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

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Dedicated to Corresponding Member M. Zikmund, in honour of his 65th birthday

Using a precursor method the melt of eutectic composition in the system $2CaO \cdot Al_2O_3 \cdot SiO_2—CaO \cdot Al_2O_3 \cdot 2SiO_2$ (30.34 mass % CaO; 36.91 mass % Al_2O_3; 32.75 mass % SiO_2) and one of the products of its crystallization, *viz.* $CaO \cdot Al_2O_3 \cdot 2SiO_2$, were prepared. 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. The temperature dependences of the specific relative enthalpy of the products of crystallization of the eutectic melt (these products being $2CaO \cdot Al_2O_3 \cdot SiO_2$ (gehlenite) and $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (anorthite)) were determined on the basis of literature data and the measured value of the specific heat of dissolution of $CaO \cdot Al_2O_3 \cdot 2SiO_2$. On the basis of the values of the specific relative enthalpy of the eutectic melt and of the phases $2CaO \cdot Al_2O_3 \cdot SiO_2$ and $CaO \cdot Al_2O_3 \cdot 2SiO_2$ related to the equilibrium temperature of crystallization of the eutectic melt 1658 K and from the material balance of the crystallization process the value of the specific enthalpy of crystallization of the eutectic melt was determined

$$\Delta h_{\mathrm{cryst}}(\text{eut. melt; } 1658\ \mathrm{K}) = (-441 \pm 23)\ \mathrm{kJ\ kg^{-1}}$$

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

С применением метода прекурсора были получены расплав эвтектического состава в системе $2CaO \cdot Al_2O_3 \cdot SiO_2—CaO \cdot Al_2O_3 \cdot 2SiO_2$ (30,34 масс. % CaO; 36,91 масс. % Al_2O_3; 32,75 масс. % SiO_2) и один из продуктов его кристаллизации, а именно, $CaO \cdot Al_2O_3 \cdot 2SiO_2$. Температурная зависимость удельной относительной энтальпии эвтектического расплава была установлена с помощью сочетания экспериментальных данных, полученных в «капельном» калориметре и в калориметре для определения теплот растворения. Температурные зависимости удельных относительных энтальпий продуктов кристаллизации эвтектического расплава (этими продуктами являются $2CaO \cdot Al_2O_3 \cdot SiO_2$ (гейленит) и $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (анортит)) были определены на основе литературных данных и измерений величины удельной теплоты растворения $CaO \cdot Al_2O_3 \cdot 2SiO_2$. Исходя из величин удельной относительной энтальпии эвтектического расплава и двух фаз $2CaO \cdot Al_2O_3 \cdot SiO_2$ и $CaO \cdot Al_2O_3 \cdot 2SiO_2$ при равновесной температуре кристаллизации эвтектического расплава 1658 K и на основании материального баланса кристаллизационного процесса, было определено значение удельной энтальпии кристаллизации эвтектического расплава

$$\Delta h_{\mathrm{cryst}}(\mathrm{eut.\ melt};\ 1658\ \mathrm{K}) = (-441 \pm 23)\ \text{кДж кг}^{-1}$$

Величина ошибки была определена при уровне значимости 95 %.

In the ternary system $2CaO \cdot Al_2O_3 \cdot SiO_2$—$CaO \cdot Al_2O_3 \cdot 2SiO_2$—$CaO \cdot SiO_2$ three binary and one ternary eutectics occur [1]. The aim of this work is to determine the enthalpy and entropy of crystallization of $2CaO \cdot Al_2O_3 \cdot SiO_2$ (C_2AS) and $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (CAS_2) from the binary eutectic melt (eut. melt) having composition 30.34 mass % CaO, 36.91 mass % Al_2O_3, and 32.75 mass % SiO_2 at the equilibrium temperature of 1385 °C [1]. Further the heat of crystallization of this melt at its cooling from the temperature of 1385 °C to 25 °C will be evaluated. (For CaO, Al_2O_3, and SiO_2 the symbols C, A, and S, respectively, are used.) Determination of the mentioned thermodynamic data is a contribution to the enthalpic analysis of the system CaO—Al_2O_3—SiO_2 which is important in the technology of cements, glass, and slags.

