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RHEOLOGICAL PROPERTIES OF AQUEOUS SUSPENSIONS OF Si₃N₄-Si-Al₂O₃-ZrO₂ POWDERS

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Abstract - The forming process is very important in the production of ceramics because the defects introduced during this manufacturing step will remain in the product even after the sintering process.In this work the rheological properties of aqueous suspensions of Si₃N₄-Si-Al₂O₃-ZrO₂ powders are studied in order to define the appropriate conditions for preparing good slips for the production of high temperature ceramics.

I - INTRODUCTION

Reaction sintering is proposed as an useful intermediate stage to obtain sintered silicon nitride based compacts in order to decrease the total shrinkage, to allow the finishing of the presintered bodies, to obtain higher density in the initial sintering stage. Reducing the nitridation time and the complexity of the nitriding atmosphere, the addition of silicon nitride to the powder mixture leads to an easier reaction bonding process. The presence of sintering and toughening agent in the powder mixture must be taken into account for the sintering stage and to improve the mechanical properties of the bodies, which are in any case strictly related to texture of green body's microstructure, i.e. to the forging technology. Well known and currently used in the traditional ceramic field, slip casting is a suited way for shaping complex geometry, but a lack of knowledge exists on the controlling microstructure parameters during casting on plaster mould. The present work is a first approach to the characterization of the rheological properties and the castability features of the slips with the final aim to find

(1)Si₃N₄ Starck,BET=15.0 m²/g,d=3.18 g/cm³;Si Starck,BET=0.5 m²/g,d=2.32 g/cm³;Al₂O₃ Alcoa,BET=17.7 m²/g,d=3.98 g/cm³;ZrO₂ Harsaw (U.S.A.),BET=28 m²/g,d=5.89 g/cm³.
suitable and accessible controlling parameters and their correlation to the microstructure.

II - EXPERIMENTAL METHODS

a) Materials.
All experiments were performed with a powder mixture of 31.1 wt% Si$_3$N$_4$, 46.6 wt% Si, 6.6 wt% Al$_2$O$_3$ and 15.7 wt% ZrO$_2$ dispersed in distilled water and different amounts of industrial deflocculants.

b) Rheological tests.
The suspensions were prepared through dispersion with an impeller of the powders mixture. The solid concentrations were 60, 65 and 70 wt%. The deflocculants concentrations were calculated on a dry material basis. The rheological tests were carried out at 25°C, with a rotational viscometer Rotowisko RV 100: measuring device a bob/cup system ZB 15; shear rate range: 3-700 s$^{-1}$.

c) Casting measurements.
The suspensions were prepared by dispersion of the components in a horizontal roller using Al$_2$O$_3$ balls and a polythene container. The pH was checked ranging between 7.0 to 7.3 for all the tested systems. The kinetics of the slip casting was followed using an apparatus proposed by Melton et al./1/. It was designed in order to determine the rate of removal of water from the slip by the mould. The apparatus consists in a plaster mould (plaster/water ratio: 100/64) which is put in contact with the suspension held in a cup. The volume of water abstracted from the slip is replaced by a reservoir burette, and so it is possible to take readings of volume against the time. The measurements were performed during not over few minutes immediately after the slip preparation in order to avoid the hydrogen evolution. Bulk densities of cast bodies were measured according to mercury picnometry technique.

III - RESULTS AND DISCUSSION

Rheological properties
The possibility of formulating concentrated suspensions having satisfactory stability and fluidity and, consequently, of obtaining cast bodies with high bulk density strongly depends upon the use of powerful dispersing agents which control the aggregation conditions of the solid phase because of their adsorption onto the particle surfaces. The rheological measurements are the best quantitative method to achieve informations on both fluidity and stability of concentrated suspensions. Therefore, the ability of various commercial deflocculants (2) was tested by examining the rheological behaviour of a number of suspensions, having the same solids content (60 wt%) and the same deflocculant concentration (0.3 wt%), according to the Camina-Roffey procedure /2/. It consists in the alternate and sequential application of the same reference shear rate and of different shear rates. Each shear rate is applied until a steady value of the shear stress is attained. So, the shear- and the time- dependent properties of the slips can be investigated and, at the same time, their stability can be measured by comparing the shear stress values attained at the reference shear rate, repeatedly applied during the experimental test. A progressive decrease of the shear stress clearly indicates

(2) Fratelli Lamberti: Reotan LA, Reotan 747, Reotan LA/7, Reotan LP4.
scarce stability of the slip and the occurrence of settling. The most promising results were obtained with ammonium alginates (A50 and A500) (*), since they allow stable slips to be prepared without collateral and detrimental aerating effects. Alginate solutions are pseudoplastic fluids at the concentration examined in the present work. The use of A50 alginate allows castable suspensions with high solids content up to 70 wt% to be easily prepared. Figure 1 reports the experimental data for the systems with a solid phase content of 60, 65 and 70 wt% and 0.3 wt% of A50.

