CHARACTERISTIC CONCENTRATIONS OF CERAMIC SLIPS IN SLIP-CASTING TECHNOLOGY

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For the purpose of mathematical modelling of the green body formation and solidification process, the characteristic concentrations of the suspension or slip were determined in the decisive stages of pouring into porous moulds, namely the initial concentration, the coagulating concentration and the body solidification one. The method developed was used to determine the characteristic concentrations for an aqueous suspension of α-Al_2O_3.

SELECTION OF THE CHARACTERISTIC CONCENTRATIONS

Mathematical modelling of the forming technology of slip casting into porous moulds involves the use of concentrations characteristic of the given operation, that is formation of a crust or body of the desired thickness, and its solidification [1-4].

The characteristic quantities should describe well the state of the ceramic mix, and be readily measurable. For this purpose, use can be made of slip concentrations in the decisive phases of the casting technology.

The first one is C_0, describing the initial state of the suspension, i.e. the content of liquid in the mix as prepared.

The second step is represented by the slip-body convesrsion. This involves a considerable decrease in the content of the liquid phase. Rheologically, the liquid turns into a viscoplastic material, that is the viscosity and flow properties change significantly. The liquid content in the mix, at which the body is formed, is characterized by the so-called coagulating concentration C_k.

On describing mathematically the body forming by pouring into porous moulds by means of the diffusion theory, the C_0 and C_k concentrations are used as the initial and boundary conditions in the resolving of transfer equations. In addition to these two, also the concentration C_s, defining the liquid content at the body-mould interface, is employed. Another characteristic concentration, C_z, describes the state at which the body is capable of keeping its given shape and has acquired a green strength sufficient for removing it from the mould [5]. C_z characterizes the condition of the body on its separation from the mould and interruption of liquid flow into the mould. On introducing the assumption that this separation results from body shrinkage, then the C_z concentration describes the content of liquid in the body at the moment the changes in body volume are over.

THE METHOD OF DETERMINING THE COAGULATING CONCENTRATION

The method of C_k determination is based on the assumption that the suspension is an incompressible isotropic liquid characterized generally by apparent viscosity μ_z. On attainment of C_k, the decrease of the liquid phase content in the suspension will result in a steepwise increase in apparent viscosity according to equation $\mu_z = \mathrm{f}(C)$, corresponding to the conversion of the liquid to a viscoplastic material. This transition must also result in a significant decrease of volume flow $\dot{V}$, in terms of the concentration of liquid in the suspension. The $\dot{V} = \dot{V}(C)$ relationship can be determined by means of a viscometer cup for various concentrations C.

The relationship $\mu_z = \mathrm{f}(C)$ can be established by using a rotary viscometer with two coaxial cylinders. The apparent viscosity is calculated from the experimental dependence of the deformation rate gradient Γ on shear stress T, using the equation

$$\mu_z = T/\Gamma \tag{1}$$

for a certain value of Γ.

THE METHOD OF DETERMINING THE BODY SOLIDIFICATION CONCENTRATION

The method for C_z determination is based on the assuption that C_z corresponds to a body in which the shrinkage has already been concluded. It consists of measuring the relationship between relative body shrinkage and liquid concentration, according to the equation

$$a = (l_0 - l(t)) \times 100/l_0\,, \tag{2}$$

where l_0 in the initial body thickness and l(t) is the body thickness at time t. The $a = a(C)$ dependence can be established by drying the body at a rate identical with the surface flux of liquid occurring during the body solidification in a porous mould.

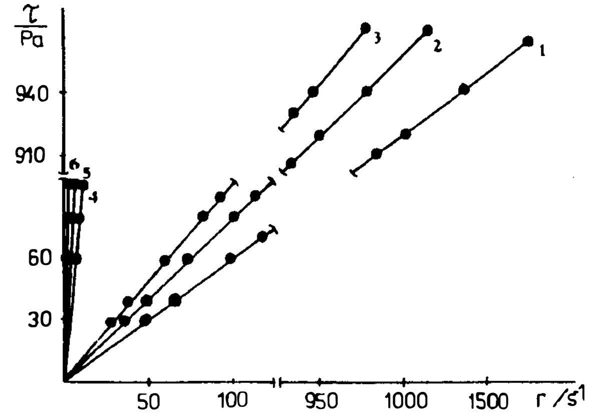

Fig. 1. Shear stress vs. deformation rate gradient.
1 – C = 0.6280 $m^3 m^{-3}$; 2 – C = 0.5677 $m^3 m^{-3}$;
3 – C = 0.4962 $m^3 m^{-3}$; 4 – C = 0.4803 $m^3 m^{-3}$;
5 – C = 0.4637 $m^3 m^{-3}$; 6 – C = 0.4420 $m^3 m^{-3}$.