For the determination of the enthalpy of crystallization of C_2AS and CAS_2 from the eutectic melt the undirect calorimetric method was used. Using this method one needs to know the values of the relative enthalpy (h_{rel}) of the phases taking part at the crystallization process at the equilibrium temperature 1658 K (related to the same reference state) and the material balance of this process. The masses of C_2AS and CAS_2 crystallizing from 1 kg of the eutectic melt were determined on the basis of balance of CaO, Al_2O_3, and SiO_2 in the phases taking part in the crystallization process. It follows

$$1\ \mathrm{kg\ eut.\ melt} \rightarrow 0.4908\ \mathrm{kg}\ C_2AS + 0.5092\ \mathrm{kg}\ CAS_2 \qquad (A)$$

The specific enthalpy of crystallization of the eutectic melt at the equilibrium temperature $T_{\mathrm{eq}} = 1658$ K (it is denoted $\Delta h_{\mathrm{cryst}}$(eut. melt; 1658 K)) is then calculated using the Hess law according to the relationship

$$\frac{\Delta h_{\mathrm{cryst}}(\mathrm{eut.\ melt};\ 1658\ \mathrm{K})}{\mathrm{kJ\ kg}^{-1}} = 0.4908\,\frac{h_{\mathrm{rel}}(C_2AS;\ 1658\ \mathrm{K})}{\mathrm{kJ\ kg}^{-1}} +$$

$$+ 0.5092 \frac{h_{\text{rel}}(\text{CAS}_2;\ 1658\ \text{K})}{\text{kJ kg}^{-1}} - 1 \frac{h_{\text{rel}}(\text{eut. melt};\ 1658\ \text{K})}{\text{kJ kg}^{-1}} \qquad (1)$$

The specific relative enthalpy of the corresponding phase at chosen temperature equals (except for sign) the sum of the specific changes in enthalpy at cooling the phase from chosen temperature to the temperature of 298 K (Δh_{cool}) and dissolution of the cooled phase at 298 K in suitable mixture of solvents (Δh_{sol}) [2, 3]

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

The necessity of determination of the heat of dissolution of phases follows from the unreproducibility of structure of glass which is formed at cooling of the eutectic melt. Thus the quantity Δh_{cool} has for the eutectic melt no physical meaning. Using the same solvent for determination of the heats of dissolution of all phases taking part at the crystallization process ensures well defined reference state, which is the same for all phases. The values of h_{rel} have a physical meaning. They are only the function of temperature and it makes it possible to calculate the enthalpy of crystallization of eutectic melt on the basis of eqn (*1*).

The values of specific relative enthalpy of the eutectic melt, C_2AS and CAS_2 at the temperature of 1658 K were determined from the temperature dependences of the specific relative enthalpy of these phases determined in suitably chosen temperature intervals. The temperature dependence h_{rel}(eut. melt) was calculated from the values of Δh_{cool}(eut. melt) measured at cooling the samples from chosen temperatures to 298 K in the drop calorimeter and from the values of the arithmetic mean of the specific heat of dissolution of products of cooling of each sample in the “dissolution” calorimeter at 298 K. For the calculation of the temperature dependences of h_{rel} of C_2AS and CAS_2 the temperature dependences of their heat capacities published in tables [4], the value of arithmetic mean of heat of dissolution of C_2AS [5], and the value of the arithmetic mean of the specific heat of dissolution of CAS_2 were used. The latter quantity was obtained in this work from the measurements of $\Delta h_{\text{sol}}(CAS_2)$.

Eqn (*1*) is also used for calculation of the error in determination of the specific enthalpy of crystallization of the eutectic melt. This error is denoted as $\delta(\Delta h_{\text{cryst}}(\text{eut. melt};\ 1658\ \text{K}))$. It is calculated from the errors in determination of h_{rel} of the phases X taking part in the crystallization process at 1658 K (these are denoted as $\delta(h_{\text{rel}}(\text{X};\ 1658\ \text{K}))$) using the Gauss law of spreading of errors. It follows

$$\delta(\Delta h_{\text{cryst}}(\text{eut. melt};\ 1658\ \text{K})) = \sqrt{\sum_{\text{X}} [w(\text{X}) \cdot \delta(h_{\text{rel}}(\text{X};\ 1658\ \text{K}))]^2} \qquad (3)$$

where $w(\text{X})$ is the mass fraction of the corresponding phase (X) in the reaction scheme (*A*).

