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Thermochimica Acta 302 (1997) 189–193

thermochimica acta

Determination of the heat capacity, enthalpy and entropy of crystallisation of ternary eutectic melt in the system $3CaO.2SiO_2(C_3S_2)$-$CaO.SiO_2(CS)$-$2CaO.Al_2O_3.SiO_2(C_2AS)$

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Received 14 February 1997; received in revised form 18 February 1997; accepted 30 May 1997

Abstract

Inverse drop calorimetry performed in a SETARAM HTC 1800 K was used to measure the values of relative enthalpy of the ternary eutectic melt in the system C_3S_2-CS-C_2AS in the temperature interval 1653–1773 K with regard to the reference state of a mechanical mixture of γ-C_2S, CS, and C_2AS crystals of corresponding composition at 298 K. The linear temperature dependence of specific relative enthalpy and the temperature-independent value of specific heat capacity of the eutectic melt (eut.melt)

$$c_p(\text{eut.melt})/(\text{J g}^{-1}\ \text{K}^{-1}) = 1.760 \pm 0.089$$

were determined from measured data.

The specific enthalpy of crystallisation of eutectic melt at 1583 K

$$\Delta_{\text{cryst}}h(\text{eut.melt}; 1583\ \text{K}) = (-324.6 \pm 14.4)\text{J g}^{-1}$$

was calculated using specific relative enthalpy of eutectic melt at 1583 K determined experimentally, enthalpies of formation of C_3S_2, γ-C_2S and CS at 298 K, and enthalpy increases on heating of C_3S_2, CS, and C_2AS from 298 to 1583 K taken from literature. The material balance of the process was also used. The value of specific enthalpy of crystallisation of eutectic melt at 1583 K represents about 25% of the heat released on subsequent cooling of the separated crystals of C_3S_2, CS, and C_2AS from 1583 to 298 K. © 1997 Elsevier Science B.V.

Keywords: Heat capacity; Heat of crystallisation; High-temperature calorimeter; System C_3S_2-CS-C_2AS

1. Introduction

Study of the thermodynamic properties of oxide systems is important for appreciating the energetical effectivity of basic production processes of some inorganic oxidic materials. Thermodynamic quantities of components and phases of the systems are substantial for describing the equilibrium relations between liquids and crystals and the modelling their pressure, temperature and composition dependences. Study of geochemical and geophysical processes is also improved by new data for databases of thermodynamic quantities.

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PII S0040-6031(97)00219-0

The system C_3S_2-CS-C_2AS is part of the system CaO(C)-Al_2O_3(A)-SiO_2(S) which is important for the production of cement, glass and the formation of slags. In the following text symbols C, A and S will be used for oxides CaO, Al_2O_3 and SiO_2, respectively. As a consequence of the existence of incongruently melting rankinite (C_3S_2) in the system C_3S_2-CS-C_2AS beside eutectic points also two peritectic points are present in this system [1]. From a thermodynamic point of view only properties of the binary subsystem CS-C_2AS are well known [2]. Enthalpies of fusion of pseudo-wollastonite (CS) [3,4] and gehlenite (C_2AS) [5], and enthalpy of crystallisation of the eutectic melt in the system CS-C_2AS [6] are known. Relative enthalpies of melts in the system CS-C_2AS were determined in enthalpic analysis of the ternary system CS-CAS_2-C_2AS [7]. The aim of the present work is to determine the heat capacity, enthalpy and entropy of crystallisation of the ternary eutectic melt in the system C_3S_2-CS-C_2AS at the eutectic temperature of 1583 K using an indirect calorimetric method.

When using the indirect calorimetric method for the determination of the enthalpy change at phase conversions and chemical reactions in the silicate systems, it is necessary to known the values of the relative enthalpies (h_{rel}) of the phases and the components of the system, respectively. The values of the relative enthalpies of the glass-forming silicate melts are obtained by a combination of measurements in the high-temperature drop calorimeter and in the solution calorimeter (e.g. by the double calorimetry method for the same sample [8]) or, in some cases, by the inverse drop calorimetry. Inverse drop calorimetry performed in a SETARAM HT 1500 calorimeter was used, for example, by Ziegler and Navrotsky [9] to measure the enthalpy of fusion of diopside ($CaO.MgO.2SiO_2$). Using this method Navrotsky et al.[10] and Tarina et al.[4] have measured relative enthalpies of melts formed from two- and three-phase mixtures of minerals at 1500°C, respectively. They have utilised the measured data to determine enthalpies of the mixing of melts and enthalpies of fusion of forsterite and pseudo-wollastonite. Applying their experience we also used inverse drop calorimetry to measure relative enthalpies of ternary eutectic melt in the system C_3S_2-CS-C_2AS, related to the reference state of the mixture of crystalline phases γ-C_2S, CS and C_2AS at 298 K.

