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THE EFFECT OF PARTICLE SIZE ON THE RHEOLOGICAL PROPERTIES OF CERAMIC PASTE

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The capillary viscometer method was used to determine the constitutive equation for two α-Al_2O_3 *pastes with different submicron particle sizes. Over the shear rate interval measured the two pastes are described by the constitutive equation for the generalized viscoplastic liquid. With increasing shear rate, the paste with the larger particle size shows a change in rheological behaviour and exhibits dilatancy. It was also found that the critical stress corresponding to the rapid increase in the paste viscosity and subsequent forcing the plasticizer out of the paste, increases with decreasing particle size.*

INTRODUCTION

The preparation of high — tech. ceramics with a controlled and reproducible microstructure depends on the state of the initial powdered mixtures and on mastering the respective technological processes. Attainment of the theoretical density and fine-grained microstructure necessitates employment of powdered mixtures with a monodisperse submicron particle size. Such powdered mixtures exhibit high sintering activity which, together with attainment of minimum porosity before sintering, is a prerequisite for the preparation of high-density products. Compliance with this requirement is associated with the forming technology chosen. In the case of forming of ceramic pastes it is necessary to resolve plastification of the powder and control of the paste flow in agreement with the microstructure required. The uniformity of densification in the body volume determined by orientation of particles, distribution uniformity of additives and pores, etc., depend on the velocity field arising during the paste flow. Control of the paste flow is related to quantitative description of the process which in turn requires the constitutive equation of the ceramic paste to be known.

The present study is aimed at determining to what extent a change in the particle size in the submicron region affects the rheological behaviour of ceramic paste.

Evidence on the effect of particle size on the behaviour of ceramic pastes during flow is provided by the fact that, with increasing particle size, there occurs a decrease of the critical stress corresponding to an abrupt and rapid rise in viscosity, when the plasticizer is forced out of the body and the paste ceases to flow [1]. The so-called volume expansion [2, 3, 4] is usually held responsible for this dilatant behaviour of suspensions or pastes. As follows from the schematic representation of this phenomenon in Fig. 1, the attainment of the critical stress or critical shear

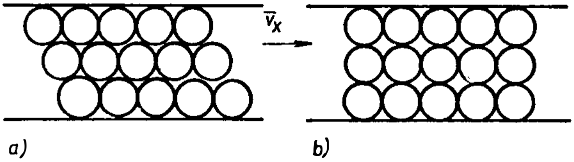

Fig. 1. Volume expansion in concentrated suspensions.

rate brings about restructuring of the mutual arrangement of particles. At standstill or at low shear rates, the particles are densely packed with a plasticizer layer on the surface (cf. Fig. 1a). At high shear rates the arrangement of particles is looser (cf. Fig. 1b), i.e. the particles are incapable of filling in the gaps, volume expansion occurs, and mutual friction between the particles inhibits flow and the plasticizer is forced out into free areas.

EXPERIMENTAL

The effect of particle size on the rheological behaviour of ceramic pastes, characterized by differences in their particle size, was assessed by comparing the constitutive equations of the paste. The measurements were carried out on two α-Al_2O_3 pastes having the parameters listed in Table I. The powders were worked into paste form by mixing with a plasticizer (Al_2O_3 (J) — 10 wt. %; Al_2O_3 (H) — 8 wt. %). Owing to the greater specific surface of the Al_2O_3 (J) particles, the optimum pasty state was achieved with a plasticizer addition higher by 2 wt. %. The paste obtained was evacuated and tempered at $T = 23\ ^{\circ}C$. The capillary viscometer method [5] was used to evaluate the constitutive equations of the pastes. The Al_2O_3 (J) paste was measured with capillaries having the lengths $L_1 = 10 \times 10^{-2}$ m and $L_2 = 4 \times 10^{-2}$ m with a diameter $D = 4.2 \times 10^{-3}$ m over the range of medium paste flow rate through the capillary, $\bar{v}_x \in \langle 9.12 \times 10^{-4}\ \mathrm{m\ s^{-1}};\ 3.92 \times 10^{-2}\ \mathrm{m\ s^{-1}} \rangle$. In the case of the Al_2O_3 (H) paste, use was made of capillaries with $L_1 = 5 \times 10^{-2}$ m, $L_2 = 4 \times 10^{-2}$ m and $D = 4.2 \times 10^{-3}$ m and $L_3 = 8 \times 10^{-2}$ m, $L_4 = 5 \times 10^{-2}$ m with $D = 6.9 \times 10^{-3}$ m over the range of $\bar{v}_x \in \langle 3.68 \times 10^{-4}\ \mathrm{m\ s^{-1}};\ 7.11 \times 10^{-2}\ \mathrm{m\ s^{-1}} \rangle$. The experimentally established relationship