Experimental

Preparation of samples

The eutectic melt of the system C_2AS—CAS_2 (its composition was taken from [1]) and CAS_2 were prepared by the precursor method [6]. The following reagents were used: $CaCO_3$ (Specpure, JMC), metal Al ($w(\text{Al}) = 99.999\ \%$) (The Research Institute of Metals, Panenské Břežany), and sol of silica acid which had been prepared from commercial water glass using the ion exchanger DOWEX 50W × 8 [5]. By heating the precursor having the composition of the eutectic mixture or CAS_2 (this was prepared by the method similar to that described in [6]) to the temperature of 500—600 °C homogeneous mixtures of oxides CaO, Al_2O_3, and SiO_2 were obtained. Anorthite (CAS_2) was prepared by heating the corresponding mixture of oxides at 1000 °C for 4 h. Its purity was checked by X-ray diffraction analysis. In the case of the eutectic mixture the homogeneous mixture of oxides was firstly kept at 1000 °C for 4 h and then after sealing into a crucible made of the alloy PtRh 10 it was kept at 1500 °C for 4 h. In despite of quenching the sample in liquid nitrogen it partly crystallizes. The X-ray pattern showed the presence of C_2AS and CAS_2 in the products of quenching of the eutectic melt. This partial crystallization, however, makes no troubles because the whole sample is homogenized. Furthermore the samples weighed for measurement are melted in the furnace of the drop calorimeter.

Apparatus

The drop calorimeter used for measurement of the change in enthalpy at cooling of the eutectic melt is described in paper [7]. The heats of dissolution of CAS_2 and of the products of cooling of the eutectic melt were measured at the temperature of 298 K in the calorimeter for the determination of the heats of dissolution which has been described in paper [8]. As the solvent the mixture of aqueous solutions of hydrofluoric acid ($w(\text{HF}) = 40\ \%$) and hydrochloric acid (1 volume part of HCl ($w(\text{HCl}) = 35$—$38\ \%$) and 1 volume part of H_2O) in the volume ratio 2 : 1 was used. The solvent was saturated with CaF_2 by adding 150 mg $CaCO_3$ to 1 dm^3 of this mixture [5].

Results and calculations

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

Determination of $h_{\text{rel},\varphi}$(eut. melt; T) (φ denotes the mean of the 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

Table 1

Experimental data of $(-\Delta h_{\mathrm{cool}})$, $(-\Delta h_{\mathrm{sol},\varphi})$, and h_{rel} for the eutectic melt and the calculated values of $h_{\mathrm{rel},\varphi}$(eut. melt) at chosen temperatures from the interval ⟨1685 K; 1802 K⟩

$\frac{T}{\mathrm{K}}$	$\frac{-\Delta h_{\mathrm{cool}}(\text{eut. melt})}{\mathrm{kJ\,kg^{-1}}}$	$\frac{-\Delta h_{\mathrm{sol},\varphi}(\text{eut. melt})}{\mathrm{kJ\,kg^{-1}}}$	$\frac{h_{\mathrm{rel}}(\text{eut. melt})}{\mathrm{kJ\,kg^{-1}}}$	$\frac{h_{\mathrm{rel},\varphi}(\text{eut. melt})}{\mathrm{kJ\,kg^{-1}}}$
1685	1693	3279	4972	4968
1704	1721	3274	4995	5000
1736	1760	3284	5044	5053
1764	1824	3293	5117	5100
1802	1881	3275	5156	5163

the interval 1685—1802 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 samples cooled in the block of the drop calorimeter give no evidence of crystallization of C_2AS or CAS_2. 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 three or four times and the means of the experimental heats of dissolution are summarized in Table 1 as well.

The experimental values of the specific relative enthalpy of the eutectic melt h_{rel}(eut. melt) were obtained as function of temperature by adding the values of $(-\Delta h_{\mathrm{cool}}$(eut. melt)) and $(-\Delta h_{\mathrm{sol},\varphi}$(eut. melt)). Treating the experimental data of h_{rel}(eut. melt) by the least-squares method the temperature dependence of the specific relative enthalpy ($h_{\mathrm{rel},\varphi}$(eut. melt; T)) was obtained in the form of the following regression function

$$\frac{h_{\mathrm{rel},\varphi}(\text{eut. melt; }T)}{\mathrm{kJ\,kg^{-1}}} = 2.1663 \times 10^3 + 1.6629\frac{T}{\mathrm{K}} \qquad (4)$$

The error was determined to be $\delta(h_{\mathrm{rel},\varphi}$(eut. melt; T)) = 18 kJ kg^{-1}. This error was determined in the following way. The error of the regression eqn (*4*) was divided by the square root of the number of measurements and multiplied by the Student coefficient taken from tables [9]. All the errors of measurement reported in this paper were determined on the level of significance of 95 %. The values of $h_{\mathrm{rel},\varphi}$(eut. melt) calculated for chosen temperatures on the basis of the relationship (*4*) are presented in Table 1.

