Determination of the enthalpy of crystallization of eutectic melt in the system $2CaO \cdot Al_2O_3 \cdot SiO_2$—$CaO \cdot SiO_2$

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Using a precursor method the melt of eutectic composition in the system $2CaO \cdot Al_2O_3 \cdot SiO_2$— $CaO \cdot SiO_2$ (45.6 mass % CaO; 13.4 mass % Al_2O_3; 41.0 mass % SiO_2) was prepared. The temperature dependence of the specific relative enthalpy of the eutectic melt was determined using the experimental data obtained in "drop" calorimeter and in the calorimeter for determination of heats of dissolution. Preparation of gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) and wollastonite ($CaO \cdot SiO_2$) which are the products of crystallization of the eutectic melt and the temperature dependences of their specific relative enthalpy were published in the previous papers. On the basis of the values of the specific relative enthalpy of the eutectic melt, gehlenite, and wollastonite at the equilibrium temperature of crystallization of the eutectic melt 1591 K and from the material balance of this crystallization the specific enthalpy of crystallization of the eutectic melt was determined

$$\Delta h_{cryst}(\text{eut. melt}; 1591\ \text{K}) = (-286 \pm 18)\ \text{kJ kg}^{-1}$$

The error was determined on the level of significance equal to 95 %.

С использованием метода прекурсора был получен расплав эвтектического состава в системе $2CaO \cdot Al_2O_3 \cdot SiO_2$—$CaO \cdot SiO_2$ (45,6 масс. % CaO; 13,4 масс. % Al_2O_3; 41,0 масс. % SiO_2). Применяя экспериментальные данные, полученные на «капельном» калориметре и на калориметре для определения теплот растворения, была установлена температурная зависимость удельной относительной энтальпии эвтектического расплава. Получение геленита ($2CaO \cdot Al_2O_3 \cdot SiO_2$) и воластонита ($CaO \cdot SiO_2$), являющихся продуктами кристаллизации эвтектического расплава, а также температурные зависимости их удельных относительных энтальпий были описаны в предыдущих работах. На основе величин удельной относительной энтальпии эвтектического расплава, геленита и воластонита при равновесной температуре кристаллизации эвтектического расплава 1591 К, а также исходя из материального баланса этой кристаллизации, определено значение удельной энтальпии кристаллизации эвтектического расплава

$$\Delta h_{cryst}(\text{eut. melt}; 1591\ \text{K}) = (-286 \pm 18)\ \text{кДж кг}^{-1}$$

Величина ошибки была определена на 95 % уровне значимости.

This work is the continuation of the enthalpic balance of the system 2CaO Al$_2$O$_3$ SiO$_2$—CaO Al$_2$O$_3$ 2SiO$_2$—CaO SiO$_2$ [1—3]. Its aim is to determine the enthalpy and entropy of crystallization of gehlenite 2CaO Al$_2$O$_3$ SiO$_2$ (C$_2$AS) and wollastonite CaO SiO$_2$ (CS) from the binary eutectic melt of the composition 45.6 mass % CaO; 13.4 mass % Al$_2$O$_3$; 41.0 mass % SiO$_2$ at the equilibrium temperature 1318 °C [4]. Further, heat of crystallization of this melt at its cooling from the temperature of 1318 °C to 25 °C was determined. In both cases the enthalpies were calculated using the values of the specific relative enthalpy (h_{rel}) determined in the way which has been described in papers [5, 6].

Material balance of crystallization of gehlenite and wollastonite from the eutectic melt is given by the relationship

$$1 \text{ kg eut. melt} \rightarrow 0.360 \text{ kg C}_2\text{AS} + 0.640 \text{ kg CS} \qquad (A)$$

The specific enthalpy of crystallization of the eutectic melt at the equilibrium temperature $T_{eq} = 1591$ K (it is denoted as Δh_{cryst}(eut. melt; 1591 K)) was calculated according to the Hess law

$$\frac{\Delta h_{cryst}(\text{eut. melt; 1591 K})}{\text{kJ kg}^{-1}} = 0.360 \frac{h_{rel}(\text{C}_2\text{AS; 1591 K})}{\text{kJ kg}^{-1}} +$$

$$+ 0.640 \frac{h_{rel}(\text{CS; 1591 K})}{\text{kJ kg}^{-1}} - 1 \frac{h_{rel}(\text{eut. melt; 1591 K})}{\text{kJ kg}^{-1}} \qquad (1)$$

The values of terms in the sum (1) were determined in the same way as in paper [2].

