J Therm Anal Calorim (2015) 119:191–195
DOI 10.1007/s10973-014-4086-7

A novel method for quantitative phase determination of cristobalite in ceramic cores using differential scanning calorimeter

R. Naghizadeh · F. Kazemi · F. Arianpour · R. Ghaderi · M. Haj Fathalian · M. Taheri · H. R. Rezaie

Received: 30 May 2014 / Accepted: 10 August 2014 / Published online: 4 September 2014

Abstract The present research aims at developing a new quantitative thermal analysis method based on differential scanning calorimeter for determination of cristobalite phase content in ceramic cores. For this purpose, various control samples with different amounts of cristobalite phase were made based on the chemical composition of silica-based ceramic cores and analyzed via differential scanning calorimetry (DSC) technique. The surface area under the $\alpha \rightarrow \beta$ cristobalite transition peak in the DSC curves was calculated via numerical integral of the peaks area, and the ratio of this area to the samples weight (A/W) was calibrated by cristobalite content of the samples. Afterward, for determining the cristobalite content of some industrial samples, the DSC patterns were plotted, and the A/W ratio of these samples was determined by the same method. Then the A/W ratios of the industrial samples were fitted on the calibration line, and the cristobalite content was derived using the equation of the calibration line. The method showed good accuracy, and the error values of the estimated cristobalite content of the industrial samples were below 2 %.

Keywords Cristobalite · Ceramic core · Differential scanning calorimeter · Silica

R. Naghizadeh (✉) · F. Kazemi · F. Arianpour · M. Taheri · H. R. Rezaie
School of Metallurgy and Materials Engineering, Iran University of Science and Technology (IUST), Tehran, Iran
e-mail: rnaghizadeh@iust.ac.ir

R. Ghaderi · M. Haj Fathalian
Researches and Development (R&D), Mapna Turbine Blade Eng. and Man. Company (PARTO), Karaj, Iran

Introduction

In the manufacturing of the superalloy gas turbine, the proper design of internal structures such as cooling passages is very important. Ceramic cores based on fused silica or cristobalite are attractive choices because of their unique properties such as resistance to thermal shock, low creep, chemical compatibility with the molten metal, open porosity (>20 % to facilitate chemical dissolution after casting), and finally near-zero sintering shrinkage in order to retain the highly precise shape and size of the cast part [1]. Since cristobalite content of the ceramic cores could change during sintering, determination of the cristobalite phase content after sintering is a key parameter to control the quality of the cores [2]. Therefore, quantitative analysis of the cristobalite and other polymorphs of silica were developed in several researches using different methods such as X-ray diffraction and differential scanning calorimetry [3, 4]. The transition of $\alpha \rightarrow \beta$ cristobalite phases has been extensively investigated from a structural point of view [5–7]. Hand et al. [8] showed that the smaller particle sizes lead to the formation of cristobalite with lower inversion temperatures, smaller degree of hysteresis, and broader inversion peaks in DSC curves.

Watson et al. [9] described the relationship between the area under the transition peak and the enthalpy of phase transformation of materials. Further researches of Ibrahim et al. [4] developed a method to calculate the phase contents of quartz and cristobalite directly without plotting a calibration line. Although such methods need a calibrated device, Ibrahim et al. measured cristobalite and quartzite phase contents in the samples with unknown phase compositions and did not determine the accuracy level of the method.

Through the recent decade, many studies can be found in the literature focusing on DSC and quantitative analysis

of organic and inorganic materials [10–13]. Since enthalpy of the reactions or transformations was calculated via DSC analysis, the literature was in lack of reliable reports relating the phase content to enthalpy of the reaction or transformation. In the present research, a novel method based on numerical integral calculation of specified samples using DSC patterns is developed, and a calibration line is derived determining cristobalite phase content in silica-based ceramic cores.

Experimental

Raw materials used in this research are presented in Table 1. The powders were prepared according to the formulations mentioned in Table 2 and mixed in PTFE jars using alumina balls and methanol as mixing media for 24 h. The mixtures were dried and sieved to pass from a 325 mesh sieve. The used DSC system was a Pyris 6 system with platinum pans under nitrogen gas flow 20 mL min^{-1}. Two different heating and cooling rates of 0.166 (S_1) and 0.333 (S_2) °C S^{-1} (equal to 10 and 20 °C min^{-1}, respectively) were adjusted in all characterizations. Since the cristobalite transformation peak of some samples, specifically those containing low amount of cristobalite phase, were not very clear during the heating period, the cooling patterns were investigated for all measurements.