2. Experimental

2.1. Sample preparation

From the ternary eutectic melt composed of oxides expressed in mass fractions $w(C) = 0.4738$; $w(A) = 0.1182$ and $w(S) = 0.408$ [1], the mixture of the minerals C_3S_2, CS, and C_2AS in the mass fraction ratio 0.1439 : 0.5382 : 0.3179 crystallizes at eutectic temperature. For measurement of relative enthalpies of the eutectic melt in the mixture of minerals using rankinite was replaced by an equimolar mixture of γ-C_2S and CS. This procedure was chosen with regard to better reliability of preparing γ-C_2S and CS against C_3S_2.

Pseudo-wollastonite and gehlenite have been prepared by the precursor method [11]. As starting components $CaCO_3$ (Specpure JMC), metallic Al ($w(Al) = 99.999$, Research Institute of Metals, Panenské Břežany, Czech Republic) and sol of silicic acid were used. The sol of silicic acid was prepared from commercial water glass using the ion exchanger DOWEX 50W × 8 and was stabilised by the addition of ammonia [5].

By heating the dry rests of aqueous solutions prepared from citric acid and weighed – in amounts of sol of silicic acid and $Ca(NO_3)_2$ and $Al(NO_3)_3$ salts (corresponding to the desired composition of pseudo-wollastonite or gehlenite) at 500–600°C homogeneous mixtures of oxides were obtained.

The oxide mixture for pseudo-wollastonite was heated (4 h) at 1000°C and after that at 1300°C for 4 h [12]. When preparing gehlenite the oxide mixture was heated for 8 h at 1300°C and subsequently for 8 h at 1400°C. The purity of both samples and also that of γ-C_2S (OZKC, Podolsk, Russia) was verified by X-ray diffraction analysis.

The mechanical mixture of γ-C_2S, CS, and C_2AS (1 g), suspended in toluene, was homogenized by stirring for 4 h. After drying at 60°C cylindrical pellets with 4 mm diameter and about 2 mm height (approximately 50 mg) were pressed from the mixture and used for calorimetric measurements.

To control complete melting of dropped pellets the conditions of melting have been simulated outside the calorimeter. $Pt_{90}Rh_{10}$ crucibles with pellets of samples were put into the furnace and heated to the respective calorimeter temperature for 15 min. This time was chosen because a typical calorimetric peak is finished in 8–10 min. Then the samples were rapidly cooled in liquid nitrogen. Subsequent X-ray analysis showed that samples heated at 1500 and 1400°C had melted completely (no crystalline phase was found in rapidly cooled samples). However, in samples cooled from 1350°C crystalline phase was present. It was not possible to distinguish if the crystallisation occurred during cooling or if the samples had not been completely melted before cooling. With regard to the results of these preliminary experiments the relative enthalpies of eutectic melt have been measured at six temperatures in the range 1380–1500°C.

2.2. Apparatus

Relative enthalpies of eutectic melts at temperatures above the crystallisation temperature have been measured by inverse drop calorimetry performed in a SETARAM HTC 1800 K. In this calorimeter the temperature difference between two crucibles is measured. The crucibles were placed one above the other in the calorimetric cell which is located in a vertical calorimetric furnace heated at constant temperature. The sintered alumina crucibles are lined by $Pt_{90}Rh_{10}$ crucibles. The lower (reference) crucible contains small pieces of sintered alumina.

Sample and calibration substance are dropped alternating into the upper crucible using the special equipment of the calorimeter. The temperature difference between the middle parts of the crucibles is measured by a set of 18 thermocouples connected in series. It is recorded along with the temperature at constant time intervals. From the measured data (the data treatment was described in Ref. [13]) the area below the curve is calculated, which is proportional to the heat flow between the crucibles.

As calibration substance we used Pt cylindrical bodies with 4 mm diameter, 1 mm of height and around 400 mg weight. The heat capacity of Pt was taken from Ref. [14]. Using the calibration substance the calibration factor is determined. Individual average calibration factor was used for each one-day series of measurements. Most values of relative enthalpies of the eutectic melt have been obtained from the dropping of three samples and two calibration bodies during one day in an isothermal experiment.

Some valuable practical experiences concerning the use of a high-temperature SETARAM calorimeter are given by Ziegler and Navrotsky [9].

