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COMPLEX THERMOANALYTICAL INVESTIGATION OF THE BEHAVIOUR OF CERAMIC BATCHES FOR NONPLASTIC SHAPING DURING HEAT TREATMENT

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ABSTRACT

Ceramic batches for nonplastic shaping usually contain polymeric organic compounds (e.g.polyethylene glycol, cellulose ether, polyvinyl alcohol) or mixtures therof as forming aids. These organic admixtures must be driven out during heat treatment before sintering takes place. Decomposition and oxidation of the different compounds in ceramic mixtures can be followed by thermal methods (DTA,TG,DTG) and by this it is possible to characterize the compounds and to decide their applicability for shaping processes. Information about the sintering process can be obtained from dilatometric measurements. The basic relationships are discussed on experimental results from corundum-glass-batches.

INTRODUCTION

Several physicochemical reactions proceed during the heat treatment in the production of sintered materials from corundum-glass mixtures. These reactions can be followed by thermal methods. The main aspects of corresponding investigations are summarized in the following table:

process	method
1. Burn-out of additives by decomposition/oxidation	DTA, TG, DTG (simultaneously)
2. Sintering	
densification, shrinkage	DTA - "sintering effect"[1] Dilatometer - linear shrinkage
crystallization of glass	DTA - crystallization heat[1]
solution of crystalline phase	Dilatometer - temperatur of glasstransformation range[2]

Of special interest are the burn-out of additives and the onset periode of sintering.

EXPERIMENTAL

1. Sample preparation. The main steps are: grinding of the raw materials alumina and glass to fine powders with a 50% quantile of their grain size distribution (d_{50}) between 2 - 5 um.

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Proportioning and dry mixing. Slip preparation with admixing of 3 - 5% of additives (polyethylene glycol-PEG, cellulose ether-CE, polyvinyl alcohol-PVA). Spray drying.

2. Conditions of the thermal investigations.

a. Behaviour during burn-out.-Substances:Spray-dried powders. Apparatus: Derivatograph Q-1500d, MOM/Hungary. Atmosphere: Air, flow rate 10 l/h. Heating rate: 5 K/min. Sample holder: Standard corundum crucible. Reference material: Al_2O_3. Sample weight: 0,3 - 0,7 g

b. Shrinkage.-Sample: Test bars (4 x 4 x 15 mm^3) dry pressed from spray dried powders. Apparatus: Dilatometer L73/30, Linseis/BRD. Sample holder: Corundum system. Atmosphere: Air, stagnant. Heating rate: 5 K/min.

c. Densification.-Sample: Cylinders (Ø 20mm,h=3 mm) dry pressed from spray dried powders. Heat treatment: Heating rate 2 K/min until t_B, soaking time at t_B = 1 h. Cooling in furnace. Parameter for description: Relative density vs. t_B.

RESULTS AND DISCUSSION

1. Burn-out of additives. Simultaneously recorded DTA and TG of three powders containing different additives are shown in Fig.1. The curves correspond to the following admixtures: 1 - PEG (5% Oxidwachs A, Buna/DDR, stabilized), 2 - CE (3% Tylose H 4000, Hoechst/BRD), 3 - PVA (3% Mowiol 04/M1, Hoechst/BRD). Differences in decomposition and oxidation behaviour can clearly be seen. Reactions start in all three cases above 180°C. Reaction speed depends upon the chemical character of the additives and their molar weight distribution. The reactions are completed at 500°C. An example for a powder suitable in production is shown in Fig.2, curve 1. The additives are 4% PEG stabilized and0,7% CE. The thermal effects are superpositions of the corresponding effects of the components. For comparence curve 2 in Fig.3 shows the behaviour of a powder with the same amount of an addition of unstabilized PEG. In that case decomposition allready starts immediately above room temperature and the rate of weight-loss has a maximum between 100 and 180°C. The latter additive is not exeptable for practical use because allready during spray drying it shows some decomposition and because of its instability during storage.

2. Sintering. Linear shrinkage of bars prepared from 80 Vol-% alumina (99% α-Al_2O_3, d_{50} = 2,8 µm) and 20 Vol-% powdered glass (alkalialumoborosilicate-glass, d_{50} = 2,5 µm) with an addition of 3% PVA, recorded with the dilatometer is shown in Fig.3. For a better demonstration of the shrinkage, the scale of the curve b is five times that of curve a. Densification, which is inverse to the shrinkage, is also shown in Fig.3, curve c. As can be seen from curve b the burn-out of additives is allready accompanied by a small shrinkage. The onset temperature of sintering is determined by the viscosity of the glass. In the example shown it is at about 600°C but sintering in that case is retarded in the region between 700 - 850°C. This retardation is caused by the crystallization of some feldspare from the glass phase as has been confirmed by X-ray examination. Increasing the temperature leads to solution of feldspare and an undisturbed sintering. Densification is completed by reaction liquid phase sintering[3]. As can be seen from shrinkage- and densification-curve this is attained at about 1500°C.

