Determination of the enthalpy of crystallization of ternary eutectic melt in the system 2CaO · Al₂O₃ · SiO₂—CaO · Al₂O₃ · · 2SiO₂—CaO · SiO₂

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Using a precursor method the ternary eutectic melt of the system $2CaO \cdot Al_2O_3 \cdot SiO_2$—$CaO \cdot Al_2O_3 \cdot 2SiO_2$—$CaO \cdot SiO_2$ (composition 38.0 mass % CaO, 20.1 mass % Al_2O_3, 41.9 mass % SiO_2) and wollastonite ($CaO \cdot SiO_2$) were prepared. Besides wollastonite, gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) and anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) crystallize from the eutectic melt at equilibrium temperature of 1538 K.

Using a drop calorimeter the values of change in enthalpy at cooling of the eutectic melt were determined. The values of heat of dissolution of wollastonite and products of cooled eutectic melt were measured in a solution calorimeter. On the basis of these data and tabulated data on the temperature dependence of heat capacity of wollastonite dependences of the specific relative enthalpy of the eutectic melt and wollastonite on temperature were obtained. The temperature dependences of the specific relative enthalpy of gehlenite and anorthite were taken from paper [5].

On the basis of material balance of crystallization of the ternary eutectic melt and the values of the specific relative enthalpy of the above-mentioned phases at the temperature of 1538 K the specific enthalpy of crystallization of the eutectic melt was determined

$$\Delta h_{cryst}(\text{eut. melt}; 1538 \text{ K}) = (-308 \pm 20) \text{ kJ kg}^{-1}$$

The error of this quantity was determined at the significance level of 95 %.

С помощью метода прекурсора был получен тройной эвтектический расплав системы $2CaO \cdot Al_2O_3 \cdot SiO_2$—$CaO \cdot Al_2O_3 \cdot 2SiO_2$—$CaO \cdot$ · SiO_2 (состав: 38 масс. % CaO; 20,1 масс. % Al_2O_3; 41,9 масс. % SiO_2) и волластонит ($CaO \cdot SiO_2$), который наряду с геленитом ($2CaO \cdot Al_2O_3 \cdot$ · SiO_2) и анортитом ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) является продуктом его кристаллизации при равновесной температуре 1538 К.

Измерены величины изменения энтальпии при охлаждении эвтектического расплава (в капельном калориметре), значения теплоты растворения волластонита и продуктов охлаждения эвтектического расплава (в калориметре для определения теплот растворения). На основании этих величин и табличных данных по температурной зависимости тепловой емкости волластонита были определены тем-

пературные зависимости удельной относительной энтальпии эвтектического расплава и волластонита. Температурные зависимости удельной относительной энтальпии геленита и анортита были взяты из работы [5].
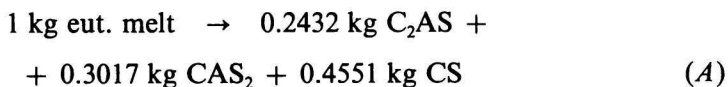
На основании материального баланса кристаллизации тройного эвтектического расплава и величин удельной относительной энтальпии эвтектического расплава, волластонита, геленита и анортита при температуре 1538 K было определено значение удельной энтальпии кристаллизации эвтектического расплава

$$\Delta h_{cryst}(\text{eut. melt; } 1538 \text{ K}) = (-308 \pm 20) \text{ кДж кг}^{-1}$$

Ошибка в определении этой величины была установлена на уровне значимости 95 %.

In the ternary system $2CaO \cdot Al_2O_3 \cdot SiO_2$ (C_2AS)—$CaO \cdot Al_2O_3 \cdot 2SiO_2$ (CAS_2)—$CaO \cdot SiO_2$ (CS) (C, A, and S are the symbols for CaO, Al_2O_3, and SiO_2, respectively) three binary and one ternary eutectic points exist [1]. The aim of this work is to determine the enthalpy and entropy of crystallization of the eutectic mixture composed of gehlenite (C_2AS), anorthite (CAS_2), and wollastonite (CS) at the equilibrium temperature of 1265 °C [1] and the total heat of crystallization of the ternary eutectic melt. The latter quantity consists of the heat of crystallization of the eutectic melt at the equilibrium temperature and the heat liberated at cooling the solid eutectic mixture from the temperature of 1265 °C to 25 °C. Composition of the eutectic mixture was determined to be 38.0 mass % CaO, 20.1 mass % Al_2O_3, 41.9 mass % SiO_2. Determination of the values of these quantities is a contribution to the enthalpic analysis of the system CaO—Al_2O_3—SiO_2 which is important in production of cement, glass, and slags.