In the shear rate range explored, the rheological behaviour of the first two systems is plastic, whereas at the highest solids content it is plastic-dilatant and resembles that of other very concentrated suspensions /3-5/.

Fig. 1 - Shear rate vs. shear stress for the slips examined (the first two number are referred to the solids content, the last to the A50 concentration).

In order to evaluate the deflocculant amount to be added for optimum fluidification, the shear-dependent behaviour of a number of slips with 70 wt% of solid phase and different deflocculant concentrations was examined. As reported in Fig. 1, all the systems exhibit plastic-dilatant behaviour. It can be described satisfactorily by the Herschel-Bülowkey equation.

\[ \tau = \tau_0 + k \dot{\gamma}^n \]

The alginate concentration does not affect appreciably the yield value \( \tau_0 \) and the exponent \( n \).

All the systems examined show thixotropic properties which are significant at low shear rates (\( \dot{\gamma} \leq 10 \text{ s}^{-1} \)). When a sudden decrease of the shear rate is applied, a progressive shear stress increase at the lower constant shear rate is generally observed, as a consequence of structural buildup processes which take place inside the system. Interesting results can be obtained by applying the Tapeznikov-Fedotova procedure /6/ with the aim of investigating the buildup properties in rest conditions. Accordingly, the system is subjected to a constant shear rate until a steady value of the shear stress is attained, and then the shear is stopped. The same shear rate

(*) CECA Algum A 50, Algum A 500.
is applied after a given rest time $t_r$ and the initial stress value $\tau_{max}$ is recorded. The procedure is repeated for different rest times. The increase of $\tau_{max}$ with $t_r$, that is the viscosity buildup with rest time, gives an insight of the thixotropic processes which involve the disperse phase of the system when it suddenly passes from shear to no-shear conditions. Figure 2 reports an example of the pronounced viscosity buildup for the system 704.

The shear-dependent behaviour of the slips results from the non-Newtonian contribution of the dispersing medium and the aggregation state of the disperse phase. A first estimate of the aggregation state can be derived from the relative viscosity $\eta_r$ (the viscosity of the slip divided by the viscosity of the dispersing medium).

![Graph showing viscosity buildup over rest time](image)

**Fig. 2** - Viscosity buildup in rest conditions for the system 704 (after the application of constant shear rate: a) $\dot{\gamma}=90$ s$^{-1}$, b) $\dot{\gamma}=30$ s$^{-1}$, c) $\dot{\gamma}=9$ s$^{-1}$).

Figure 3 reports a comparison between the relative viscosities of the systems with 0.2 wt% and 0.5 wt% deflocculant concentrations and with the same solid content (70 wt%). One can see that, while the 0.5 wt% system is more viscous than the 0.2 wt% one in the whole shear rate range, its relative viscosity is sensibly lower at any shear rate. It means that at higher alginate concentrations the disperse phase is less aggregated, that is the particles are better dispersed, and the more effective dispersing action, due to the 0.5 wt% alginate addition, is simply hidden by the corresponding viscosity enhancement.

**Casting properties**

Casting tests were performed with the above mentioned apparatus, for suspensions containing 60, 65 and 70 wt% of solid phase and different amount of A 50 and A 500 deflocculant. Casting kinetics are usually described by the relationship:

$$L^2 = K\tau t$$

where $L$ is the thickness of the cast at the time $t$. If the initial data, relative to the time during which the gap between the suspension and the plaster mould is filled, are excluded and if the cast produced has constant density throughout its thickness
the above equation can be adapted to the experimental data by the following one, as described by /7/:

$$V = K t^{1/2}$$

where $K$ is the casting constant and $V$ is the volume of water abstracted at time $t$ from the slip by the mould, normalized to the unit area of the mould/slip interface. The casting constants result to be strictly related to the deflocculant concentration and to the porosity of the cast (Fig.4), higher casting rate being obtained with lower deflocculant concentration and higher density being obtained with lower casting rate. Anomalous behaviour of this general trend has been verified and are pointed out by the anomalous values of cast body's porosity (see system 655 and 705 in Fig.4).

Fig. 3 - Relative viscosity vs. shear rate for the systems 702 and 705.

Fig. 4 - Dependence of the casting constant on the relative density for the systems with A 50 and A 500 deflocculants (theoretical density = 2.92 g/cm$^3$).
They are probably related to the variation of the effectiveness of the deflocculant on dispersing the solid phase. The different dispersing degree of the solid phase, also confirmed by the viscosity measurements, directly influences the microstructure of the cast bodies as shown in Fig. 5 where only the concentration of 0.6 wt% gives satisfactory microstructure. The general trend and the anomalous behaviours can be explained according to the Carman-Kozeny model /8/. In fact the permeability of the cast (that is casting constant) is strictly related both to the amount and to the distribution of the porosity, being the stress to remove water from the pores inversely proportional to the pore radius.

Fig. 5 - Microstructure of cast bodies for systems: a) 603/A50 (K=4.7); b) 703/A50 (K=2.1); c) 656/A500 (K=1.2).

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