Determination of the temperature dependence of the specific relative enthalpy of C_2AS ($h_{\mathrm{rel},\varphi}(C_2AS; T)$) and CAS_2 ($h_{\mathrm{rel},\varphi}(CAS_2; T)$)

For the determination of the temperature dependence of the enthalpic content of C_2AS and CAS_2 the following temperature dependences of their molar heat capacities $C_{\mathrm{m}}(T)$ [4] were used

$$C_{\mathrm{m}}(T) = A + B \cdot 10^{-3}\,T + C \cdot 10^{5}\,T^{-2} + D \cdot 10^{-6}\,T^{2} \qquad (5)$$

A, B, C, and D are the constants taken from tables [4]. (In the case of C_2AS and CAS_2 the constant $D = 0$.) Integrating this equation in the temperature limits $T_0 = 298\ \mathrm{K}$ and T and introducing numerical values of the constants A, B, and C the following relationships for $\Delta h_{\mathrm{cool},\varphi}(C_2AS; T)$ and $\Delta h_{\mathrm{cool},\varphi}(CAS_2; T)$ were obtained

$$\frac{-\Delta h_{\mathrm{cool},\varphi}(C_2AS; T)}{\mathrm{kJ\,kg^{-1}}} = -3.999 \times 10^{2} + 1.0053\frac{T}{\mathrm{K}} + 5.092 \times 10^{-5}\frac{T^{2}}{\mathrm{K}^{2}} + 2.854 \times 10^{4}\frac{T^{-1}}{\mathrm{K}^{-1}} \qquad (6)$$

and

$$\frac{-\Delta h_{\mathrm{cool},\varphi}(CAS_2; T)}{\mathrm{kJ\,kg^{-1}}} = -4.887 \times 10^{2} + 1.0683\frac{T}{\mathrm{K}} + 7.803 \times 10^{-5}\frac{T^{2}}{\mathrm{K}^{2}} + 4.868 \times 10^{4}\frac{T^{-1}}{\mathrm{K}^{-1}} \qquad (7)$$

The value of the arithmetic mean of the specific heat of dissolution of C_2AS ($\Delta h_{\mathrm{sol},\varphi}(C_2AS)$) was taken from work [5]

$$\Delta h_{\mathrm{sol},\varphi}(C_2AS) = (-3100 \pm 18)\ \mathrm{kJ\,kg^{-1}} \qquad (8)$$

This value can be used for the calculation because it was obtained in the same solvent mixture as that used in this work for the determination of the heats of dissolution of cooled products of the eutectic melt and CAS_2. The values of the heats of dissolution obtained at 298 K for CAS_2 ($\Delta h_{\mathrm{sol}}(CAS_2)$) are given in Table 2. Here also the value of the arithmetic mean obtained from seven values of $\Delta h_{\mathrm{sol}}(CAS_2)$ is presented together with the error in its determination. These quantities are denoted $\Delta h_{\mathrm{sol},\varphi}(CAS_2)$ and $\delta(\Delta h_{\mathrm{sol},\varphi}(CAS_2))$, respectively.

After adding the negative values of $\Delta h_{\mathrm{sol},\varphi}(C_2AS)$ (eqn (*8*)) or $\Delta h_{\mathrm{sol},\varphi}(CAS_2)$ (Table 2) to the right-hand side of eqn (*6*) or eqn (*7*), the temperature dependence of the specific relative enthalpy of C_2AS ($h_{\mathrm{rel},\varphi}(C_2AS; T)$) and CAS_2 ($h_{\mathrm{rel},\varphi}(CAS_2; T)$), respectively, was obtained

$$\frac{h_{\mathrm{rel},\varphi}(\mathrm{C_2AS};T)}{\mathrm{kJ\,kg^{-1}}} = 2.7001 \times 10^3 + 1.0053\frac{T}{\mathrm{K}} + 5.092 \times 10^{-5}\frac{T^2}{\mathrm{K}^2} + 2.854 \times 10^4\frac{T^{-1}}{\mathrm{K}^{-1}} \tag{9}$$