Table 1 The specification of the used raw materials

Materials	Purity/mass%	Mean particle size/μm	Source
Fused Silica	>98	75	Remet/UK
Cristobalite	>99	45	Sibelco/Belgium
Alumina	>99.5	4	Pechiney/France
Zircon	>98	1.5	Johnson Matthey Co./Italy

Table 2 Composition of samples

Sample code	Content/mass%			
	Cristobalite	Zircon	Alumina	Fused silica
Calibration samples				
CS1	5	20	5	70
CS2	15	20	5	60
CS3	30	20	5	45
CS4	50	20	5	25
CS5	70	20	5	5
Industrial samples				
IS1	6.5	6.5	3	84
IS2	34.5	10.5	3.5	51.5
IS3	19.5	5.5	6.5	68.5
IS4	44.5	20.5	2.5	32.5
IS5	11	17.5	1.5	70

Results and discussion

Figure 1 shows the DSC patterns of CS1 and CS5 samples in heating and cooling cycles. In order to calibrate the cristobalite content versus surface area under the transformation peak, exact determination of this area is an important point to calculate the cristobalite phase contents of samples. While the cooling patterns of these two samples show a sharp and clear peaks related to cristobalite transition at 220 °C, the heating pattern of CS1 sample shows a wide and weak peak. So the cooling patterns of all samples were selected to do all calibrations and calculations.

Figure 2 shows the DSC cooling patterns of control samples with cooling rate of S_1. By increasing the amount of cristobalite phase in the samples, the transformation peak became sharper. In addition, the transition of α → β occurred from 240 to 260 °C in the heating and from 220 to 240 °C in the cooling period which has been reported also by other researchers [13]. Hill and Roy [14] assigned the inversion temperatures at 267 °C (heating) and 242 °C (cooling) for cristobalite phase. The difference between the cristobalite transition temperature in heating and cooling could be attributed to the temperature differences which are caused by the very small heat transfer rate differences inside the DSC system; so there must be a heat transfer lag between the sample and sensor [15]. Table 3 shows the enthalpy changes (ΔH) calculated for cristobalite inversion in different researches [16–18].

According to the Eq. 1, the surface area under the inversion peak (A) refers to the amount of heat released by the α → β inversion; so the ratio of this area to the sample weight (W) gives the enthalpy (ΔH) of the α → β inversion related to the cristobalite content of sample [10]. In this equation, χ is a constant value which is related to the cell, sensitivity, and time [4] and can be calculated by above information and the enthalpy inversion.

$$\Delta H = \chi \frac{A}{W}. \quad (1)$$

Figure 3 shows the DSC curves of the control samples with cooling rate of S_2. The method of calculating the integral of α → β inversion peak is presented by Eqs. 2 and 3. In addition, a schematic of the integral calculation in graphs is displayed in Fig. 3. By comparing these two cooling rates, it is obvious that the second rate shows the inversion peak more clear than the other one. So, it seems that the integral calculation using the S_2 rate reaches to more accurate values. In addition, Hakvoort et al. [15] reported that by increasing the heating and cooling rates in

