A NOVEL METHOD TO STUDY MELTING OF FRITS AND GLAZES

JÁN MAJLING, ŠTEFAN SVETÍK, VLADIMÍR KREMNIČAN*, JOZEF CHOCHOLOUŠEK**

Department of Ceramics, Glass and Cement,
Faculty of Chemical Technology, Slovak University of Technology,
Radlinského 9, 812 37 Bratislava, Slovak Republic

**Data System Laboratory, s.r.o.,*
Budovateľská 15, 821 08 Bratislava, Slovak Republic

***Technical Glass, a.s.,*
Agátová 22, 844 03 Bratislava, Slovak Republic

Submitted May 5, 1998; accepted November 19, 1998.

A method providing measurement of melting temperature of glaze powder particles is described. The principle of the method is a direct measurement of the light transmittance through a layer of frit powder at a constant heating rate. Examples are given to measure melting temperatures of a commercially produced frit and sodium chloride and sodium phosphate ($NaPO_3$) chemicals, respectively. Specific features of the present measurement method are discussed with respect to the other similar methods.

INTRODUCTION

Ceramic glazes in solid or in liquid state exhibit a set of properties, the most important include their coefficients of thermal expansion, softening and melting temperatures, contact angles at solid surfaces, viscosity and surface tensions [1, 2].

At quality tests a measurement of their melting phenomena including determination of melting temperatures proceeds usually in an indirect way, e.g. by heating of the bulk or powdered glaze frits to specified temperatures followed by their cooling and an ambient temperature microscopy examination.

Hot stage microscopes (Erhitzungmikroskope Leitz Wetzlar, Hochtemperaturmikroskop MHO 2, Carlzeiss, Jena, to mention as examples) seem to be much helpful and preferred instruments for corresponding studies. In spite of their multi-functional design [2,3], the temperature of a first liquid appearance is not a quite sharply determinable parameter when measuring bulk specimens. Glass melting or melting of the polyphase solids is not restricted to a specific temperature but to a temperature interval. Its macroscopic manifestation will depend then on the heating rate of a sample, its shape and quantity, viscosity of the melt, the wettability of the substrate phase, etc.

The other kinds of hot stage microscopes can be applied either only in the low temperature range (up to ca 600 °C) (KSPS 1000, A.Krüss Optronic, FP82HT, Mettler Toledo, or HCS 600 of Instec) not sufficient for melting of glazes, or also at sufficiently high temperatures but on samples (metallic, or ceramic) observed in the reflected light (Mikroskop-Heiztisch 1750, Leitz Wetzlar, or the HSM of CERAM research). In addition, the first appearance of the liquid is not so easily observable. Melting phenomena and liquidus temperatures of systems rendering transparent liquids can be observed also by rarely applied Griffin-Telin hot stage microscope [4].

Gradient temperature furnaces, DTA, DSC, or dilatometric instruments are also appropriate methods for furnishing the additional information on the glaze properties at their Tg temperatures and at temperatures of their melting.

It is believed that a variety of mentioned experimental techniques to study glaze powders can be appropriately complemented by a present method of the specific thermo-optical measurement, consisting in a measurement of changes in the light transmittance of samples with temperature. The mentioned instrument is capable to measure the transmittance changes up to 1200 °C.

EXPERIMENTAL PART

A drop of a glaze powder suspension is deposited on a sapphire transparent thin, small area (diameter12 mm) circular support plate and the liquid medium is left to be evaporated. The support plate with a homogeneous layer of glassy powder particles (height approx. 0.2 mm) is positioned inside the electrical furnace of the thermo-optical instrument (DSL, s.r.o.,) which was basically described in [5]. The sample is illuminated from its upper side by an efficient LED (light emitting diode). The transmitted light is collected by an objective of a camera and fed to a Si photodiode. The temperature control, data acquisition and storing of measured transmittance is made by an icon - based software, which runs under Windows on a PC.

The thermo-optical measurements self were performed using the commercial glaze frit (TS Bratislava, a.s.) and sodium chloride and sodium phosphate compounds (reagent grade chemicals with nominal melting point temperatures 800 and 627 °C).