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

The errors in determination of $h_{\mathrm{rel},\varphi}(\mathrm{C_2AS};T)$ and $h_{\mathrm{rel},\varphi}(\mathrm{CAS_2};T)$ were calculated from the corresponding errors in determination of $\Delta h_{\mathrm{cool},\varphi}$ and $\Delta h_{\mathrm{sol},\varphi}$ on the basis of the Gauss law of spreading of errors. They are as follows

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

As in the tables [4] the errors are not presented we assumed that the relative error in the determination of $\Delta h_{\mathrm{cool},\varphi}$ of $\mathrm{C_2AS}$ or $\mathrm{CAS_2}$ at the equilibrium temperature 1658 K equals 1 %. Further we assumed that the values of $\delta(\Delta h_{\mathrm{cool},\varphi})$ of $\mathrm{C_2AS}$ and $\mathrm{CAS_2}$ do not depend on temperature.

Table 2

Values of the specific heat of dissolution of $\mathrm{CAS_2}$ and the error in its determination

$\frac{-\Delta h_{\mathrm{sol}}(\mathrm{CAS_2})}{\mathrm{kJ\,kg^{-1}}}$	$\frac{-\Delta h_{\mathrm{sol},\varphi}(\mathrm{CAS_2})}{\mathrm{kJ\,kg^{-1}}}$	$\frac{\delta(\Delta h_{\mathrm{sol},\varphi}(\mathrm{CAS_2}))}{\mathrm{kJ\,kg^{-1}}}$
2916	2916	8
2921		
2910		
2901		
2925		
2924		
2913		

Calculation of the specific enthalpy of crystallization of $\mathrm{C_2AS}$ and $\mathrm{CAS_2}$ from the eutectic melt

Using the relationships (*4*), (*9*), and (*10*) the values of $h_{\mathrm{rel},\varphi}$ of the eutectic melt, $\mathrm{C_2AS}$ and $\mathrm{CAS_2}$, respectively, were determined at the equilibrium tem-

Table 3

Values of $h_{\mathrm{rel},\varphi}(\mathrm{X}; 1658\ \mathrm{K})$ of the eutectic melt, C_2AS, and CAS_2

Phase	$\frac{h_{\mathrm{rel},\varphi}(\mathrm{X}; 1658\ \mathrm{K})}{\mathrm{kJ\ kg^{-1}}}$
Eut. melt	4923 ± 18
C_2AS	4524 ± 23
CAS_2	4442 ± 17

perature of crystallization $T_{\mathrm{eq}} = 1658\ \mathrm{K}$. These data are together with the errors of their determination presented in Table 3. Introducing these values into eqn (*1*) the value of specific enthalpy of crystallization of the eutectic melt in the system C_2AS—CAS_2 was calculated at the temperature of 1658 K.

$$\Delta h_{\mathrm{cryst},\varphi}(\mathrm{eut.\ melt}; 1658\ \mathrm{K}) = (-441 \pm 23)\ \mathrm{kJ\ kg^{-1}} \qquad (11)$$

The error in the determination of the specific enthalpy of crystallization of the eutectic melt was calculated from the errors in determination of the specific relative enthalpy of each phase according to the relationship (*3*).

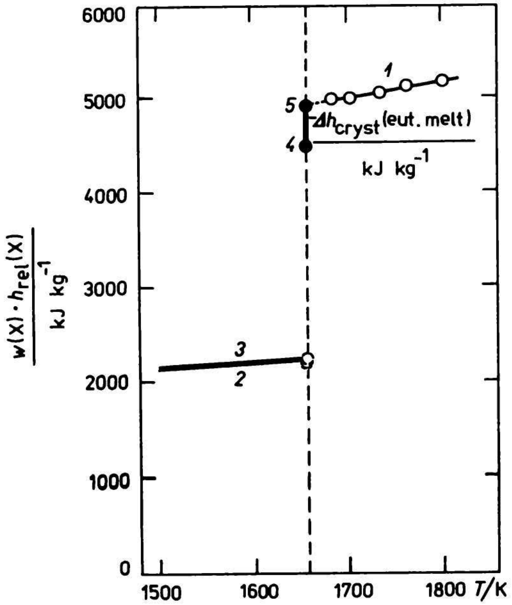

Fig. 1. Temperature dependences of $w(\mathrm{X}) \cdot h_{\mathrm{rel}}(\mathrm{X})$.
1. Eut. melt ($w(\mathrm{X}) = 1$); *2.* C_2AS ($w(C_2AS) = 0.4908$); *3.* CAS_2 ($w(CAS_2) = 0.5092$).
The value of $(-\Delta h_{\mathrm{cryst}}(\mathrm{eut.\ melt}; 1658\ \mathrm{K}))$ is given as the difference between the specific relative enthalpy of the eutectic melt at $T_{\mathrm{eq}} = 1658\ \mathrm{K}$ (point *5*) and the sum of specific relative enthalpies of the products of crystallization of the eutectic melt (C_2AS, CAS_2) at the same temperature multiplied by corresponding mass fractions of phases C_2AS and CAS_2 (point *4*).