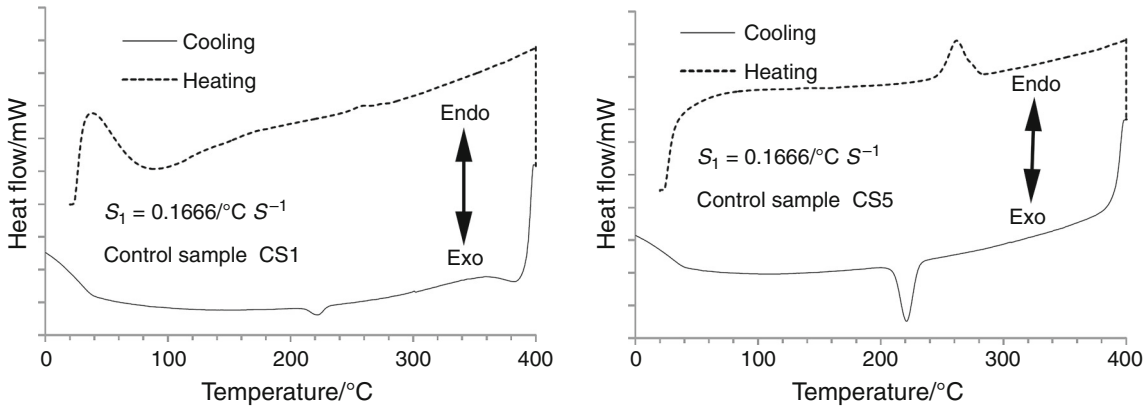

Fig. 1 The DSC heating and cooling patterns of CS1 and CS5 samples

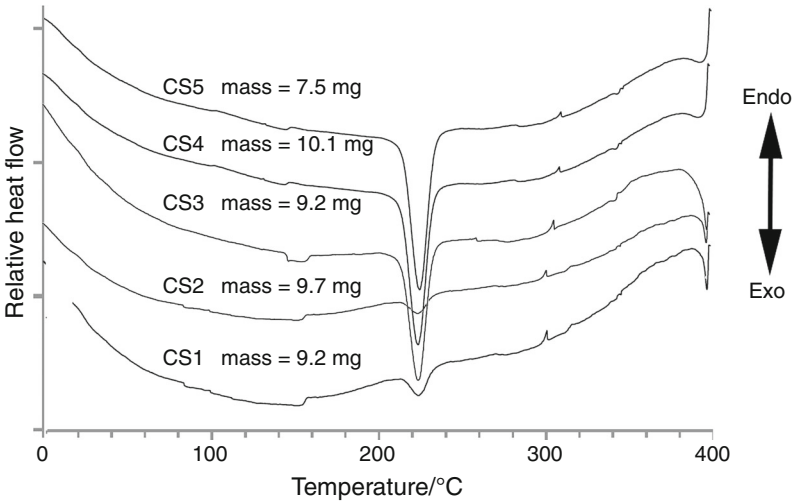

Fig. 2 DSC patterns of control samples with cooling rate of S_1

Table 3 The enthalpy changes in cristobalite inversion

ΔH/J g^{-1}	Source	Year	Reference
18.392	Sabatier	1957	[16]
13.794	Majumdar et al.	1964	[17]
13.376	Lakoday et al.	1956	[18]

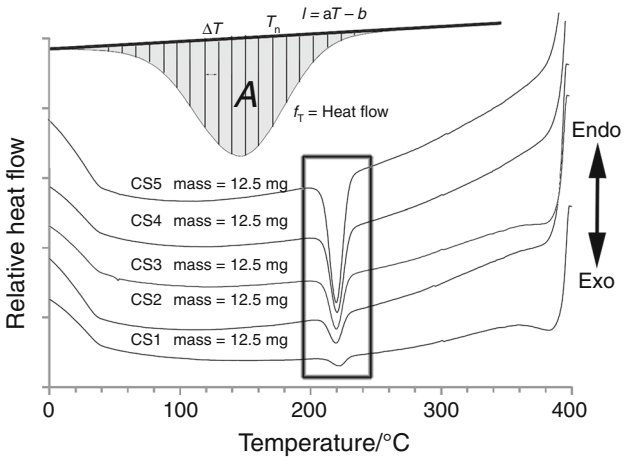

Fig. 3 DSC patterns of control samples with cooling rate of S_2 and a schematic of integral calculation. L is the base line as a function of temperature

differential scanning calorimetry, the calculated enthalpy of the reactions from the DSC curves has better accuracy. Furthermore, by increasing the heating or cooling rate of the samples, the inversion time could be decreased. However, according to Eq. 1, if χ factor decreases, because of the constant amount of ΔH and the equal amount of mass, the A (Area of the inversion peak) will be increased.

In the Eqs. 2 and 3, A is the calculated area of the cristobalite transformation peak, T is temperature, T_1 and T_2 are the starting and finishing temperature of the inversion, ΔT is equal to 0.3333 °C, T_n is the temperature in nth step, l is base line, f_T is heat flow during cooling period as a function of temperature, and finally n_f is the number of steps.