Table I

The characteristics of the oxides employed

Designation	Particle size, μm	Content %	Specific area $g\ m^{-2}$
Al_2O_3 (J)	0.1—0.4	83	10.8
Al_2O_3 (H)	0.1—0.8	76	7.1

$$p = f(4\bar{v}_x/R), \tag{1}$$

where R is the capillary radius and p is the pressure, was corrected for terminal effects ($\Delta p = p_{Li} - p_{Li+1}$; $\Delta L = L_i - L_{i+1}$). Introduction of

$$\tau_s = R\ \Delta p/2L, \tag{2}$$

where τ_s is shear stress at the capillary wall, produced the dependence

$$\tau_s = f(4\bar{v}_x/R). \tag{3}$$

Conversion of the quantity $(4\bar{v}_x/R)$ to the shear rate at the wall provided a plot of the constitutive equation, i.e. the relationship

$$\tau_s = f(\mathrm{d}v_x/\mathrm{d}r)_s. \tag{4}$$

The experimental relationship (1) and the evaluated ones (3), (4) are plotted in Figs. 2, 3 and 4 for Al_2O_3 (J), and in Figs. 5, 6 and 7 for Al_2O_3 (H).

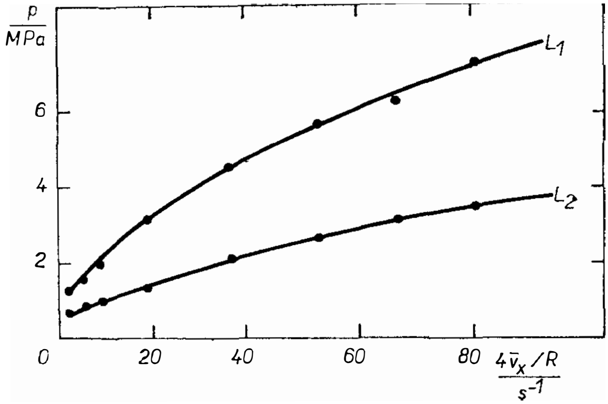

Fig. 2. Relationship $p = f(4\bar{v}_x/R)$ *for* Al_2O_3 (J).

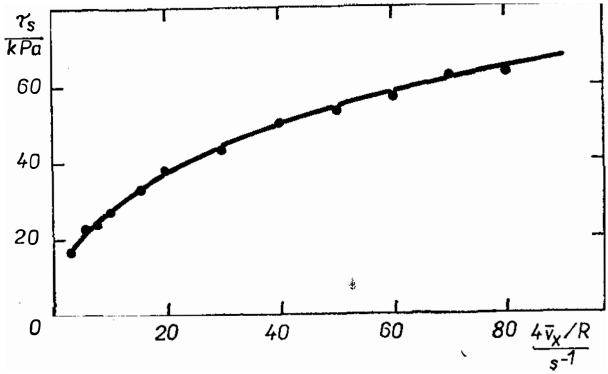

Fig. 3. Relationship $\tau_s = f(4\bar{v}_x/R)$ *for* Al_2O_3 (J).

