nagoya, Japan) or polyoxyethylene nonylphenyl ether (EA-170, Daiichi Kogyo Seiyaku, Tokyo, Japan) was used as a deflocculant. For preparation of the slips, sialon/4 wt % Y_2O_3 powder mixtures were milled for 24 h in 2-propanol, and then dried in a spray-dryer at 80 °C.

Sedimentation suspensions were prepared as follows. The mixed sialon/Y_2O_3 powder was stirred into deionized water, with 0.5 wt % deflocculant. The solid content of the suspensions was 5 vol %. The pH of the suspensions were controlled over the range 4.5–12 using HCl or NH_4OH. Particles in the suspensions were dispersed ultrasonically in a type VS-150 (Iuchi, Tokyo, Japan) for 15 min. The suspensions in the test tubes were left for 72 h at 20 °C, and the heights of the resultant dispersion were measured, to observe the dispersion of sialon particles.

The zeta potential was determined using a zetasizer ZP-10B (Shimadzu Seisakusho, Tokyo, Japan). The

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slips for zeta potential measurement were prepared as follows. The mixed sialon/Y_2O_3 powder was stirred into deionized water, with 0.3 wt % deflocculant, and then the slips were mixed in a polyethylene mill, with a few 15 mm polyethylene balls, for 16 h. The solid content of the slips was 40 vol %. The pH of the slips were controlled over the range 4.5–12 using HCl or NH_4OH.

Aqueous slips for viscosity measurement were prepared by mixing with deionized water, deflocculant and organic binder in a polyethylene mill, with a few 15 mm polyethylene balls, for 16 h. Polyacrylic resin (WA-320, Mitsui Toatsu, Tokyo, Japan) was used as the organic binder. The solid content of the samples was 40 or 45 vol %.

The apparent viscosity was measured on a VT-04 rotation viscometer (Rion, Tokyo, Japan). The rheogram was measured as a function of shear rate for each slip, using a Visconic Ed (Tokyo Keiki, Tokyo, Japan).

The slips were cast in moulds of plaster (Aoyama Ceramold, Seto, Japan). Standard plaster moulds (150 × 150 × 20 mm) were used for measurement of the green density of cast ware. The slips were degassed for 2 h under a rotary pump vacuum and pressure casting was carried out by applying a 2 kg cm^{-2} air pressure to the top free surface of the slip for 3 h. The green densities of the casts ware were determined by the Archimedean method using kerosene.

The cast ware was fired at 1740 °C for 3 h in a carbon crucible under 101.3 MPa pressure of nitrogen. From room temperature to 1000 °C the heating rate was 20 °C min^{-1}, from 1000 to 1650 °C the heating rate was 10 °C min^{-1}, and from 1650 to 1740 °C the heating rate was 5 °C min^{-1}. The density of the sintered body was determined by the Archimedean method, using water.

3. Results and discussion

The pH values of sedimentation suspensions were adjusted from 4.5 to 12. The heights of the resultant dispersion are shown in Table I. As can be seen in Table I, the pH values of suspensions have an effect on the height of the sialon particles dispersion. Sedimentation of the sialon particles occurred at pH 4.5 with ammonium polyacrylate. Good dispersion is achieved with pH > 10. On the other hand, the pH values of the suspensions with polyoxyethylene nonylphenyl ether do not affect the heights of sialon particles dispersion significantly. Obvious sedimentation of the sialon particles was not observed.

In Fig. 1, the results from the zeta potential measurements on the sialon slips are presented. The zeta potential is negative for pH > 7. The slips with pH 10 turned out to be easy to cast, which can be expected because the magnitude of zeta potential is greater than another pH. The negative value indicates that the anionic deflocculant is effective at this pH value. Slightly less negative values of zeta potential were obtained at pH 12 compared with pH 10.

The results of the apparent viscosity measurements at six concentrations of ammonium polyacrylate for slips with solid content 40 vol % are shown in Fig. 2a.

TABLE I The height of the sialon particles dispersion (mm)

	pH				
Deflocculant	4.5	6	8	10	12
Ammonium polyacrylate	30	78	78	84	75
Polyoxyethylene nonylphenyl ether	75	75	81	84	84

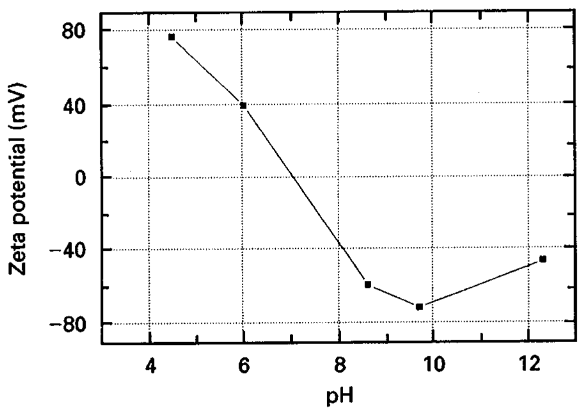

Figure 1 Zeta potential of the sialon slip with ammonium polyacrylate as a function of pH.