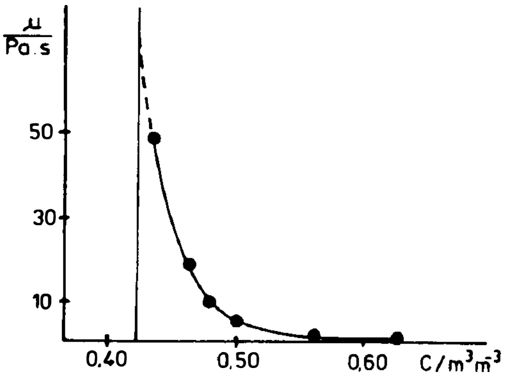

Fig. 2. Dynamic viscosity vs. concentration of the liquid phase in the suspension.

EXPERIMENTAL DETERMINATION OF THE CHARACTERISTIC CONCENTRATIONS

The characteristic concentrations were measured on an aqueous suspension of α-Al_2O_3 with a particle size over the interval of ⟨0.1 μm; 0.4 μm⟩. The electrolyte (deflocculating agent) employed allowed a high-grade suspension containing 82 wt. % of solids to be prepared, i.e. with $C_0 = 0.53$ m^3m^{-3}. The measurements were carried out with suspensions over the solids content interval of ⟨70 wt. %; 84 wt. %⟩. The content of the liquid phase in the suspension or body or gypsum mould is expressed by volume concentration C, defined by the equation.

$$C = V_L/V_M\,, \tag{3}$$

where V_L is the volume of the liquid phase and V_M is the volume of the mix. The relationship between volume concentration C and the absolute moisture content w, i.e. $w = m_L/m_S$, where m_L is the weight of the liquid phase and m_S that of the solid phase, has the form

$$C = w\left[(\rho_l/\rho_s) + w\right]^{-1} \tag{4}$$

where ρ_L is the density of the liquid phase and ρ_s is that of the solid phase $\rho_s = 3490$ kg m^{-3}.

DETERMINATION OF THE COAGULATING CONCENTRATION C_k FROM THE VISCOSITY AND VOLUME FLOW MEASUREMENTS

In the case of coagulating concentration, the α-Al_2O_3 suspension was measured on the Rheotest 2, type RV 2 rotary viscometer with two coaxial cylinders, over the deformation rate gradient range $\Gamma \in \langle 0.3\ s^{-1};\ 1312\ s^{-1}\rangle$.

The experimental relationships $\tau = \tau(\Gamma)$ for the suspensions with various C are plotted in Fig. 1.

The linear source of the dependence shown in Fig. 1 indicates that over the interval in question, the flow behaviour of the suspensions corresponds to the rheological behaviour of a Newtonian liquid. In that case the suspensions can be characterized by dynamic viscosity μ constant for a given suspension over the entire gradient of the deformation rate gradient. The μ evaluated according to the equation

$$\mu = \mathrm{d}T/\mathrm{d}\Gamma \tag{5}$$

in terms of the content of the liquid phase in the suspension, C, is plotted in Fig. 2.

The volume flow of the suspension was measured on a cup viscometer of 0.3-litre capacity. The resulting relationship $\dot{V} = \dot{V}(C)$ is plotted in Fig. 3.

The relationships shown in Figs 2 and 3 indicate that the slip viscosity begins to rise at $C < 0.4962$ m^3m^{-3}. The flow behaviour of a Newtonian liquid is retained over the concentration interval $C \in \langle 0.425$

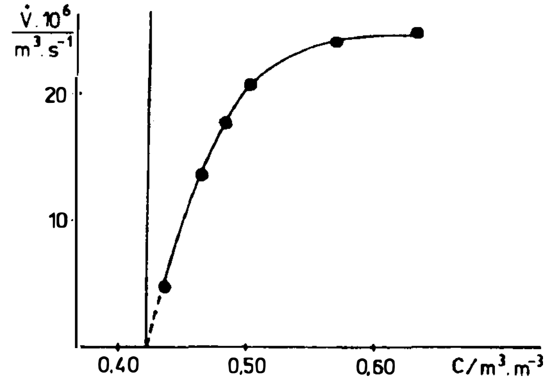

Fig. 3. Volume rate of flow of suspension vs. concentration of the liquid phase.