CONCLUSIONS

The main physicochemical processes during heat treatment of glass bonded alumina are accompanied by a specific behaviour in dilatation or shrinkage and are therefore observable by dilatometric examination. Decomposition and oxidation relations which can be followed by simultaneous DTA and TG are determining factors for the suitability of additives. The optimal heat treatment can be derived by the combination of the different thermal measurements.

REFERENCES

1 W.Schiller, C.-H.Horte, J.Wiegmann, Thermische Analysenverfahren in Industrie und Forschung, Wiss.Beitr.Friedrich-Schiller-Univ. Jena 1981, S 45 - 52.
2 W.Schiller, C.-H.Horte, I.Schiemann, ibd. 1983, S.16 - 25
3 W.D.Kingery, J.Appl.Physics 30(1954) S. 301 - 310

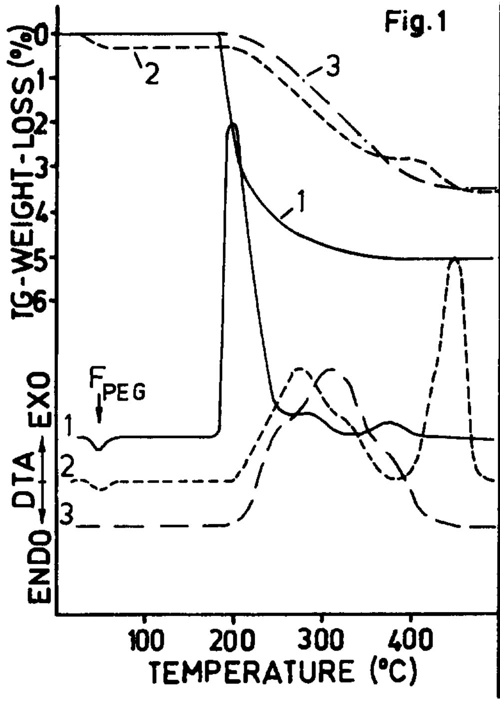

Fig.1

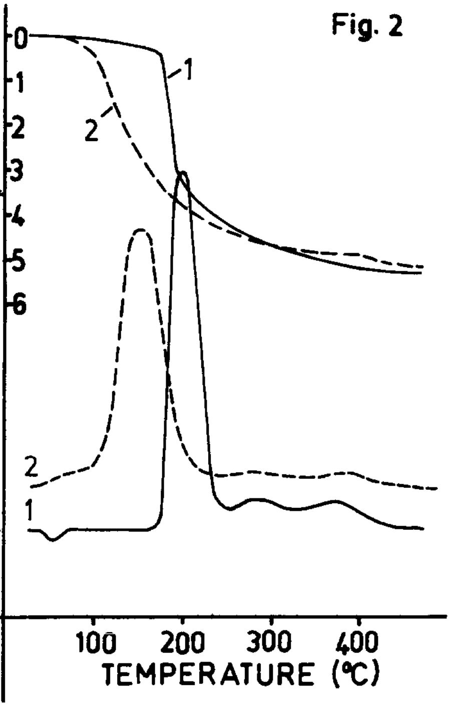

Fig. 2

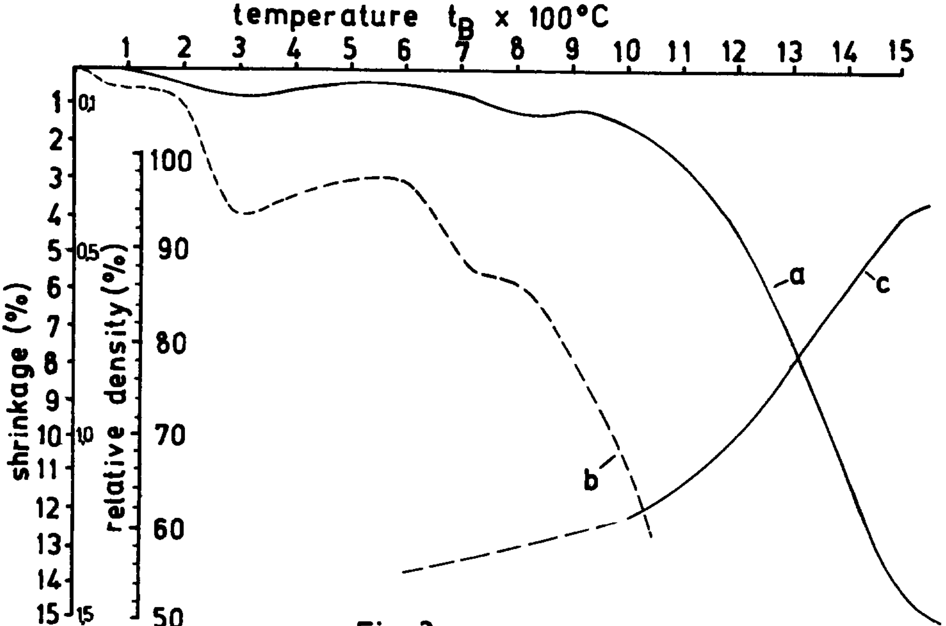

Fig 3