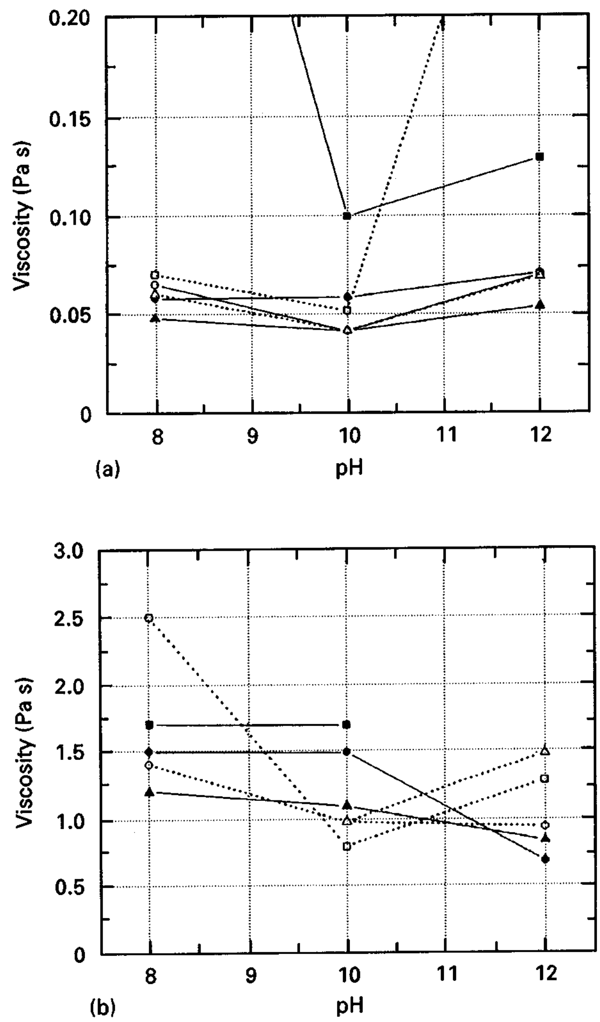

Figure 2 Apparent viscosity of slips with ammonium polyacrylate as a function of pH: (a) solid content 40 vol %; (b) solid content 45 vol %. Concentration of deflocculant: (●) 0%; (▲) 0.1%; (○) 0.2%; (△) 0.3%; (□) 0.5%; (■) 1.0%.