For determination of the enthalpy of crystallization of the ternary eutectic melt in the system C_2AS—CAS_2—CS at the equilibrium temperature $T_{eq} = 1538$ K (1265 °C) an undirect calorimetric method was used. This method consists in determination of the values of relative enthalpy of all phases taking part in the process of crystallization at 1538 K related to the same reference state. The material balance of the process, *i.e.* masses of C_2AS, CAS_2, and CS which crystallize from 1 kg of the eutectic melt (eut. melt), was determined from the analysis of CaO, Al_2O_3, and SiO_2 in C_2AS, CAS_2, CS and in the eutectic melt. The following reaction scheme was obtained

$$1 \text{ kg eut. melt} \quad \rightarrow \quad 0.2432 \text{ kg } C_2AS +$$
$$+ \ 0.3017 \text{ kg } CAS_2 + 0.4551 \text{ kg CS} \tag{A}$$

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Thus the specific enthalpy of crystallization of the eutectic melt at $T_{eq} = 1538$ K (Δh_{cryst}(eut. melt; 1538 K)) can be determined from the Hess law

$$\frac{\Delta h_{cryst}(\text{eut. melt; 1538 K})}{\text{kJ kg}^{-1}} = 0.2432 \frac{h_{rel}(C_2AS; 1538 \text{ K})}{\text{kJ kg}^{-1}} +$$

$$+ 0.3017 \frac{h_{rel}(CAS_2; 1538 \text{ K})}{\text{kJ kg}^{-1}} + 0.4551 \frac{h_{rel}(CS; 1538 \text{ K})}{\text{kJ kg}^{-1}} -$$

$$- 1 \frac{h_{rel}(\text{eut. melt; 1538 K})}{\text{kJ kg}^{-1}} \tag{1}$$

The values of the specific relative enthalpy (h_{rel}) of eut. melt, C_2AS, CAS_2, and CS at 1538 K were calculated from the temperature dependences of h_{rel} of these phases. For the method used in this work the specific relative enthalpy of corresponding phase at given temperature equals the negative sum of the specific changes in enthalpy at cooling the phase from chosen temperature to the temperature of 298 K (Δh_{cool}) and the heat of dissolution of this phase at 298 K in suitable solving mixture (Δh_{sol}) [2, 3].

$$h_{rel} = - (\Delta h_{cool} + \Delta h_{sol}) \tag{2}$$

Temperature dependence of the specific relative enthalpy of the eutectic melt was obtained from the values of h_{rel}(eut. melt) determined from measured values of Δh_{cool}(eut. melt) and measured values of the specific heat of dissolution of products of cooled eutectic melt (Δh_{sol}(eut. melt)). For determination of the temperature dependence of the specific relative enthalpy of CS the temperature dependence of Δh_{cool}(CS) (determined on the basis of [4]) and measured values of Δh_{sol}(CS) were used. Temperature dependences of h_{rel} for C_2AS and CAS_2 were taken from paper [5]. This was possible because the heats of dissolution of CS and products of cooled eutectic melt were measured in the same solvent mixture as the heats of dissolution of C_2AS and CAS_2. Eqn (1) is used also for estimation of the error in determination of the specific enthalpy of crystallization of the eutectic melt $\delta(\Delta h_{cryst}$(eut. melt; 1538 K)). This error was calculated from the errors in determination of the specific relative enthalpies of corresponding phases ($\delta(h_{rel}(X; 1538 \text{ K}))$) taking part in the crystallization process at equilibrium temperature using the "Gauss law of spreading of errors"

$$\delta(\Delta h_{cryst}(\text{eut. melt})) = \sqrt{\sum_X [w(X) \cdot \delta(h_{rel}(X))]^2} \tag{3}$$

where $w(X)$ is the mass fraction of corresponding phase (X) in eqn (1).

