A CALORIMETRIC METHOD FOR DETERMINATION OF HEAT CAPACITY OF CERAMICS FOR CONCENTRATED SOLAR THERMAL SYSTEMS

J. Kalnačs¹, V. Grehovs¹, G. Mežinskis², L. Bidermanis²¹Institute of Physical Energetics,

21 Aizkraukles Str., LV-1006, Riga, LATVIA,

²Institute of Silicate Materials of the Riga Technical University,

1 Kaļķu Str., LV-1658, Riga, LATVIA

e-mail: jkalnacs@edi.lv

Differential scanning calorimetry was carried out to determine the heat capacity (C_p) of the high temperature resistant ceramic materials to be used as protective coatings for stainless steel tubes of parabolic trough solar collectors in concentrated solar power (CSP) systems. The $C_p(T)$ measurements and calculations were performed at continuous scanning in the temperature range 20-800 °C. In the work, calibration curves have been derived for conversion of measuring units from mcV into mW. To achieve a better repeatability of measurements, methods for stabilization of the thermal contact between the sample-containing vessel and the probe have been developed. The $C_p(T)$ dependence was obtained for different ceramic materials.

Keywords: concentrated solar power (CSP) systems, ceramics, enamels, heat capacity, differential scanning calorimetry (DSC).

1. INTRODUCTION

Usually, determination of heat capacity by differential scanning calorimetry (DSC) of ceramics and enamels (applicable as high temperature resistant materials for stainless steel tubes of a parabolic trough solar collector) involves two tests carried out under the same experimental conditions: the first test with two empty vessels (blank), and the second – with one empty vessel and the other containing a sample. The difference between two corresponding signals (proportional to the specific heat of the sample) is converted directly into the heat flow (HF) using the known DSC calibration curve.

In a real measurement practice, deriving the temperature dependence of heat capacity ($C_p(T)$) is a difficult and labour-consuming task, since graduation of an experimental curve needs careful consideration of various factors. In particular, the calibration curves for conversion of HF experimental values in mcV into the energy ones in mW are always unknown, since they depend on the conditions of a particular experiment. This is due to the fact that the values measured in mcV by a differential thermocouple of a DSC probe are determined by the temperature of substance in a vessel (provided there is a constant and reproducible/stable thermal

contact between the vessel and the probe) as well as by the temperature range, heating rate, etc.. However, the thermal contact between the vessel and the probe is not always reproducible and stable.

In this work, a three-test method is proposed: the first test being the same, while for the next two the material-containing vessels are taken: with the sample to be tested and with a reference sample. For the thermal contact stabilization special techniques have been elaborated. Therefore, the aim of this work was to improve the method for DSC heat capacity determination in the cases of ceramics to be used in concentrated solar power (CSP) systems.

2. EXPERIMENTAL

Experimental curves obtained in three tests are shown in Fig.1.

Fig. 1. Heat flow in vessels with sample under test (1), reference sample (2) and without samples (blank) (3), under the same temperature conditions (4).

The calorimetric signals received in the tests are in volts (V). At each temperature T_i the $C_p(T)$ dependence of a sample will be [1]:

$$C_p(T_i) = \frac{HF_{sample}(T_i) - HF_{blank}(T_i)}{HF_{ref}(T_i) - HF_{blank}(T_i)} \cdot \frac{Mass_{ref}}{Mass_{sample}} \cdot C_{p,ref}(T_i) \quad (1)$$

In Eq.(1), $C_{p,ref}(T_i)$ and $C_p(T_i)$ are in $J \cdot kg^{-1} \cdot K^{-1}$, and mass – in kg.

The calorimetric signals from a sample (the reference and the blank) were received under the same conditions. For each point, it was necessary to calculate C_p of the reference material from the coefficients of the known function $C_{p,ref}(T)$. The $C_p(T)$ measurements were taken in the range from 20 to 800° C, under nitrogen flow (20 ml/min) at the heating rate of 10°C/min in a 100 mcl Pt vessel (crucible). As the reference material the Al_2O_3 (99.98%) powder was used. The $C_{p,ref}(T)$ values were calculated by polynomial using the data of NIST Chemistry Web Book [2]. The control of measurements was performed on samples of quartz sand. The measurement data were compared with the calculated by polynomial for SiO_2 [2].

The corresponding calibration curves for the DSC1500 probe are shown in Fig. 2. Initially, their repeatability was rather poor owing to the low reproducibility

of the thermal contact between the crucible and the probe. In our experiments it was found that the thermal contact stabilized after 2-4 times repeated heating to 800°C and after a single heating up to 1200°C.

Fig. 2. Calibration curves (mW/mcV) for DSC1500 probe in experiments with Al_2O_3 powder (nitrogen flow 20 ml/min, heating rate 10°C/min, 100 μl Pt crucible):
 1 – C_p in the units of experimental measurements (mcV·s/mg·°C);
 2 – C_p calculated by polynomial [2] (J/g·°C) for Al_2O_3 ;
 3 – calculated calibration curves (mW/mcV) from four different experiments.