Experimental

Preparation of samples

The eutectic melt of the system C$_2$AS—CS was prepared by the precursor method using a modified procedure described in [7]. The following reagents were used: CaCO$_3$ (Specpure, JMC), metallic Al (w(Al) = 99.999 %, The Research Institute of Metals, Panenské Břežany), and sol of silicic acid which had been prepared from commercial water glass using the ion exchanger DOWEX 50W × 8 [1]. By heating the dry rest of aqueous solution prepared from organic substance and weighed-in amounts of salts corresponding to the desired composition of the eutectic mixture at the temperature of 500—600 °C the precursor, i.e. the homogeneous mixture of oxides CaO, Al$_2$O$_3$, and SiO$_2$ was obtained. This mixture was further heated for 4 h at 1000 °C and then after sealing into a crucible made of the alloy PtRh 10 it was kept at 1500 °C for 4 h. The eutectic mixture of the system C$_2$AS—CS was then quenched in liquid nitrogen. No crystallization of the melt was observed.

Apparatus

The changes in enthalpy at cooling of the eutectic melt were measured by the "drop" calorimeter which has been described in [8]. The heats of dissolution of the products of cooling of the eutectic melt were measured in the calorimeter for determination of the heats of dissolution which has been described in paper [9]. Composition of the dissolving mixture was the same as that used in works [1—3].

Results and calculations

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

Determination of $h_{rel,\varphi}$(eut. melt; T) (φ denotes the mean of experimental values) is based on two sets of measured data: the values of Δh_{cool}(eut. melt) and Δh_{sol}(eut. melt). With the drop calorimeter the changes in enthalpy of five samples of the eutectic melt at their cooling from the temperatures chosen from the interval 1622 K—1823 K to the temperature of 298 K were measured. The experimental data of Δh_{cool}(eut. melt) are given in Table 1. The X-ray patterns of the cooled samples of the eutectic melt gave no evidence of crystal phases. In despite of that (and in order to avoid a possible difference in the structure of glass) for each sample its heat of dissolution Δh_{sol}(eut. melt) was measured. This measurement was repeated four times and the arithmetic mean of these values is denoted as $\Delta h_{sol,\varphi}$(eut. melt). The obtained data are presented in Table 1.

The experimental values of h_{rel}(eut. melt) were obtained as the sum of the values of $(-\Delta h_{cool}$(eut. melt)) and $(-\Delta h_{sol,\varphi}$(eut. melt)) at corresponding temperatures. The results are summarized in Table 1. Treating the experimental data of h_{rel}(eut. melt) by the least-squares method the temperature dependence of the specific relative enthalpy $h_{rel,\varphi}$(eut. melt; T) was obtained in the form of the following regression function

$$\frac{h_{rel,\varphi}(\text{eut. melt; } T)}{\text{kJ kg}^{-1}} = 2.0146 \times 10^3 + 1.5011 \frac{T}{\text{K}} \qquad (2)$$

The error was determined to be $\delta(h_{rel,\varphi}$(eut. melt)) = 11 kJ kg^{-1} by the procedure described in [2]. All errors of measurements reported in this paper were determined on the level of significance of 95 %. The values of $h_{rel,\varphi}$(eut. melt) calculated at chosen temperatures on the basis of the relationship (2) are presented in Table 1.

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Table 1

Experimental data of $(-\Delta h_{cool})$, $(-\Delta h_{sol,\varphi})$, and h_{rel} for the eutectic melt and the calculated values of $h_{rel,\varphi}$(eut. melt) at chosen temperatures from the interval $\langle 1622\ K;\ 1823\ K \rangle$

$\dfrac{T}{K}$	$-\Delta h_{cool}$(eut. melt) $kJ\ kg^{-1}$	$-\Delta h_{sol,\varphi}$(eut. melt) $kJ\ kg^{-1}$	h_{rel}(eut. melt) $kJ\ kg^{-1}$	$h_{rel,\varphi}$(eut. melt) $kJ\ kg^{-1}$
1622	1535	2911	4446	4449
1667	1604	2923	4527	4517
1724	1692	2901	4593	4602
1767	1746	2922	4668	4667
1823	1831	2922	4753	4751

*Calculation of the specific enthalpy of crystallization of gehlenite and wollastonite
from the eutectic melt of the system C_2AS—CS*

Using the relationship (2) and the equations describing the temperature
dependence of the specific relative enthalpy of gehlenite (eqn (3)) and wollastonite (eqn (4)), the values of h_{rel} of each phase at the equilibrium temperature
of crystallization of the eutectic melt $T_{eq} = 1591$ K were obtained. The relationships (3) and (4) were taken from papers [2] and [3], respectively.

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

$$+ 2.854 \times 10^4 \frac{T^{-1}}{K^{-1}} \qquad (3)$$

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

$$+ 2.036 \times 10^4 \frac{T^{-1}}{K^{-1}} \qquad (4)$$

The calculated data and the errors in their determination are presented in
Table 2. By introducing these data into eqn (1) we obtain

$$\Delta h_{cryst,\varphi}(\text{eut. melt};\ 1591\ \text{K}) = (-286 \pm 18)\ kJ\,kg^{-1} \qquad (5)$$

The error in determination of the specific enthalpy of crystallization of the
eutectic melt was calculated in the same way as it has been described in [2].