Experimental

Preparation of samples

The ternary eutectic melt of the system C_2AS—CAS_2—CS and wollastonite were prepared by a precursor method similar to that described in [6]. The following reagents were used: $CaCO_3$ (Specpure, JMC), metal Al ($w(Al) = 99.999$ %) (The Research Institute of Metals, Panenské Břežany) and sol of silica acid which was prepared from commercially available water glass using the ion exchanger DOWEX 50 W × 8 [7]. By heating the dry rests of aqueous solutions prepared from organic substance and weighed--in amounts of salts (the composition corresponded to the desired composition of the eutectic mixture or wollastonite) at 500—600 °C precursors, *i.e.* the homogeneous mixtures of oxides CaO, Al_2O_3, and SiO_2 were obtained. In the case of the eutectic mixture, precursor was first heated at *ca.* 1000 °C for 4 h, then sealed into a crucible made of Pt Rh10 alloy and heated again at 1500 °C for 4 h. Finally the sample was quenched in liquid nitrogen. Wollastonite was prepared by heating the precursor of composition corresponding to CS at 1000 °C and then at the temperature of 1300 °C for 4 h. Purity of the product was checked by X-ray diffraction analysis.

Apparatus

Changes in enthalpy at cooling of the eutectic melt from chosen temperatures to 298 K were measured in the drop calorimeter which has been described in [8]. Heats of dissolution of wollastonite and products of cooled eutectic melt were measured at 298 K in the solution calorimeter [9]. Heats of dissolution of all samples were measured in dissolving mixture prepared by mixing aqueous solutions of hydrofluoric acid ($w(HF) = 40$ %) and hydrochloric acid (1 volume part of HCl ($w(HCl) = 35$—38 %) and 1 volume part of H_2O) in the volume ratio 2 : 1. The solvent mixture was saturated with CaF_2 by adding 150 mg of $CaCO_3$ to 1 dm^3 of this mixture. In result of that Ca^{2+} ions were quantitatively precipitated from the dissolved sample.

Results

Determination of the temperature dependence of the specific relative enthalpy of the eutectic melt ($h_{rel.\varphi}$(eut. melt; T))

Using the drop calorimeter the values of specific change in enthalpy at cooling of five samples of eutectic melt from the temperatures chosen in the interval 1583 K—1807 K to 298 K were measured. Obtained values of Δh_{cool}(eut. melt) are presented in Table 1.

The products of cooling of each sample of the eutectic melt were investigated by X-ray diffraction analysis. Despite of finding no crystallic phases in the

Table 1

Experimental values $(-\Delta h_{cool})$, $(-\Delta h_{sol,\varphi})$, and h_{rel} of the eutectic melt and the calculated values of $h_{rel,\varphi}$(eut. melt) at different temperatures chosen from the range $\langle$ 1583 K; 1807 K $\rangle$

$\dfrac{T}{K}$	$\dfrac{-\Delta h_{cool}\text{(eut. melt)}}{\text{kJ kg}^{-1}}$	$\dfrac{-\Delta h_{sol,\varphi}\text{(eut. melt)}}{\text{kJ kg}^{-1}}$	$\dfrac{h_{rel}\text{(eut. melt)}}{\text{kJ kg}^{-1}}$	$\dfrac{h_{rel,\varphi}\text{(eut. melt)}}{\text{kJ kg}^{-1}}$
1583	1514	2982	4496	4499
1615	1563	2983	4546	4548
1680	1653	3011	4664	4648
1742	1747	2983	4730	4743
1807	1846	3000	4846	4843

samples heats of dissolution of all these samples were measured. This eliminates possible differences in structure of glasses obtained at cooling of the eutectic melt. For each sample of cooled eutectic melt four values of heat of dissolution were determined. The arithmetic mean of these values was calculated: $(\Delta h_{\text{sol},\varphi}(\text{eut. melt}))$ (Symbol φ denotes the mean of the experimental values.). The obtained data are summarized in Table 1.