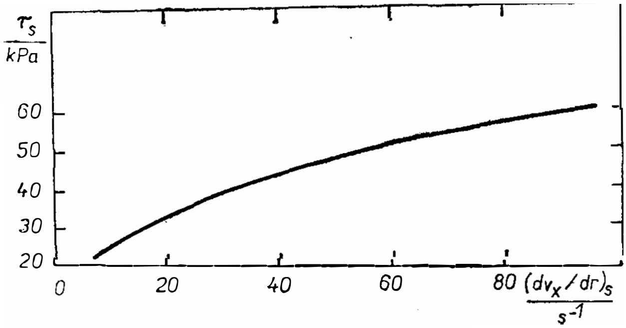

Fig. 4. Relationship $\tau_s = f(dv_x/dr)_s$ *for* Al_2O_3 (J).

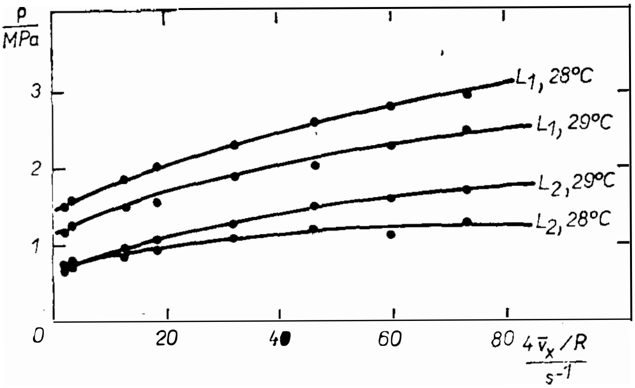

Fig. 5. Relationship $p = f(4\bar{v}_x/R)$ *for* Al_2O_3 (H).

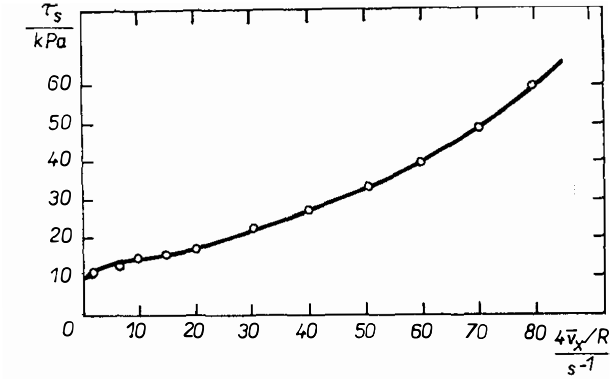

Fig. 6. Relationship $\tau_s = f(4\bar{v}_x/R)$ *for* Al_2O_3 (H).

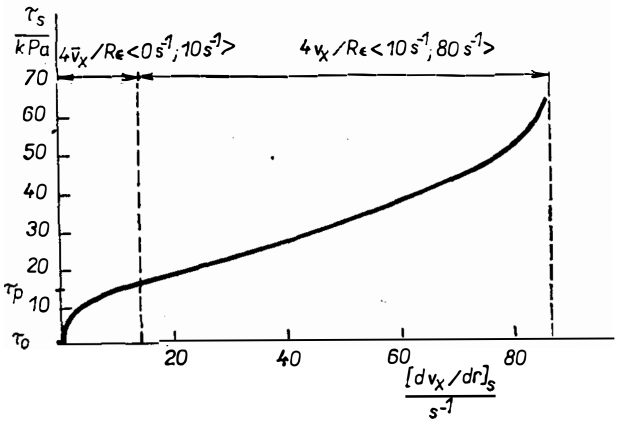

Fig. 7. Relationship $\tau_s = f(\mathrm{d}v_x/\mathrm{d}r)_s$ *for* Al_2O_3 (H).

