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

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Melt of the eutectic composition in the system $CaO \cdot Al_2O_3 \cdot 2SiO_2$—$CaO \cdot SiO_2$ (33.9 mass % CaO; 18.7 mass % Al_2O_3; 47.4 mass % SiO_2) was prepared by heating of oxide precursor. The temperature dependence of the specific relative enthalpy of the eutectic melt was determined using combination of the experimental data obtained in "drop" calorimeter and in the calorimeter for determination of heats of dissolution. On the basis of the values of the specific relative enthalpy of the eutectic melt, anorthite and wollastonite at the equilibrium temperature of crystallization of the eutectic melt at 1580 K and from the material balance of crystallization of this melt the specific enthalpy of crystallization of the eutectic melt was determined

$$\Delta h_{cryst}(\text{eut. melt}; 1580 \text{ K}) = (-297 \pm 14) \text{ kJ kg}^{-1}$$

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

Получен расплав эвтектического состава в системе $CaO \cdot Al_2O_3 \cdot 2SiO_2$—$CaO \cdot SiO_2$ (33,9 масс. % CaO; 18,7 масс. % Al_2O_3; 47,4 масс. % SiO_2) посредством нагрева окисного прекурсора. Температурная зависимость удельной относительной энтальпии эвтектического расплава была установлена с использованием экспериментальных данных, полученных в капельном калориметре, а также в калориметре для определения теплот растворения. На основе значений удельной относительной энтальпии эвтектического расплава, анортита и воластонита при равновесной температуре кристаллизации эвтектического расплава 1580 К и исходя из материального баланса кристаллизации этого расплава, было определено значение удельной энтальпии кристаллизации эвтектического расплава

$$\Delta h_{cryst}(\text{eut. melt}; 1580 \text{ K}) = (-297 \pm 14) \text{ кДж кг}^{-1}$$

Величина ошибки была определена на уровне значимости 95 %.

This paper is a continuation of the study of enthalpic balance of the system $2CaO \cdot Al_2O_3 \cdot SiO_2$—$CaO \cdot Al_2O_3 \cdot 2SiO_2$—$CaO \cdot SiO_2$, the part of which has been published in papers [1—4]. Its aim is to determine the enthalpy and entropy of crystallization of the eutectic mixture in the system $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (CAS_2 — anorthite)—$CaO \cdot SiO_2$ (CS — wollastonite). Composition of the binary eutectic

melt (eut. melt) is 33.9 mass % CaO; 18.7 mass % Al_2O_3; 47.4 mass % SiO_2 at the equilibrium temperature of 1307 °C [5]. Further, the heat of crystallization of this melt at its cooling from the temperature of 1307 °C to 25 °C was evaluated. Both enthalpic quantities were calculated using the values of relative enthalpy (h_{rel}), determination of which has been described in [6, 7].

The material balance of crystallization of the eutectic mixture of anorthite and wollastonite from the eutectic melt is given by the relation

$$1 \text{ kg eut. melt} \rightarrow 0.510 \text{ kg } CAS_2 + 0.490 \text{ kg CS} \qquad (A)$$

The specific enthalpy of crystallization of the eutectic melt at the equilibrium temperature $T_{eq} = 1580$ K (it is denoted Δh_{cryst}(eut. melt; 1580 K)) was calculated using the Hess law according to the relationship

$$\frac{\Delta h_{cryst}(\text{eut. melt}; 1580 \text{ K})}{\text{kJ kg}^{-1}} = 0.510 \frac{h_{rel}(CAS_2; 1580 \text{ K})}{\text{kJ kg}^{-1}} +$$

$$+ 0.490 \frac{h_{rel}(CS; 1580 \text{ K})}{\text{kJ kg}^{-1}} - 1 \frac{h_{rel}(\text{eut. melt}; 1580 \text{ K})}{\text{kJ kg}^{-1}} \qquad (1)$$

The terms in the relationship (1) were determined in the same way as it has been described in paper [2].

Experimental

Preparation of sample

The eutectic melt of the system CAS_2—CS was prepared by the precursor method [8] in the same procedure which has been given in paper [4] for the preparation of the eutectic melt of the system C_2AS—CS.