By adding the values of $(-\Delta h_{\text{cool}}(\text{eut. melt}))$ and $(-\Delta h_{\text{sol},\varphi}(\text{eut. melt}))$ for relevant temperatures the experimental data of the specific relative enthalpy of the eutectic melt $h_{\text{rel}}(\text{eut. melt})$ were obtained. Also these data are presented in Table 1. Using the method of least squares the temperature dependence of the specific relative enthalpy of the eutectic melt was obtained in the form of a linear regression function

$$\frac{h_{\text{rel},\varphi}(\text{eut. melt}; T)}{\text{kJ kg}^{-1}} = 2.0686 \times 10^3 + 1.5354 \frac{T}{K} \qquad (4)$$

The error in determination of the specific relative enthalpy of the eutectic melt was determined to be $\delta(h_{\text{rel},\varphi}(\text{eut. melt}; T)) = 17 \text{ kJ kg}^{-1}$. It was calculated according to the relation

$$\delta(h_{\text{rel},\varphi}(\text{eut. melt}; T)) = \frac{1}{\sqrt{n}} \cdot \sqrt{\frac{S_0}{n-p}} \cdot t \qquad (5)$$

where n is the number of experimental values of h_{rel}, S_0 is the residual sum of squares, p is the number of independent coefficients of the regression, and t is the Student coefficient taken from tables [10] for corresponding number of degree of freedom and coefficient of reliability $(1 - \alpha) = 0.95$. (All errors of measurement presented in this paper were determined on the level of significance 95 %.) The values of $h_{\text{rel},\varphi}(\text{eut. melt})$ calculated for relevant temperatures according to eqn (4) are compared with experimental values of these quantities $h_{\text{rel}}(\text{eut. melt})$ in Table 1.

Determination of the temperature dependence of the specific relative enthalpy of CS ($h_{\text{rel},\varphi}(\text{CS}; T)$)

The temperature dependence of the specific change in enthalpy at cooling of wollastonite was calculated by the integration of the temperature dependence of the specific heat capacity of wollastonite. The constants of this dependence were taken from tables [4]. In the limits T and $T_0 = 298$ K it holds

$$\frac{-\Delta h_{\text{cool},\varphi}(\text{CS}; T)}{\text{kJ kg}^{-1}} = -3.523 \times 10^2 + 9.317 \times 10^{-1} \frac{T}{K} +$$

$$+ 7.100 \times 10^{-5} \frac{T^2}{K^2} + 2.036 \times 10^4 \frac{T^{-1}}{K^{-1}} \tag{6}$$

Heat of dissolution of wollastonite ($\Delta h_{sol}(CS)$) was determined experimentally. From seven experimental values of this quantity the arithmetic mean of the specific heat of dissolution of wollastonite ($\Delta h_{sol,\varphi}(CS)$) and the error of the arithmetic mean ($\delta(\Delta h_{sol,\varphi}(CS))$) were calculated. Similarly as in the previous case the Student coefficient was used at the calculation of the error. Results of the experimental measurements and of calculations are summarized in Table 2.

Table 2

Experimental values of the specific heat of dissolution of wollastonite and the error in determination of this quantity

$-\Delta h_{sol}(CS)$ kJ kg^{-1}	$-\Delta h_{sol,\varphi}(CS)$ kJ kg^{-1}	$\delta(\Delta h_{sol,\varphi}(CS))$ kJ kg^{-1}
2597	2609	12
2594		
2623		
2609		
2626		
2616		
2596		

By adding the negatively taken value of the arithmetic mean of the specific heat of dissolution of wollastonite to the right-hand side of eqn (6) the temperature dependence of the specific relative enthalpy of wollastonite was obtained

$$\frac{h_{rel,\varphi}(CS; T)}{kJ\,kg^{-1}} = 2.2567 \times 10^3 + 9.317 \times 10^{-1} \frac{T}{K} + 7.100 \times 10^{-5} \frac{T^2}{K^2} +$$

$$+ 2.036 \times 10^4 \frac{T^{-1}}{K^{-1}} \tag{7}$$

The error in determination of the specific relative enthalpy of wollastonite was determined according to the "Gauss law of spreading of errors" from the errors in $\Delta h_{sol,\varphi}(CS)$ and $\Delta h_{cool,\varphi}(CS)$. It equals $\delta(h_{rel,\varphi}(CS; T)) = 18$ kJ kg^{-1}. (At the calculation of $\delta(\Delta h_{cool,\varphi}(CS))$ it was assumed that the value of $\Delta h_{cool,\varphi}(CS)$ at 1538 K was obtained with 1 % relative error and that $\delta(\Delta h_{cool,\varphi}(CS))$ does not depend on temperature.)