The dilatometric examination of the frit powder pressed to a cylinder (diameter 5 mm, height 10 mm) was performed using Netsch 402 E equipment at a heating rate 10 °C min^{-1}.

RESULTS AND DISCUSSION

The present results are achieved using an improved version of the instrument primarily designed to study the changes in the optical transmittance of polycrystalline translucent or transparent plates (films) on their thermal treatment [5].

Three different samples were measured in present work for changes in their light transmittance with temperature. One commercial glaze frit and two chemicals were used as test materials. The change in the light transmittance of samples heated at a rate of 20 °C min^{-1} is given in figure 1.

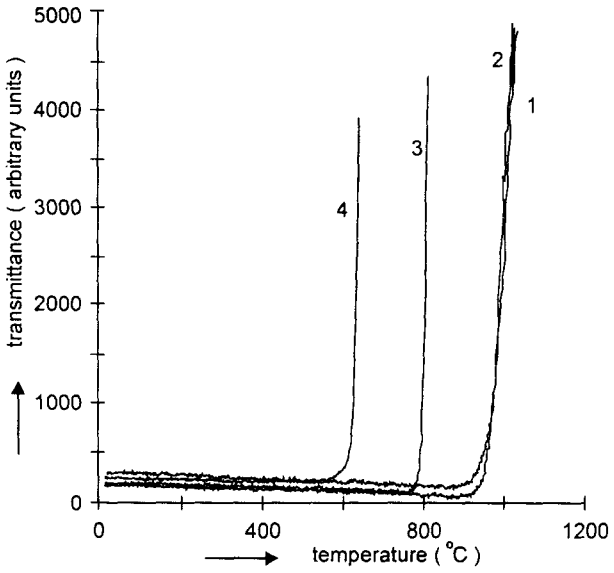

Figure 1. Light transmittance-temperature dependencies.
1, 2 - glaze frit TS; 3 - NaCl; 4 - $NaPO_3$

All samples, in a form of a layer of rather densely packed powder particles, were nearly opaque at the beginning of experiments. The opaqueness of samples was essentially unchanged up to the temperature of a first melt appearance. At this temperature, the optical transmittance was suddenly increased. The curves 1 and 2 imply the reproducibility of measurements.

The vertical parts of curves 3 an 4 indicate the rapid changes of the transmittance inside a narrow temperature interval. The curves 1 and 2 show a slope slightly deviated from the vertical one. This fact is probably attributed to the increase of melt viscosity in comparison with samples 3 and 4 and consequently to slower liberation of bubbles from the liquid phase.

The $NaPO_3$ glass and crystallized NaCl were easily washed away from substrates after experiments, without noticing any kind of the corrosion effects. The glaze powder formed a strongly adhered glassy layer on the sapphire substrate making it inappropriate for the further use.

In figure 2 a comparison is made for an examination of the mentioned glaze frit as performed by the thermo-optical measurement and as performed by the conventional dilatometer. The dilatometric experiment was stopped before a shrinkage of the sample reached 12 %. It is supposed that the glaze glass powder sinters initially by a viscous flow, prior to melt formation, what is reflected by the initial shrinkage of the sample as measured by dilatometer.

In addition the initial increase of the light transmittance is probably also caused by partial sintering of glaze particles due to viscous flow but its strong in-

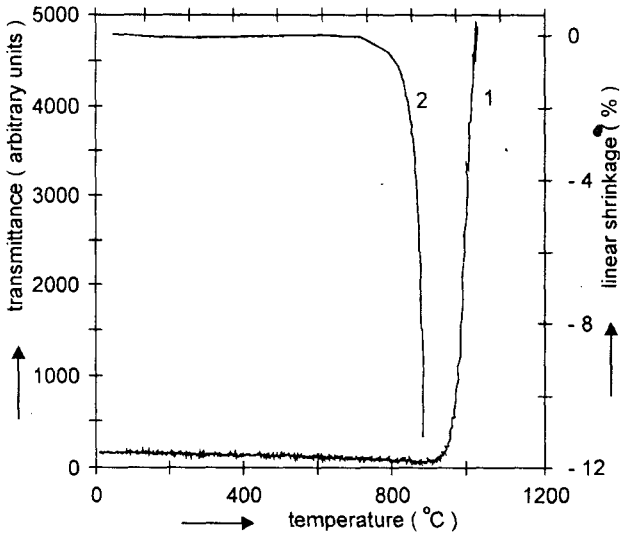

Figure 2. Light transmittance-temperature dependence (1) and the dilatometric measurement (2) for the glaze frit TS.

crease is a consequence of glaze melting. The situation can be different at slow heating rates.