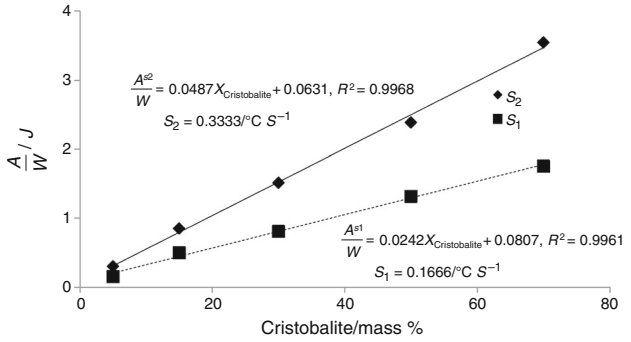

Fig. 4 Calibration lines of control samples based on the cooling rates of S_1 and S_2

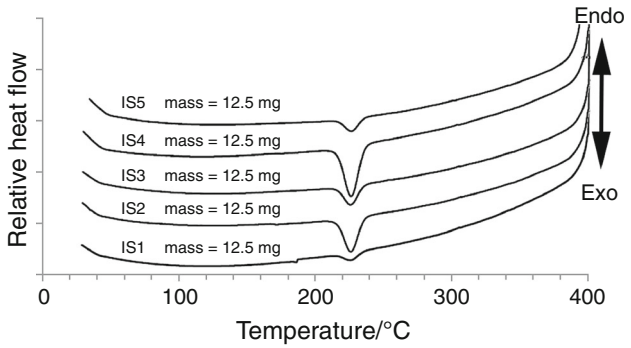

Fig. 5 DSC patterns of industrial samples based on S_2 cooling rate

$$A = \int_{T_1}^{T_2} (l - f_T)\mathrm{d}T, \quad \begin{matrix} l = aT - b \\ f_T = \text{Heat flow} \end{matrix} \tag{2}$$

$$A = \sum_{n=1}^{n=n_f} \left[(l(T_n) - f(T_n))\Delta T\right]_{n_f = \frac{T_2 - T_1}{\Delta T}}^{\Delta T = 0.3333\,^{\circ}\mathrm{C}} \tag{3}$$

According to the cristobalite contents of the control samples, two calibration lines are drawn for both cooling rates in Fig. 4. This figure shows that the A/W ratio is a linear function of cristobalite content of the control samples. In addition, the R^2 value of S_2 cooling rate is closer to 1, which indicates the accuracy of the linear functions. Finally, according to R^2 values of the lines in this study and the other available results in literature [15], the higher cooling rate (S_2) should be selected for quantitative thermal analysis of industrial sample. Figure 5 demonstrates the cooling curves of the industrial samples. Similar to the above procedure, the integral of the transition peak of cristobalite was calculated, and the A/W ratio was extracted from the Eqs. 4 and 5 and demonstrated in Fig. 6.

$$\frac{A^{S_1}}{W} = 0.0242X_{\text{cristobalite}} + 0.0807. \tag{4}$$

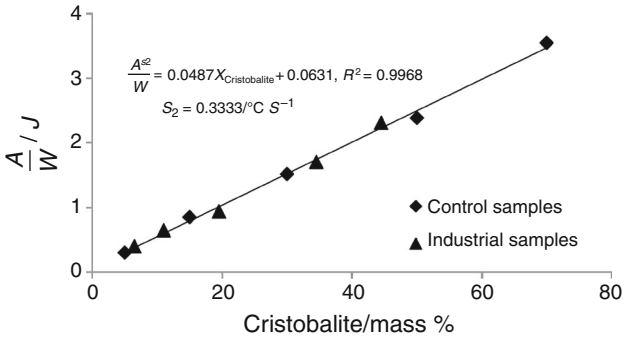

Fig. 6 Calculated A/W values of industrial samples

Table 4 Real and calculated amounts of cristobalite phase in the industrial samples

Samples code	Cristobalite content/mass%	
	Real	Calculated
IS1	6.5	6.89
IS2	34.5	33.65
IS3	19.5	17.94
IS4	44.5	46.13
IS5	11	11.93

$$\frac{A^{S_2}}{W} = 0.0487X_{\text{cristobalite}} + 0.0631. \tag{5}$$

Figure 6 indicates the A/W ratio of the industrial samples (IS1–IS5) extracted from the DSC patterns, and the calculated amounts of cristobalite phase are mentioned in Table 2. This figure shows that the calculated amounts of cristobalite phase in the industrial samples are located exactly on the calibration line, which shows the precision of this procedure. As it can be seen in Table 4, the error values of the estimated cristobalite content of the industrial samples were below 2 %, which demonstrates high accuracy of the procedure.