3. Results and discussion

Evaluating measurements of several series for each temperature the values of arithmetic means of relative enthalpies of eutectic melt ($h_{\mathrm{rel},\Phi}(\mathrm{eut.melt})$) have been obtained. These data along with doubled values of the error of the arithmetic means ($2\sigma_{\Phi}(h_{\mathrm{rel},\Phi}(\mathrm{eut.melt}))$) and the number of measurements (n) are given in Table 1.

The scattering of measured data may have several reasons. In the small samples the ratio of phases may not be kept correctly. However, the relatively large number of the measurements at each temperature by which most of the prepared mixture is used should compensate this influence. Another reason for the scattering may be a certain instability of the base line of measured curves for time dependence of temperature difference between calorimetric crucibles.

The measured data were fitted by a straight line, given in Eq. (1), using the method of weighted least squares

$$\frac{h_{\mathrm{rel}}(\mathrm{eut.melt})}{\mathrm{J\,g^{-1}}} = (-1146.8 \pm 151.9) + (1.760 \pm 0.089)\frac{T}{\mathrm{K}}$$

Standard deviations of the relative enthalpies were calculated from

$$\sigma(h_{\mathrm{rel}}) = (\mathrm{var}(b)T^2 + 2T\mathrm{cov}(a,b) + \mathrm{var}(a))^{1/2} \quad (2)$$

Table 1
Values of arithmetic means of relative enthalpy of eutectic melt, two-fold values of error of arithmetic means and corresponding number of measurements of relative enthalpy

$\frac{T}{\mathrm{K}}$	$\frac{h_{\mathrm{rel},\Phi}(\mathrm{eut.melt})}{\mathrm{J\,g^{-1}}}$	$\frac{2\sigma_{\Phi}(h_{\mathrm{rel},\Phi}(\mathrm{eut.melt}))}{\mathrm{J\,g^{-1}}}$	n
1653	1759	23	11
1675	1804	21	12
1701	1854	35	8
1722	1888	26	11
1748	1917	27	8
1773	1983	28	11

and are smaller than 7 J g^{-1}. The covariance of coefficients of Eq. (1) is (−13.514).

The value of the specific relative enthalpy of the eutectic melt obtained by extrapolation of these quantities from Eq. (1) to the temperature of crystallisation of 1583 K is

$$h_{\mathrm{rel,calc}}(\mathrm{eut.melt};\,1583\ \mathrm{K})(1639.3 \pm 11.7)\,\mathrm{J\,g^{-1}} \qquad (3)$$

Differentiating Eq. (1) with regard to temperature the specific heat capacity of eutectic melt is

$$C_p(\mathrm{eut.melt})/(\mathrm{J\,g^{-1}\ K^{-1}}) = 1.760 \pm 0.089 \qquad (4)$$

With regard to the reference state of the mixture of crystalline phases γ-C_2S, CS, and C_2AS at 298 K, the relative enthalpy of eutectic melt at temperature T can be expressed as follows

$$\begin{aligned} &h_{\mathrm{rel}}(\mathrm{eut.melt};\,T)\\ &= 0.1439\Delta_f h(\mathrm{C_3S_2};\,298\ \mathrm{K})\\ &\quad - 0.0859\Delta_f h(\gamma - \mathrm{C_2S};\,298\ \mathrm{K})\\ &\quad - 0.0580\Delta_f h(\mathrm{CS};\,298\ \mathrm{K})\\ &\quad + 0.1439\Delta_{\mathrm{heat}} h(\mathrm{C_3S_2};\,298\ \mathrm{K} \to 1583\ \mathrm{K})\\ &\quad + 0.5382\Delta_{\mathrm{heat}} h(\mathrm{CS};\,298\ \mathrm{K} \to 1583\ \mathrm{K})\\ &\quad + 0.3179\Delta_{\mathrm{heat}} h(\mathrm{C_2AS};\,298\ \mathrm{K} \to 1583\ \mathrm{K})\\ &\quad + (-\Delta_{\mathrm{cryst}} h(\mathrm{eut.melt};\,1583\ \mathrm{K}))\\ &\quad + \int_{1583\ \mathrm{K}}^{T} c_p(\mathrm{eut.melt};\,T)\mathrm{d}T \qquad (5) \end{aligned}$$

where $\Delta_f h(\mathrm{X};\,298\ \mathrm{K})$ is the specific enthalpy of formation of phase X at 298 K ($\mathrm{X} \equiv \mathrm{C_3S_2};\ \gamma - \mathrm{C_2S};\ \mathrm{CS}$)$\Delta_{\mathrm{heat}}\mathrm{h}(\mathrm{Y};\,298\ \mathrm{K} \to 1583\ \mathrm{K})$ is the specific enthalpy increase on heating of phase Y from 298 K to 1583 K ($\mathrm{Y} \equiv \mathrm{C_3S_2};\ \mathrm{CS},\ \mathrm{C_2AS}$) $\Delta_{\mathrm{cryst}} h(\mathrm{eut.melt};\,1583\,\mathrm{K})$ is the specific enthalpy of crystallisation of the eutectic melt at the eutectic temperature of 1583 K.