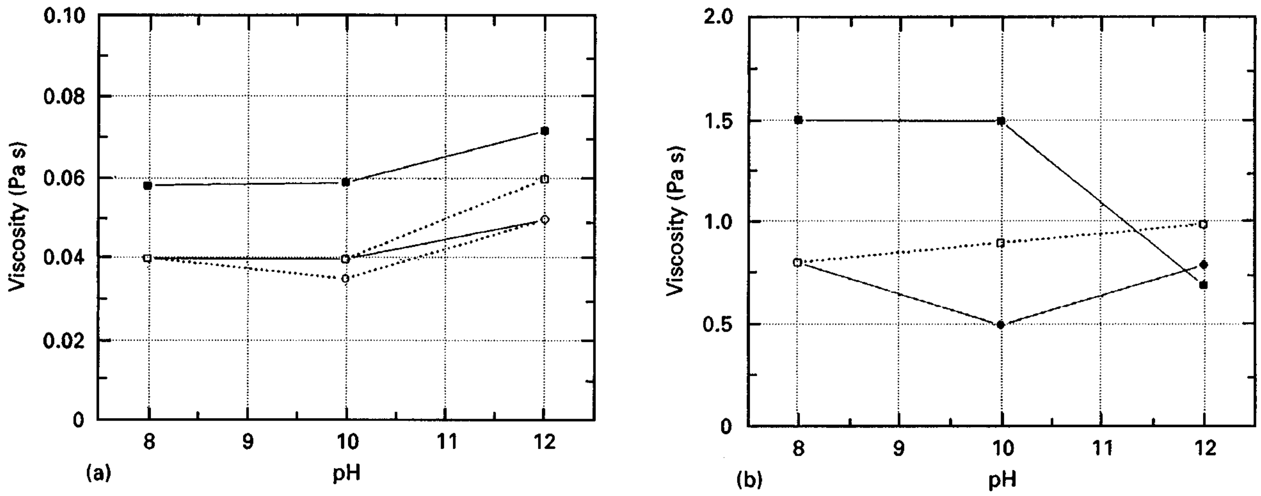

Figure 3 Apparent viscosity of slips with polyoxyethylene nonylphenyl ether as a function of pH: (a) solid content 40 vol %; (b) solid content 45 vol %. Concentration of deflocculant: (■) 0%; (●) 0.5%; (○) 1.0%; (□) 1.5%.

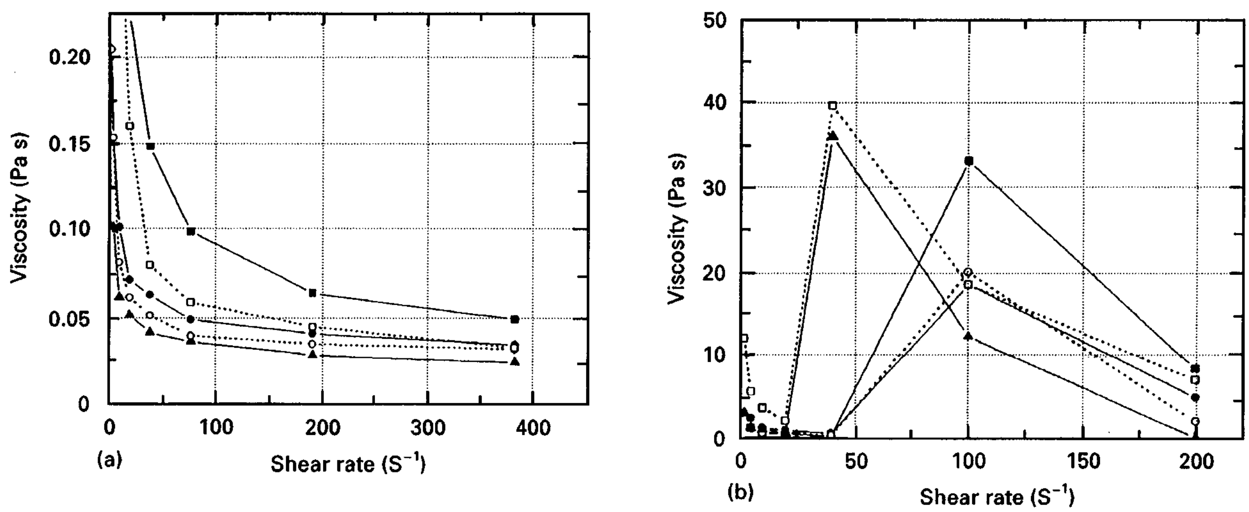

Figure 4 Apparent viscosity of slips with ammonium polyacrylate as a function of shear rate: (a) solid content 40 vol %; (b) solid content 45 vol %. Concentration of deflocculant: (●) 0%; (▲) 0.2%; (○) 0.3%; (□) 0.5%; (■) 1.0%.

As can be seen, the concentration of deflocculant and the pH value of the slips have an effect on viscosity, and a concentration of 0.2 wt % and pH 10 proved optimal. This result coincides with zeta potential measurement. An excess amount of deflocculant increases the viscosity. This may be caused by the entanglement of the polymer chains of the deflocculant [7]. The results of the apparent viscosity measurements for slips with solid content 45 vol % are shown in Fig. 2b. As can be seen, the viscosity also depends on the concentration of deflocculant and pH value of the slips, but in all cases increases significantly with respect to 40 vol %. The slips with solid content 45 vol % were very awkward to work with and difficult to cast.

The results of the apparent viscosity measurements for slips with polyoxyethylene nonylphenyl ether and solid content 40 vol % are shown in Fig. 3a. As can be seen, the concentration of deflocculant and pH value of the slips has an effect on the viscosity, and a concentration of 1.0 wt % and pH 10 proved optimal. The results of the apparent viscosity measurements for slips with solid content 45 vol % are shown in Fig. 3b. As can be seen, the viscosity also depends on the concentration of deflocculant and pH value of the slips, but is increased significantly with respect to 40 vol %. Closely similar values of viscosity were obtained compared with ammonium polyacrylate.