Conclusions

The cooling DSC patterns show strong, sharp, and clear peaks related to the cristobalite transition in 220 °C while the heating patterns of samples containing low content of cristobalite show weak and wide peaks at higher temperatures near 260 °C. Furthermore, with higher cooling rate of samples, the calibration line has a better accuracy due to the clearness of respective DSC cooling patterns. The calculated cristobalite content of industrial samples fitted exactly on the calibration line extracted from DSC cooling pattern of control samples, which caused novel accuracy in

determination of cristobalite content of industrial samples. The method shows the highly accurate measurement procedure of cristobalite phase in a wide range of cristobalite contents, and its error values is below 2 %.

Acknowledgements The authors gratefully acknowledge the MAPNA Turbine Blade Eng. & Mfg. Co. PARTO, Research and Development Department of MAPNA and PARTO for their funding, and also Mr. H. Alizade for his technical assistant.

References

1. Sachs E, Cima M, Bredt J. Intelligent design and manufacturing for prototyping. ASME PED. 1991;50:61–5.
2. Wereszczak AA, Breder K, Ferber MK, Kirkland TP, Payzant EA, et al. Dimensional changes and creep of silica core ceramics used in investment casting of superalloys. J Mater Sci. 2002;37:4235–45.
3. Kazemi A, Faghihi-Sani MA, Alizadeh HR. Investigation on cristobalite crystallization in silica-based ceramic cores for investment casting. J Eur Ceram Soc. 2013;33:3397–402.
4. Ibrahim DM, Kabish AM, Sallam EH. Quantitative determination of cristobalite by thermal methods. Thermochim Acta. 1981;45:167–76.
5. Welberry TR, Hna GL, Withers RL. An optical transform and monte carlo study of the disorder in β-cristobalite, SiO_2. J Appl Crvsr. 1989;22:87–91.
6. Withers RL, Thompson JG, Welberry TR. The structure and microstructure of α-cristobalite and its relationship to β-cristobalite. Phys Chem Min. 1989;16:517–22.
7. Hatch DM, Ghose S. The α-β phase transition in cristobalite, SiO_2. Phys Chem Min. 1991;17:554–62.
8. Hand RJ, Stevens SJ, Sharp JH. Characterisation of fired silicas. Thermochim Acta. 1998;318:115–23.
9. Watson ES, O'Neill MJ, Justin J, Brenner N. A differential scanning calorimeter for quantitative differential thermal analysis. Anal Chem. 1964;36:7–13.
10. Sajadi SA, Khaleghian M. Study of thermal behavior of CrO3 using TG and DSC. J Therm Anal Calorim. 2014;116:915–21.
11. Maggio RM, Barnaba C, Cerretani L, Paciulli M, Chiavaro E. Study of the influence of triacylglycerol composition on DSC cooling curves of extra virgin olive oil by chemo-metric data processing. J Therm Anal Calorim. 2014;115:2037–44.
12. Barrena MI, Gómez de Salazar JM, Pascual L, Soria A. Determination of the kinetic parameters in magnesium alloy using TEM and DSC techniques. J Therm Anal Calorim. 2013;113:713–20.
13. Finnie KS, Thompson G, Withers RL. Phase transitions in cristobalite and related structures studied by variable temperature infer-red emission spectroscopy. J Phys Chm Solids. 1994;55:23–9.
14. Hill VG, Roy R. Silica structure studies VI on tridymites. Trans Br Ceram Soc. 1958;57:496–502.
15. Hakvoort G, Hol CM. DSC investigation of some testing and calibration compounds, particularly during cooling. J of Therm Anal Calorim. 1998;52:195–202.
16. Sabatier G. Heats of transition forms, low temperature to high temperature forms of quartz, tridymite, and cristobalite. Bull Soc Fr Miner Crystallogr. 1957;80:444–50.
17. Majumdar AJ, McKinstrey HA, Roy R. Thermodynamic parameters for the α-β quartz and α-β cristobalite transitions. J Phys Chem Solids. 1964;25:1487–93.
18. Lakoday P, Eyraud C, Prettre M, Hebd CR. A contribution to the study of some polymorphic transformations of silica. Seances, Acad Sci. 1956;242:3071–77.