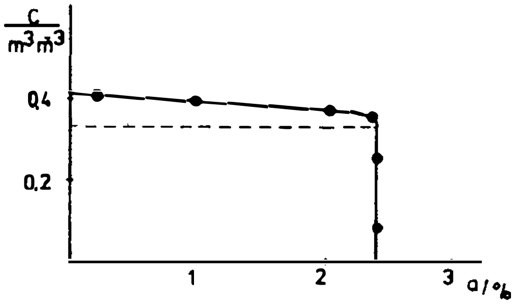

Fig. 4. Shrinkage vs. liquid concentration in the body.

Table I.

Time of body solidification in terms of its thickness

L [m]	t_z [s]	$\bar{C}$ [m^3m^{-3}]	C_z [m^3m^{-3}]
3×10^{-3}	874	0.339	0.338
5×10^{-3}	1053	0.339	
7×10^{-3}	1296	0.340	

m^3m^{-3}; 0.628 m^3m^{-3}). A suspension with $C \leq 0.42$ m^3m^{-3} exhibits the behaviour of a ceramic body. The system is no longer measurable by the rotary viscometer method. The concentration od the suspension-slip transition established is therefore regarded as the coagulating concentration, $C_k = 0.425$ m^3m^{-3}.

DETERMINATION OF THE BODY SOLIDIFICATION CONCENTRATION, C_z, BY MEASURING LINEAR SHRINKAGE

In the case of C_z, the $a = a(C)$ relationships were studied on bodies prepared from slips with various initial concentrations. The bodies were dried in an oven at controlled temperatures, relative humidity and rate of air flow. Selection of a suitable drying schedule allowed the rate of drying to be kept identical with the surface flow of the liquid in the course of body solidification in the porous mould. A typical dependece $a = a(C)$, established for a suspension with $C_0 = 0.53$ m^3m^{-3}, is plotted in Fig. 4.

The experimentally determined relationships $a = a(C)$ were used to assess the concentration corresponding to the end of the volume changes in the body, $C_z = 0.3384$ m^3m^{-3}.

To check whether the C_z concentration established in this way really corresponds to that at the time the moulding separates from the mould, the times of body solidification were determined, that is the time till the moment the body separates from the mould. The results, jointly with the corresponding mean concentration C of body solidification, are listed in Table I.

The comparison of $\bar{C}$ and C_z shows that the body separates from the mould at a mean body concentration virtually identical with the liquid concentration corresponding to the end of body shrinkage.

CONCLUSION

The methods proposed allowed the characteristic concentrations, used in the diffusion approach to the theoretical treatment of body formation and solidification, to be determined.

For an aqueous solution of α-Al_2O_3 it was found that

(i) the C_k concentration corresponds to that state of the mix when its volume flow $\dot{V} \rightarrow 0$,

(ii) the C_z concentration corresponds to that of the end of body separation from the porous mould,

(iii) for an initial slip concentration $C_0 = 0.53$ m^3m^{-3}, the coagulating concentration $C_k = 0.425$ m^3m^{-3} and the body solidification concentration $C_z = 0.3384$ m^3m^{-3}.

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CHARAKTERISTICKÉ KONCENTRACE V TECHNOLOGII LITÍ KERAMICKÝCH SUSPENZÍ

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Pro matematický popis tvorby a zatuhování střepu byly v práci určeny charakteristické koncentrace kapaliny v rozhodujících fázích technologie lití suspenze do porézní formy, tj. počáteční koncentrace suspenze, koagulační koncentrace a koncentrace zatuhnutí střepu.

Vypracovanými metodami byla pro vodnou suspenzi α-Al_2O_3 stanovena koagulační koncentrace $C_k = 0{,}425$ m^3m^{-3} a koncentrace zatuhnutí střepu $C_z = 0{,}338$ m^3m^{-3}. Pro tuto suspenzi bylo dále zjištěno, že (i) koncentrace C_k odpovídá stavu směsi, kdy objemový tok suspenze $\dot{V} \rightarrow 0$, (ii) koncentrace C_z odpovídá koncentraci konce smrštění střepu a současně i koncentraci, kdy dochází k oddělení střepu od porézní formy.