Apparatus

The changes in enthalpy at cooling of the eutectic melt (Δh_{cool}(eut. melt)) were measured by the "drop" calorimeter which has been described in [9]. The values of the heat of dissolution of the products of cooling of the eutectic melt (Δh_{sol}(eut. melt)) were measured in the calorimeter for determination of the heats of dissolution which has been described in paper [10]. 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 $\Delta h_{sol, \varphi}$(eut. melt) [2] (Table 1).

By the addition of the values $(-\Delta h_{cool}$(eut. melt)) and $(-\Delta h_{sol, \varphi}$(eut. melt)) at corresponding temperatures the values of h_{rel}(eut. melt) were obtained (Table 1). By treatment of these data by the least-squares method the following linear regression function was obtained

$$\frac{h_{rel, \varphi}(eut. melt; T)}{kJ\ kg^{-1}} = 2.0678 \times 10^3 + 1.4958\ \frac{T}{K} \qquad (2)$$

The error in the determination of this quantity equals $\delta(h_{rel, \varphi}$(eut. melt)) = $= 8\ kJ\ kg^{-1}$ The error was determined by the same procedure as described in [2]. All errors 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 according to the relationship (2) are presented in Table 1.

Calculation of the specific enthalpy of crystallization of the eutectic mixture of anorthite and wollastonite from the eutectic melt of the system CAS_2—CS

In papers [2, 3] the relationships of the temperature dependence of the specific relative enthalpy of anorthite (eqn (3)) and wollastonite (eqn (4)) were presented

$$\frac{h_{rel, \varphi}(CAS_2; T)}{kJ\ kg^{-1}} = 2.4273 \times 10^3 + 1.0683\ \frac{T}{K} + 7.803 \times 10^{-5}\ \frac{T^2}{K^2} +$$
$$+ 4.868 \times 10^4\ \frac{T^{-1}}{K^{-1}} \qquad (3)$$

$$\frac{h_{rel, \varphi}(CS; T)}{kJ\ kg^{-1}} = 2.2567 \times 10^3 + 9.317 \times 10^{-1}\ \frac{T}{K} + 7.100 \times 10^{-5}\ \frac{T^2}{K^2} +$$
$$+ 2.036 \times 10^4\ \frac{T^{-1}}{K^{-1}} \qquad (4)$$

Using the relationship (2) and eqns (3) and (4) the values of h_{rel} of corresponding phases at the equilibrium temperature of crystallization of the eutectic melt $T_{eq} = 1580\ K$ were calculated. These data are together with the errors in their

Table 1

Experimental values 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 $\langle 1622\,K;\ 1817\,K\rangle$

| $\dfrac{T}{K}$	$\dfrac{-\Delta h_{cool}\text{(eut. melt)}}{kJ\,kg^{-1}}$	$\dfrac{-\Delta h_{sol.\,\varphi}\text{(eut. melt)}}{kJ\,kg^{-1}}$	$\dfrac{h_{rel}\text{(eut. melt)}}{kJ\,kg^{-1}}$	$\dfrac{h_{rel.\,\varphi}\text{(eut. melt)}}{kJ\,kg^{-1}}$
1622	1555	2941	4496	4494
1664	1620	2933	4553	4557
1726	1711	2937	4648	4650
1769	1782	2939	4721	4714
1817	1850	2932	4782	4786

Table 2

Values of the specific relative enthalpy $h_{rel, \varphi}(X; 1580 \text{ K})$ ($X \equiv$ eut. melt; CAS_2; CS)

Phase	$\dfrac{h_{rel, \varphi}(X; 1580 \text{ K})}{\text{kJ kg}^{-1}}$
Eut. melt	4431 ± 8
CAS_2	4341 ± 16
CS	3919 ± 18

determination presented in Table 2. Introducing these values into eqn (*1*) we obtain

$$\Delta h_{cryst, \varphi}(\text{eut. melt}; 1580 \text{ K}) = (-297 \pm 14) \text{ kJ kg}^{-1} \qquad (5)$$