Table 2

Values of the specific relative enthalpy $h_{rel,\varphi}(X;\ 1591\ \text{K})$
($X \equiv$ eut. melt; C_2AS; CS)

Phase	$\dfrac{h_{rel,\varphi}(X;\ 1591\ \text{K})}{kJ\,kg^{-1}}$
Eut. melt	4403 ± 11
C_2AS	4446 ± 22
CS	3932 ± 18

The determination of the value of Δh_{cryst}(eut. melt) is illustrated in Fig. 1
where the following data and relationships are plotted:
— the experimental values of the specific relative enthalpy of the eutectic
melt, the temperature dependence of its specific relative enthalpy (curve *1*);

— the temperature dependences of h_{rel} of C_2AS and CS multiplied by corresponding mass fractions of these phases (see eqn (*1*)) (curves *2* and *3*, respectively);

— the value of the specific enthalpy of crystallization of the eutectic melt which is given as the difference of $\sum_X w(X)\, h_{rel,\varphi}(X;\ 1591\ K)$ ($X \equiv C_2AS$; CS) (point *4*) and the value of $h_{rel,\varphi}$(eut. melt; 1591 K) (point *5*).

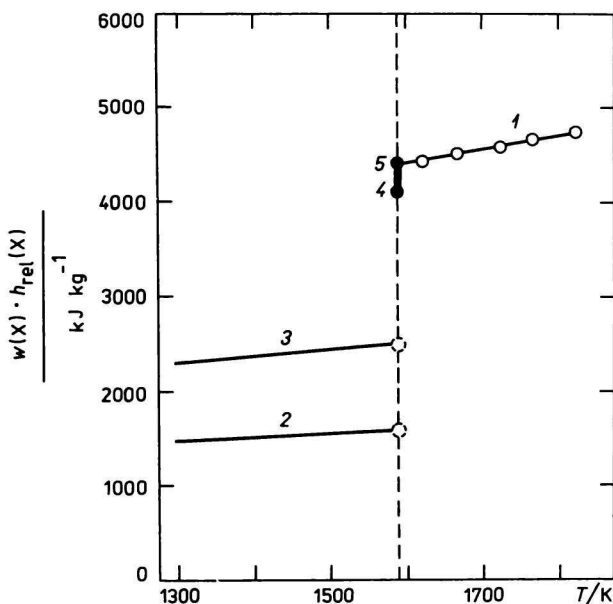*Fig. 1.* Temperature dependences of the term $(w(X)\ h_{rel}(X))$.
1. Eut. melt ($w(X) = 1$); *2.* C_2AS ($w(X) = 0.360$); *3.* CS ($w(X) = 0.640$).
The value of $(-\Delta h_{cryst}$(eut. melt; 1591 K)) is given as the difference between the specific relative enthalpy of the eutectic melt at $T_{eq} = 1591$ K (point *5*) and the sum of specific relative enthalpies of the products of crystallization of the eutectic melt (C_2AS, CS) at the same temperature multiplied by corresponding mass fractions of phases C_2AS and CS (point *4*).

The specific entropy of crystallization of the eutectic melt was obtained by dividing the value of the specific enthalpy of crystallization by the equilibrium temperature. It follows

$$\Delta s_{cryst,\varphi}(\text{eut. melt};\ 1591\ K) = \frac{\Delta h_{cryst,\varphi}(\text{eut. melt};\ 1591\ K)}{1591\ K} =$$

$$= (-180 \pm 11)\ J\,kg^{-1}K^{-1} \qquad (6)$$

Determination of the "heat of total crystallization" of the eutectic melt in the system C_2AS—CS

Heat evolved at the crystallization of the eutectic melt at the equilibrium temperature $T_{eq} = 1591$ K added to the heat evolved at cooling of gehlenite and wollastonite to the temperature of 298 K is denoted in this paper as the "heat of total crystallization" ($\Delta h_{\Sigma cryst,\varphi}$(eut. melt; 1591 K → 298 K)). Its value was determined in the same way as it has been described in paper [2] using the data presented in this paper and in papers [1, 3]. It follows

$$\Delta h_{\Sigma cryst,\varphi}(\text{eut. melt; } 1591 \text{ K} \rightarrow 298 \text{ K}) = (-1617 \pm 15) \text{ kJ kg}^{-1} \qquad (7)$$

From comparison of the values $\Delta h_{cryst,\varphi}$(eut. melt; 1591 K) and $\Delta h_{\Sigma cryst,\varphi}$(eut. melt; 1591 K → 298 K) (see eqns (5) and (7)) it follows that the heat formed at the equilibrium crystallization of the eutectic melt of the system C_2AS—CS at $T_{eq} = 1591$ K presents less than 18 % of the heat of total crystallization of the eutectic melt. Thus more than 4/5 of the heat of total crystallization of the eutectic melt of the system C_2AS—CS is evolved at cooling of gehlenite and wollastonite from the temperature of 1591 K to 298 K.

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