Obr. 1. Závislost smykového napětí na gradientu rychlosti deformace.

1 – $C = 0{,}6280\ m^3 m^{-3}$; 2 – $C = 0{,}5677\ m^3 m^{-3}$;
3 – $C = 0{,}4962\ m^3 m^{-3}$; 4 – $C = 0{,}4803\ m^3 m^{-3}$;
5 – $C = 0{,}4637\ m^3 m^{-3}$; 6 – $C = 0{,}4420\ m^3 m^{-3}$.

Obr. 2. Závislost dynamické viskozity na koncentraci kapalné fáze v suspenzi.

Obr. 3. Závislost objemového průtoku suspenze na koncentraci kapalné fáze.

Obr. 4. Závislost smrštění na koncentraci kapaliny ve střepu.

Recenze knih

E. D. ŠČUKIN, A. V. PERCOV, E. A. AMELINOVÁ: KOLOIDNÍ CHEMIE. Academia, Praha 1990. 484 stran, 70 Kčs.

Kniha je upraveným překladem ruského originálu Koloidnaja chimija z roku 1982. Změny v textu překladu proti originálu byly provedeny v součinnosti a se souhlasem autorů.

Text, který je rozdělen do 11 kapitol je podán uspořádanou a srozumitelnou formou s odpovídajícím využitím nezbytného matematického aparátu. Všechny použité specifické pojmy jsou v jednotlivých kapitolách důsledně definovány a případně dále objasněny na praktických příkladech. K snadnějšímu pochopení textu jsou také účelně využívány názorné obrázky. Ve vztazích použité rozměry důsledně odpovídají SI soustavě. Za každou kapitolou je souhrn literatury a na závěr textu knihy je uveden předmětový rejstřík.

1. kapitola je věnována povrchovým jevům a struktuře fázového rozhraní v jednosložkových soustavách. Uvádí se zde potřebné termodynamické vztahy, je zde např. definována povrchová energie, je pojednáno o vlivu zakřivení povrchu na rovnováhu fází a ve stručnosti jsou zde uvedeny principy základních metod ke stanovení specifické volné povrchové energie.

2. kapitola shrnuje adsorpční jevy a rozebírá vztahy mezi strukturou a vlastnostmi adsorpčních vrstev v soustavách pevná látka - plyn a pevná látka - kapalina. Vedle termodynamiky adsorpce je zde uvedena i základní klasifikace povrchově aktivních látek.

3. kapitola: Rozhraní kondenzovaných fází mimo jiné pojednává o problematice smáčení, o použití povrchově aktivních látek a také stručně o základech flotace.

Vznik disperzních soustav, jejich molekulárně kinetické, optické a elektrické vlastnosti jsou zevrubně popsány v kapitolách 4 až 7. Zde jsou např. mimo jiné vysvětleny základy teorie elektrické dvojvrstvy a elektrokinetických dějů, vliv elektrolytů na uspořádání elektrické dvojvrstvy apod.

Vlastnosti lyofilních koloidních soustav jsou studovány v kapitole 8. Je zde objasněna např. tvorba micel v roztocích tenzidů (povrchově aktivních látek).

Kapitola 9 je věnována příčinám destrukce a relativní stability lyofóbních disperzních soustav. Vysvětlena je zde např. sedimentační a agregátní stálost disperzních soustav apod.

V kapitole 10 se pojednává o zvláštnostech struktury, stability a destrukce různých lyofóbních disperzních soustav např. aerosolů, pěn, suspenzí, solů apod.

Kapitola 11 probírá velmi přehlednou a názornou formou základy fyzikálně chemické mechaniky. Jsou zde tedy objasňovány základy reologie, vytváření struktur a reologické vlastnosti disperzních soustav, fyzikálně chemické jevy probíhají při deformaci a destrukci pevných látek apod.

V knize, která přináší vedle základních znalostí i nové cenné zkušenosti a poznatky, je zdařile sklouben teoretický výklad nezbytný k pochopení principů koloidní chemie s řadou praktických poznatků z technické i běžné praxe. Tato publikace byla napsána především jako učebnice pro studenty chemických fakult, je možné ji však doporučit všem odborníkům, kteří pracují v oborech, kde je nezbytné využívat poznatků z aplikované fyzikální a koloidní chemie.

V. Hanykýř