The temperature dependences of the specific relative enthalpy of the further two phases which crystallize from the eutectic melt, *i.e.* gehlenite and anorthite, were taken from paper [5]. It holds

$$\frac{h_{\text{rel.}\varphi}(C_2AS; T)}{kJ\,kg^{-1}} = 2.7001 \times 10^3 + 1.0053\,\frac{T}{K} + 5.092 \times 10^{-5}\,\frac{T^2}{K^2} +$$

$$+ 2.854 \times 10^4\,\frac{T^{-1}}{K^{-1}} \qquad (8)$$

$$\frac{h_{\text{rel.}\varphi}(CAS_2; T)}{kJ\,kg^{-1}} = 2.4273 \times 10^3 + 1.0683\,\frac{T}{K} + 7.803 \times 10^{-5}\,\frac{T^2}{K^2} +$$

$$+ 4.868 \times 10^4\,\frac{T^{-1}}{K^{-1}} \qquad (9)$$

The errors in determination of these quantities are as follows [5]

$$\frac{\delta(h_{\text{rel.}\varphi}(C_2AS; T))}{kJ\,kg^{-1}} = 23; \qquad \frac{\delta(h_{\text{rel.}\varphi}(CAS_2; T))}{kJ\,kg^{-1}} = 17$$

Calculation of the specific enthalpy of crystallization of the ternary eutectic melt in the system C_2AS—CAS_2—CS

Using the relationships (8), (9), (7), and (4) the values of the specific relative enthalpy of gehlenite, anorthite, wollastonite, and of the eutectic melt at the equilibrium temperature of 1538 K were determined. These data and the errors in their determination are presented in Table 3.

Table 3

Values of the specific relative enthalpy $h_{\text{rel.}\varphi}(X; 1538\,K)$
$X \equiv C_2AS,\ CAS_2,\ CS,$ and eut. melt, respectively

Phase	$\dfrac{h_{\text{rel.}\varphi}(X;\,1538\,K)}{kJ\,kg^{-1}}$
C_2AS	4385 ± 23
CAS_2	4287 ± 17
CS	3871 ± 18
Eut. melt	4430 ± 17

Introducing the values $h_{\text{rel},\varphi}(X; 1538 \text{ K})$ into eqn (1) the value of the specific enthalpy of crystallization of the eutectic melt was calculated

$$\Delta h_{\text{cryst},\varphi}(\text{eut. melt; } 1538 \text{ K}) = (-308 \pm 20) \text{ kJ kg}^{-1} \qquad (10)$$

In Fig. 1, the experimental values of the specific relative enthalpy of the eutectic melt, the temperature dependence of this specific relative enthalpy (curve 1), and the temperature dependences of the specific relative enthalpies of C_2AS, CAS_2, and CS multiplied by corresponding mass fractions from eqn (1) (curves 2, 3, and 4, respectively) are plotted. The value of the specific relative enthalpy of crystallization of the ternary eutectic melt is given by the difference of $\sum_{X} w(X)h_{\text{rel},\varphi}(X; 1538 \text{ K})$ ($X \equiv C_2AS$, CAS_2, CS) (point 5) and the value of $h_{\text{rel},\varphi}(\text{eut. melt; } 1538 \text{ K})$ (point 6).
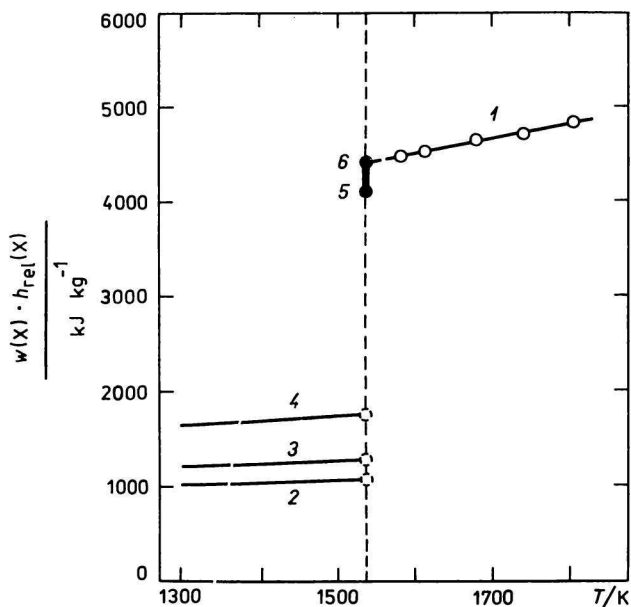