Stabilization of the HF blank curve after heating to 1200°C between any two processes from four different experiments is shown in Fig. 3.

Fig.3. Stabilization of HF (blank) curve after heating to 1200 °C in four steps.

3. RESULTS AND DISCUSSION

After stabilizing the thermal contact between the crucible and the probe good results were obtained in the control experiments at measuring C_p of quartz sand (see example in Fig.4).

Fig.4. Example of deriving C_p (J/g·°C) for SiO_2 (quartz sand):

1 – C_p in J/g·°C; 2 – C_p in J/g·°C (calculated from measurements and calibration curves);
3 – C_p data from [2]; 4 – calibration curve (mW/mcV) calculated for Al_2O_3 .

After thermal contact stabilization, without removing the crucible the test powder was put into it, and two-cycle measurements were taken. During the first heating a partial or complete powder vitrification occurred, and a stable thermal contact with the crucible was set.

The resultant $C_p(T)$ dependence of enamel (ceramic) samples (E3, E19, P100, and P15K45) is shown in Fig.5.

Fig.5. Heat capacity of enamel (ceramic) samples: 1 – E3, 2 – E19, 3 – P100, 4 – P15K45 in absolute units (J/g·K), 5 – sensitivity curve from Al_2O_3 powder measurements and data [2].

In the obtained $C_p(T)$ dependences common features were observed (Fig.5: domains I, II, III). The appearance of peaks (I) at ~ 100 °C and ~ 200 °C is possibly connected with evaporation of the physically and chemically bound water at heating the material. In domain (II) for all samples a span is characteristic where a steep C_p rise is observed on the background of its general increase with temperature. This manifests itself independently of the preliminary heating. At the temperatures 460-500 °C, obviously a transition occurs from a vitrified condition of the ceramics to a rubber-wise. This transition can be characterized by the vitrification temperature T_g and by the heat capacity jump ΔC_p . The values obtained for ceramic (enamel) materials are presented in Fig.5. The appearance of maximum (III) on the curve $C_p(T)$ at the temperature ~ 571 °C is connected with the α - β transition in the quartz particles (arises at heating the quartz sand, see Fig.4) .

4. CONCLUSIONS

1. An improved method of differential scanning calorimetry has been elaborated for measuring the heat capacity of ceramics (enamels) to be used as protective coatings for stainless steel tubes of parabolic trough solar collectors in CSP systems. The $C_p(T)$ measurements and calculations were carried out at continuous scanning in the range 20-800°C.
2. A strong influence of instable thermal contact on the repeatability of measurements has been revealed.
3. The methods for thermal contact stabilization have been developed.
4. The $C_p(T)$ dependence has been obtained for different ceramic (enamel) materials: E3, E19, P100, and P15K45.

ACKNOWLEDGEMENT

We acknowledge the financial support of the European Regional Development Fund in the framework of programme "Development of solar heat absorbing materials by means of sol-gel and vacuum technologies" (Project No 2010/0243/2DP/2.1.1.1.0/10/APIA/VIAA/156).

REFERENCES

1. Akts Engineering AG (2012). *Advanced Kinetics and Technology Solutions*. Programme Package „Calisto”.
2. National Institute of Standards and Technology (NIST) Chemistry Web Book. Standard Reference Database 69.
3. Chraska, T., Hostomsk, J., Klementova, M., & Dubsky, J. (2009). Crystallization kinetics of amorphous alumina–zirconia–silica ceramics. *Journal of the European Ceramic Society*, 29, 3159–3165.
4. Wurth, R., Pascual, M.J., Mather, G.C., Pablos-Martin, A., Munoz, F., Duran, A., Cuello, G.J., & Russel C. (2012). Crystallisation mechanism of a multicomponent lithium alumino-silicate glass. *Materials Chemistry and Physics*, 134, 1001-1006.

SKENĒJOŠĀS KALORIMETRIJAS METODE SILTUMIETILPĪBAS NOTEIKŠANAI SAULES KOLEKTORU KERAMIKĀ

J. Kalnačs, V. Grehovs, G. Mežinskis, L. Bidermanis

Kopsavilkums

Rakstā izklāstīta izstrādātā metodika keramikas un emalju siltumietilpības noteikšanai pēc diferenciālās skenējošās kalorimetrijas mērījumiem. Parādīta virkne traucējošo faktoru kalibrēšanas līknes un mērījumu veikšanai, piedāvātas metodes to samazināšanai vai novēršanai, precīzāku rezultātu ieguvei. Noteikta siltumietilpības atkarība no temperatūras virknei emalju, kas var tikt izmantotas saules siltuma kolektoros, kā aizsargpārklājumi. Parādīta siltumietilpības noteikšanas atkārtojamības atkarība no siltuma kontakta. Izstrādāta metode termiskā kontakta stabilizācijai. Virknei emalju noteikta siltumietilpības atkarība no temperatūras diapazonā 20 - 800°C.

05.10.2013.