The error in determination of the specific enthalpy of crystallization of the eutectic melt was calculated in the same way as in paper [2].
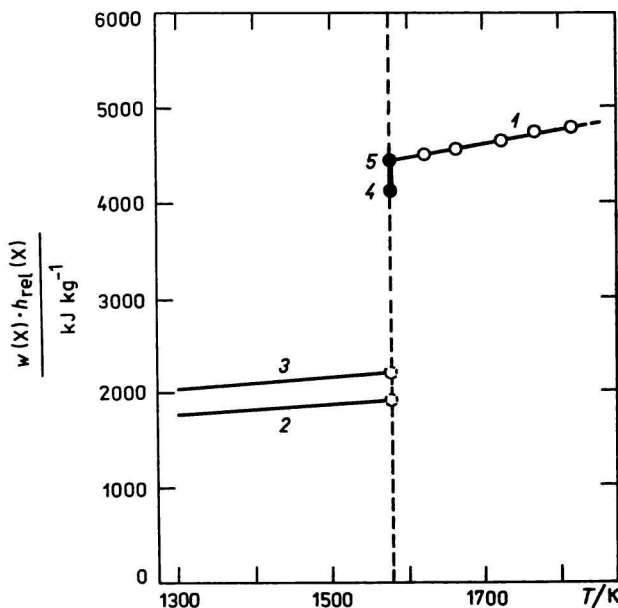
Fig. *1*. Temperature dependences of $w(X) \cdot h_{rel}(X)$.
1. Eut. melt ($w(X) = 1$); *2*. CS ($w(X) = 0.490$); *3*. CAS_2 ($w(X) = 0.510$).
The value of $-\Delta h_{cryst}$(eut. melt; 1580 K) is given as the difference between the specific relative enthalpy of the eutectic melt at $T_{eq} = 1580$ K (point *5*) and the sum of specific relative enthalpies of products of crystallization of the eutectic melt (CS, CAS_2) at 1580 K multiplied by corresponding mass fractions of phases CS and CAS_2 (point *4*).

Determination of Δh_{cryst}(eut. melt) is illustrated in Fig. 1 where the following values and curves are plotted:

— the experimental values of the specific relative enthalpy of eutectic melt, the temperature dependence of its specific relative enthalpy (curve *1*);

— the temperature dependences of h_{rel} of CS and CAS_2 multiplied by corresponding mass fractions of these phases (eqn (*1*)) (curves *2* and *3*);

— the value of the specific enthalpy of crystallization of the eutectic melt which is given as difference of $\sum_X w(X) h_{rel, \varphi}(X; 1580\,K)$ ($X \equiv CS; CAS_2$) (point *4*) and the value of $h_{rel, \varphi}$(eut. melt; 1580 K) (point *5*).

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

$$\Delta s_{cryst, \varphi}(\text{eut. melt}; 1580\,K) = \frac{\Delta h_{cryst, \varphi}(\text{eut. melt}; 1580\,K)}{1580\,K} =$$

$$= (-188 \pm 9)\,J\,kg^{-1}\,K^{-1} \tag{6}$$

Determination of the "heat of total crystallization" of the eutectic melt in the system CAS_2—CS

Heat evolved at the crystallization of the eutectic melt at the equilibrium temperature $T_{eq} = 1580\,K$ added to the heat evolved at cooling of the products of crystallization, *viz.* anorthite 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; 1580 K → 298 K)). Its value can be determined in the same way as it has been described in [2] using the data presented in this work and in papers [2, 3]. It follows

$$\Delta h_{\Sigma cryst, \varphi}(\text{eut. melt}; 1580\,K \rightarrow 298\,K) = (-1665 \pm 11)\,kJ\,kg^{-1} \tag{7}$$

From comparison of the values of $\Delta h_{cryst, \varphi}$(eut. melt; 1580 K) and $\Delta h_{\Sigma cryst, \varphi}$(eut. melt; 1580 K → 298 K) (the relationships (*5*) and (*7*)) it follows that the heat formed at the equilibrium crystallization of the eutectic melt of the system CAS_2—CS at the temperature of 1580 K presents less than 18 % of the heat evolved at the total crystallization of this melt. Thus more than 4/5 of the heat of total crystallization of the eutectic melt of the system CAS_2—CS is evolved at the cooling of anorthite and wollastonite from the temperature of 1580 K to 298 K.

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