In Fig. 1 the following data and relationships 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 dependence of h_{rel} of C_2AS and CAS_2 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 difference of $\sum_X w(X) h_{\text{rel},\varphi}(X;\ 1658\ \text{K})$ ($X \equiv C_2AS; CAS_2$) (point *4*) and the value of $h_{\text{rel},\varphi}(\text{eut. melt; } 1658\ \text{K})$ (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

$$\Delta s_{\text{cryst},\varphi}(\text{eut. melt; } 1658\ \text{K}) = \frac{\Delta h_{\text{cryst},\varphi}(\text{eut. melt; } 1658\ \text{K})}{1658\ \text{K}} =$$

$$= (-266 \pm 14)\ \text{J kg}^{-1}\ \text{K}^{-1} \qquad (12)$$

Determination of the heat of "total crystallization" of the eutectic melt in the system C_2AS—CAS_2

Heat evolved at the crystallization of the eutectic melt at $T_{\text{eq}} = 1658\ \text{K}$ added to the heat evolved at cooling of the products of crystallization (C_2AS and CAS_2) to the temperature of 298 K is denoted in this work as the "heat of total crystallization" ($\Delta h_{\Sigma\text{cryst},\varphi}(\text{eut. melt; } 1658\ \text{K} \rightarrow 298\ \text{K})$). Its value can be determined on the basis of the Hess law from the values of $h_{\text{rel},\varphi}$ of C_2AS and CAS_2 at the temperature of 298 K and the value $h_{\text{rel},\varphi}$ of the eutectic melt at the temperature of 1658 K. It follows

$$\frac{\Delta h_{\Sigma\text{cryst},\varphi}(\text{eut. melt; } 1658\ \text{K} \rightarrow 298\ \text{K})}{\text{kJ kg}^{-1}} = 0.4908\ \frac{h_{\text{rel},\varphi}(C_2AS;\ 298\ \text{K})}{\text{kJ kg}^{-1}} +$$

$$+ 0.5092\frac{h_{\text{rel},\varphi}(CAS_2;\ 298\ \text{K})}{\text{kJ kg}^{-1}} - 1 \cdot \frac{h_{\text{rel},\varphi}(\text{eut. melt; } 1658\ \text{K})}{\text{kJ kg}^{-1}} \qquad (13)$$

The values of $h_{\text{rel},\varphi}$ of C_2AS and CAS_2 at the temperature 298 K are in reality the negative values of the arithmetic mean of their specific heats of dissolution at this temperature.

Introducing the negative values of $\Delta h_{\text{sol},\varphi}(C_2AS)$ (eqn (*8*)) and $\Delta h_{\text{sol},\varphi}(CAS_2)$ (Table 2) and the value of $h_{\text{rel},\varphi}(\text{eut. melt; } 1658\ \text{K})$ (Table 3) into eqn (*13*) we obtain the value of the "heat of total crystallization" of the eutectic melt

$$\Delta h_{\Sigma \mathrm{cryst},\varphi}(\text{eut. melt; } 1658\ \mathrm{K} \rightarrow 298\ \mathrm{K}) = (-1917 \pm 20)\ \mathrm{kJ\ kg^{-1}} \qquad (14)$$

From comparison of the values of $\Delta h_{\mathrm{cryst},\varphi}$(eut. melt; 1658 K) and $\Delta h_{\Sigma \mathrm{cryst},\varphi}$(eut. melt; 1658 K → 298 K) (the relationships (*11*) and (*14*)) it follows that the heat formed at the crystallization of C_2AS and CAS_2 from the eutectic melt at the temperature of 1658 K presents only one quarter of the value of $\Delta h_{\Sigma \mathrm{cryst},\varphi}$(eut. melt; 1658 K → 298 K), while the heat evolved at cooling the phases C_2AS and CAS_2 from the temperature of 1658 K to 298 K contributes more than by three quarters to the value of the heat of "total crystallization" of the eutectic melt.

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