From the relative enthalpy of the eutectic melt at 1583 K, the specific enthalpies of formation of C_3S_2, CS, and γ-C_2S at 298 K, tabulated in Ref. [15] and the specific enthalpy increases on heating of rankinite, pseudo-wollastonite and gehlenite from 298 K to 1583 K [16], the specific enthalpy of crystallisation of eutectic melt at 1583 K was obtained

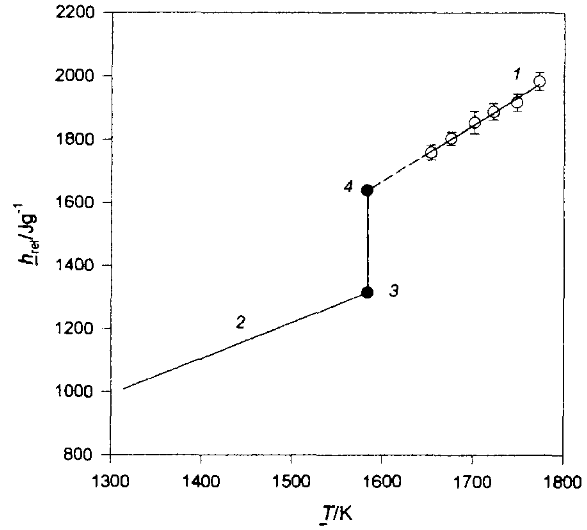

Fig. 1. Temperature dependences of $h_{\mathrm{rel}}(\mathrm{eut.melt};\,T)$ (line l) and $h_{\mathrm{rel}}(\mathrm{cryst.prod};\,T)$ (line 2). The enthalpy of crystallisation is given by the difference of relative enthalpies for points 3 and 4.

$$\Delta_{\mathrm{cryst}} h(\mathrm{eut.melt};\,1583\ \mathrm{K}) = (-324.6 \pm 14.4)\,\mathrm{J\,g^{-1}} \qquad (6)$$

The error of the relative enthalpy of eutectic melt was calculated using Gauss' law of spreading of errors and an estimated relative error of $\Delta_{\mathrm{heat}} h(\mathrm{Y};\,298\ \mathrm{K} \to 1583\,\mathrm{K})$ of 1%, neglecting errors of determination of specific enthalpies of formation.

The relative enthalpies of the eutectic melt are plotted in Fig. 1. The bars represent two-fold values of the errors. The temperature dependences of the relative enthalpy of eutectic melt and of the mixture of its crystallisation products ($h_{\mathrm{rel}}(\mathrm{cryst.prod.};\,T)$) are also displayed in Fig. 1.

The specific entropy of crystallisation is

$$\begin{aligned} &\Delta_{\mathrm{cryst}} s(\mathrm{eut.melt};\,1583\,\mathrm{K})\\ &= (0.205 \pm 0.009)\,\mathrm{J\,g^{-1}\,K^{-1}} \qquad (7) \end{aligned}$$

Using Eq. (5) 'the enthalpy of total crystallisation of eutectic melt' ($\Delta_{\mathrm{cryst},\Sigma} h$) can also be calculated. This quantity represents the sum of equilibrium crystallisation enthalpy of eutectic melt and of the heat effect by cooling of crystallisation products from 1583 to 298 K

$$\Delta_{\mathrm{cryst},\Sigma}h(\mathrm{eut.melt};\ 1583\,\mathrm{K} \rightarrow 298\,\mathrm{K}) = (-1648.0 \pm 14.4)\,\mathrm{J\,g^{-1}} \qquad (8)$$

The equilibrium crystallisation enthalpy represents around 20% of 'the enthalpy of total crystallisation of eutectic melt.' Thus 4/5 of 'the enthalpy of total crystallisation of eutectic melt' is released by the cooling of the eutectic mixture of rankinite, pseudowollastonite and gehlenite from 1583 to 298 K.

Acknowledgements

The work was financially supported by the Scientific Grant Agency of the Ministry of Education and Slovak Academy of Sciences; Grant No. 2/1170/96.

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