Fig. 1. Temperature dependences of the terms $w(X) \cdot h_{\text{rel}}(X)$.
1. Eut. melt ($w(X) = 1$); 2. C_2AS ($w(X) = 0.2432$); 3. CAS_2 ($w(X) = 0.3017$); 4. CS ($w(X) = 0.4551$). The value of $\Delta h_{\text{cryst}}(\text{eut. melt; } 1538 \text{ K})$ is given as the difference of the specific relative enthalpies corresponding to the points 5 and 6.

Dividing the specific enthalpy of crystallization of the eutectic melt by the equilibrium temperature of its crystallization one obtains the value of the specific entropy of crystallization of the eutectic melt

$$\Delta s_{\text{cryst},\varphi}(\text{eut. melt; } 1538 \text{ K}) = (-200 \pm 13) \text{ J kg}^{-1}\text{K}^{-1} \qquad (11)$$

Determination of heat of total crystallization of the ternary eutectic melt in the system C_2AS—CAS_2—CS ($\Delta h_{\Sigma\,cryst}(eut.\ melt)$)

Heat evolved at the crystallization of the eutectic melt at equilibrium temperature $T_{eq} = 1538$ K and at cooling of the products of crystallization to the temperature of 25 °C was calculated according to the "nonisothermal Hess law". It holds

$$\frac{\Delta h_{\Sigma\,cryst,\varphi}(eut.\ melt;\ 1538\ K \to 298\ K)}{kJ\ kg^{-1}} = 0.2432\,\frac{h_{rel,\varphi}(C_2AS;\ 298\ K)}{kJ\ kg^{-1}} +$$

$$+ 0.3017\,\frac{h_{rel,\varphi}(CAS_2;\ 298\ K)}{kJ\ kg^{-1}} + 0.4551\,\frac{h_{rel,\varphi}(CS;\ 298\ K)}{kJ\ kg^{-1}} -$$

$$- 1\,\frac{h_{rel,\varphi}(eut.\ melt;\ 1538\ K)}{kJ\ kg^{-1}} \tag{12}$$

Values of the specific relative enthalpy of crystal phases at 298 K equal to the negatively taken values of arithmetic mean of their specific heat of dissolution. For gehlenite it holds [7]

$$\Delta h_{sol,\varphi}(C_2AS) = (-3100 \pm 18)\ kJ\ kg^{-1} \tag{13}$$

For anorthite it holds [5]

$$\Delta h_{sol,\varphi}(CAS_2) = (-2916 \pm 8)\ kJ\ kg^{-1} \tag{14}$$

Introducing the negatively taken values of the arithmetic mean of specific heat of dissolution of gehlenite, anorthite, and wollastonite (the relationships (13) and (14), see also Table 2) and the value of the specific relative enthalpy of the eutectic melt at the temperature of 1538 K (Table 3) into eqn (12) we obtain the value of heat of total crystallization of the eutectic melt

$$\Delta h_{\Sigma\,cryst,\varphi}(eut.\ melt;\ 1538\ K \to 298\ K) = (-1609 \pm 19)\ kJ\ kg^{-1} \tag{15}$$

From comparison of the values following from eqns (10) and (15) it can be seen that the value of the specific enthalpy of crystallization of the ternary eutectic melt at $T_{eq} = 1538$ K makes less than 20 % from the value of specific enthalpy of total crystallization. Thus more than 80 % of the value of $\Delta h_{\Sigma\,cryst,\varphi}(eut.\ melt;\ 1538\ K \to 298\ K)$ corresponds to the heat liberated at cooling of gehlenite, anorthite, and wollastonite from the temperature of 1538 K to 298 K.

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