The graphic plot of the constitutive equation of the Al_2O_3 (J) paste in Fig. 4 was approximated by the equation of the general viscoplastic material model in the form

$$\tau_s = \tau_0 + K(\mathrm{d}v_x/\mathrm{d}r)_s^n, \tag{5}$$

with the following values of the constants:

$$\tau_0 = 6.0\,\mathrm{kPa}; \qquad K = 6.54\,\mathrm{kPa\,s}^n; \qquad n = 0.472. \tag{6}$$

The course of the graphic plot of the constitutive equation for the Al_2O_3 (H) paste was divided into two intervals $(4\bar{v}_x/R)$ describing the change in the rheological behaviour in terms of the shear rate. Over the interval of $(4\bar{v}_x/R) \in \langle 0\ \mathrm{s}^{-1};\ 10\ \mathrm{s}^{-1}\rangle$, the relationship was approximated by equation (5) where the constants have the following values:

$$\tau_0 = 1.07\,\mathrm{kPa}; \qquad K = 5.9\,\mathrm{kPa\,s}^n; \qquad n = 0.376. \tag{7}$$

Over the interval $(4\bar{v}_x/R) \in \langle 10\ \mathrm{s}^{-1};\ 80\ \mathrm{s}^{-1}\rangle$ the constants in equation (5) had the following values:

$$\tau_0 = 14.5\,\mathrm{kPa}; \qquad K = 0.04\,\mathrm{kPa\,s}^n; \qquad n = 1.545. \tag{8}$$

Measurement of the rheological behaviour of paste Al_2O_3 (H) showed that at the flow rates of the paste through the capillary, coresponding to the values $(4\bar{v}_x/R) > 80\ \mathrm{s}^{-1}$, there occurs an abrupt increase in shear stress, the paste ceases to flow through the capillary and the plasticizer is forced out of the paste.

CONCLUSION

On the basis of the experiments performed, the findings concerning the effect of submicron particle size on the rheological behaviour of ceramic paste can be summarized into the following points:

(i) to achieve the same pasty state with a mix containing smaller particles with a greater specific surface area it is necessary to used a higher amount of plasticizer,

(ii) over the entire range of $(4\bar{v}_x/R) \in \langle 0\ \mathrm{s}^{-1};\ 80\ \mathrm{s}^{-1}\rangle$ the constitutive equation of the Al_2O_3 (J) ceramic pastes in the form (5) with the values of the constants according to (6) corresponds to a generalized viscoplastic material over the entire range of $(4\bar{v}_x/R) \in \langle 0\ \mathrm{s}^{-1};\ 80\ \mathrm{s}^{-1}\rangle$,

(iii) the Al_2O_3 (H) ceramic paste exhibits a change in its rheological behaviour with increasing shear rate. Over the interval of $(4\bar{v}_x/R) \in \langle 0\ \mathrm{s}^{-1};\ 10\ \mathrm{s}^{-1}\rangle$ the constitutive equation corresponds to that of generalized viscoplastic material (5) with the values of the constants given in (7). Over the interval of $(4\bar{v}_x/R) \in \langle 10\ \mathrm{s}^{-1};\ 80\ \mathrm{s}^{-1}\rangle$ the paste exhibits dilatant behaviour described by equation (5) where the constants have the values given in (8),

(iv) with the ceramic pastes composed of larger submicron particles, Al_2O_3 (H), a rapid increase in viscosity followed by squeezing out of the plasticizer, occurs when exceeding the critical stress, $\tau_s > 65\,\mathrm{kPa}$. Under this stress, the Al_2O_3 (J) paste exhibits satisfactory flow properties. The value of critical stress therefore increases with decreasing particle size.