The dependence of apparent viscosity of the slips with ammonium polyacrylate and solid content 40 vol % on the shear rate is shown in Fig. 4a. This slip showed a reduction of the viscosity with increasing shear rate. As can be seen, 0.2 wt % proved optimal and the slip resulting from this is almost Newtonian. This slip proved sufficiently fluid for casting.

The dependence of apparent viscosity of the slips with ammonium polyacrylate and solid content 45 vol % on the shear rate is shown in Fig. 4b. This slip showed a totally different behaviour from those with 40 vol %, with an increase of the viscosity with increasing shear rate. As can be seen, the slip resulting from this is dilatant flow and difficult to cast.

The dependence of apparent viscosity of the slips with polyoxyethylene nonylphenyl ether and solid content 40 vol % on the shear rate is shown in Fig. 5a. This slip also showed reduction of the viscosity with increasing shear rate. As can be seen, 1.0 wt% proved

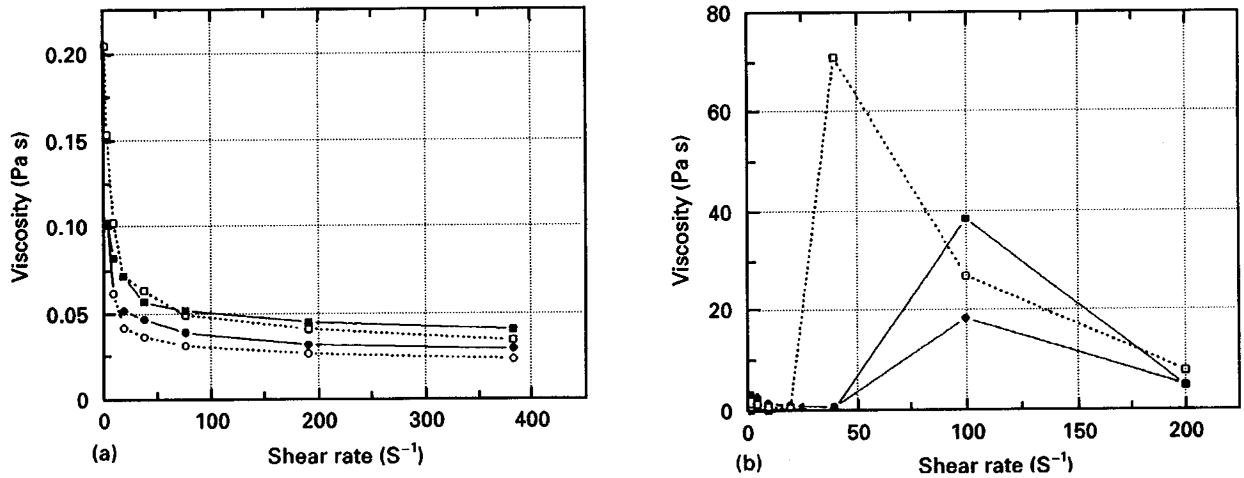

Figure 5 Apparent viscosity of slips with polyoxyethylene nonylphenyl ether as a function of shear rate: (a) solid content 40 vol %; (b) solid content 45 vol %. Concentration of deflocculant: (□) 0%; (●) 0.5%; (○) 1.0%; (■) 1.5%.

optimal and the slip resulting from this is almost Newtonian.

The dependence of the apparent viscosity of the slips with polyoxyethylene nonylphenyl ether and solid content 45 vol % on the shear rate is shown in Fig. 5b. This slip also showed increase of the viscosity with increasing shear rate. As can be seen, the slip resulting from this is dilatant flow.

The best castable slip was obtained by mixing deionized water with 0.2 wt% ammonium polyacrylate deflocculant and solid content 40 vol %. After 16 h milling, the slip had a pH of 9.7. The viscosity curve showed rather low viscosity and thixotropy. The slip with polyoxyethylene nonylphenyl ether is foamy and difficult to be degassed, and would not be expected to produce dense ceramic sintered bodies.

The green density of the cast ware was 1.78 g cm^{-3}, i.e. 55% of the theoretical density (TD), for the slip with 0.2 wt % ammonium polyacrylate deflocculant at solid content 40 vol %. The bulk density of the sintered body was 3.20 g cm^{-3}, 98% TD.

4. Conclusions

1. Sialon powder with sintering aids (4 wt % Y_2O_3) yields castable aqueous slip in the presence of a deflocculant (ammonium polyacrylate), as well as by addition of NH_4OH.

2. Aqueous sialon slip at solid content 40 vol % shows low viscosity and thixotropy.

3. Slip cast sialon ware lends itself to high bulk density (98% TD) after firing.

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