In spite of a limited number of experiments performed it can be concluded that the present experimental technique has a potential to become a useful tool for an investigation of melting behavior of frits and glazes. The planar - layer form of particles at the beginning can be mentioned as more suitable than the bulk sample forms, used by other methods of investigation.

Further experiments are conducted both at slow heating rates and at constant temperature to differentiate the pre-melting period, including sintering of the frit particles and the actual melting period.

CONCLUSION

The measurements of the light transmittance changes vs. temperature were performed by means of a newly built kind of the hot stage microscope suitable for measurements in the temperature range up to 1200 °C. Measurements were made on thin layers of the glaze powder particles and on thin layers of two model chemicals. The method presented is suitable for the determination of the initial melting temperatures of tested compounds as well as of the melting of the glaze powder particles. The present measurements only partially disclosed the potentials of this experimental technique and it is expected that its applications will be growing in future.

References

1. Hlodák P.: *Clays and Glazes in Ceramic Praxis*, Garmond spol. s.r.o., Bratislava 1993. (in Slovak)
2. Burzacchini B., Paganelli M., Christ H.G.: Ceram. Eng. Sci. Proc. *17*, 60 (1996).
3. Chocholoušek J.: Proceedings from 14th Int. Conference on Thermal Analysis, pp.102-104, CHTF STU Bratislava 1997. (in Slovak)
4. Majling J., Hanic F.: J. Solid State Chem. *7*, 370 (1973).
5. Majling J., Svetík Š., Annus J., Krištín J., Marquis P.M.: Chem. Papers *51*, 268 (1997).

Submitted in English by the authors.

NOVÁ METÓDA PRE ŠTÚDIUM TAVENIA FRÍT A GLAZÚR

JÁN MAJLING, ŠTEFAN SVETÍK, VLADIMÍR KREMNIČAN*, JOZEF CHOCHOLOUŠEK**

Katedra keramiky, skla a cementu, Chemickotechnologická fakulta, Slovenská technická univerzita, Radlinského 9, 812 37 Bratislava, Slovenská republika

**Data System Laboratory, s.r.o., Budovateľská 15, 821 08 Bratislava, Slovenská republika*

***Technické sklo, a.s., Agátová 22, 844 03 Bratislava, Slovenská republika*

V úvode práce sa stručne porovnávajú experimentálne metódy dostupné pre vyšetrovanie tavenia keramických frít a glazúr. V práci sa ďalej prezentujú pôvodné merania tavenia práškov technickej glazúry a práškov dvoch ďalších zlúčenín pri ich ohreve, pomocou novej metódy merania zmien optickej priepustnosti. Použitá experimentálna zostava, ktorá bola pôvodne opísaná v práci [5], umožňuje vykonať merania v teplotnom intervale do teploty 1200 °C.

Prášky uvedených látok, deponované v tenkej vrstve na safírovej doštičke, sa ohrievali rýchlosťou 20 °C/min. Zo získaných záznamov sa odčítali teploty počiatkov tavenia práškov a do určitej miery sa posúdil aj charakter (rýchlosť) ich tavenia. Výsledok merania tavenia prášku glazúry pomocou optickej priepustnosti vzorky je porovnaný s dilatometrickým meraním zlisovaného prášku glazúry.

Ná základe získaných predbežných skúseností je možno konštatovať, že uvedená metóda umožnuje pomerne presné meranie teplôt počiatkov topenia uvedených látok.

Dá sa predpokladať, že aplikačné oblasti tejto metódy sa budú postupne rozširovať.