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VLIV VELIKOSTI ČÁSTIC NA REOLOGICKÉ VLASTNOSTI KERAMICKÉ PASTY

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V práci byl sledován vliv velikosti částic na reologické chování keramické pasty α-Al_2O_3 vyjádřené její konstitutivní rovnicí. Dvě pasty s odlišnou submikronovou velikostí částic byly uvedeny do plastického stavu přídavkem organického plastifikátoru. Bylo zjištěno, že pasta s jemnějšími částicemi vyžadovala k dosažení stejného pastovitého stavu o 2 % hmot. větší přídavek plastifikátoru. Konstitutivní rovnice obou past byla stanovena metodou kapilárního viskozimetru. Ve stejném intervalu gradientu rychlosti smykové deformace jsou obě pasty popsány konstitutivní rovnicí obecné viskoplastické kapaliny. U pasty s větší velikostí částic dochází s rostoucím gradientem rychlosti deformace ke změně reologického chování a projevu dilatance. U této pasty při překročení kritického napětí $\tau_s > 65$ kPa dochází rovněž k vytlačování plastifikátoru z pasty. Při tomto napětí pasta s menšími částicemi vykazuje dobré tokové vlastnosti.

Obr. 1. Vznik objemové expanze v koncentrovaných suspenzích.
Obr. 2. Závislost $p = f\,(4\bar{v}_x/R)$ *pro* Al_2O_3 (J).
Obr. 3. Závislost $\tau_s = f(4\bar{v}_x/R)$ *pro* Al_2O_3 (J).
Obr. 4. Závislost $\tau_s = f(\mathrm{d}v_x/\mathrm{d}r)_s$ *pro* Al_2O_3 (J).
Obr. 5. Závislost $p = f(4\bar{v}_x/R)$ *pro* Al_2O_3 (H).
Obr. 6. Závislost $\tau_s = f(4\bar{v}_x/R)$ *pro* Al_2O_3 (H).
Obr. 7. Závislost $\tau_s = f(\mathrm{d}v_x/\mathrm{d}r)_s$ *pro* Al_2O_3 (H).

ВЛИЯНИЕ РАЗМЕРА ЧАСТИЦ НА РЕОЛОГИЧЕСКИЕ СВОЙСТВА КЕРАМИЧЕСКОЙ ПАСТЫ

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В раборе исследуется влияние размера частиц на реологическое поведение керамической пасты n-Al_2O_3, описанное с помощью конститутивного уравнения. Две пасты с различным субмикроновым размером частиц перевели в пластическое состояние добавкой органического пластификатора. Было установлено, что паста с более тонкими частицами требует для достижения одинакового постообразного состояния на 2 % по весу большее количество пластификатора. Конститутивное уравнение обеих паст было установлено методом капилярного вискозиметра. В одинаковом интервале градиента скорости деформации сдвига обе пасты описываются конститутивным уравнением общей вискозопластической жидкости. У пасты с большим размером частиц происходит с растущим градиентом скорости деформации изменение реологического поведения и дилатация. У данной пасты при превышении критического напряжения τ_s >,65 кПа происходит также вытеснение пластификатора из пасты. При таком напряжении паста с меньшими частицами обладает хорошими свойствами протока.

Рис. 1. Образование объемной экспансии в концентрированных суспенсиях.
Рис. 2. Зависимость $p = f(4\bar{v}_x/R)$ *для* Al_2O_3 (J).
Рис. 3. Зависимость $\tau_s = f(4\bar{v}_x/R)$ *для* Al_2O_3 (J).
Рис. 4. Зависимость $\tau_s = f(\mathrm{d}\bar{v}_x/\mathrm{d}r)_s$ *для* Al_2O_3 (J).
Рис. 5. Зависимость $p = f(4\bar{v}_x/R)$ *для* Al_2O_3 (H).
Рис. 6. Зависимость $\tau_s = f(4\bar{v}_x/R)$ *для* Al_2O_3 (H).
Рис. 7. Зависимость $\tau_s = f(\mathrm{d}\bar{v}_x/\mathrm{d}r)_s$ *для* Al_2O_3 (H).