

Enthalpic Analysis of Melts in the $\text{CaO} \cdot \text{SiO}_2(\text{CS})\text{—}2\text{CaO} \cdot \text{SiO}_2(\text{C}_2\text{S})\text{—}2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2(\text{C}_2\text{AS})$ System

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The heats of solution of $\gamma\text{-C}_2\text{S}$ and $\beta\text{-C}_2\text{S}$ at temperature 298 K have been measured to reach the consistency of the values of relative enthalpy of melts in the $\text{CS—C}_2\text{S—C}_2\text{AS}$ system determined by two different methods: combination of measurements with the drop and solution calorimeters and the method of inverse drop calorimetry. Assuming that the athermal solutions are formed on the connecting line $\text{CS—C}_2\text{S}$, the temperature—composition dependence of relative enthalpy in the $\text{CS—C}_2\text{S—C}_2\text{AS}$ system has been determined by regressive analysis. On the basis of this dependence the enthalpies of mixing on formation of melts in part of the $\text{CS—C}_2\text{S—C}_2\text{AS}$ system, *i.e.* the $\text{C}_3\text{S}_2\text{—CS—C}_2\text{AS}$ subsystem, from the melts of CS , C_2S , and C_2AS at temperature 1873 K were calculated. The obtained values point to exothermic character of reactions on formation of the melts of this subsystem from the CS , C_2S , and C_2AS melts.

The experimental base of the enthalpic analysis of the melts in the $\text{CaO} \cdot \text{SiO}_2\text{—}2\text{CaO} \cdot \text{SiO}_2\text{—}2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ system are the values of the relative enthalpy of melts determined by two different calorimetric methods: double calorimetry from one sample [1—5] and inverse drop calorimetry [6, 7]. In further text, the symbols C, A, and S will be used for the CaO , Al_2O_3 , and SiO_2 oxides, respectively.

The relative enthalpy value of the silicate melt (H_{rel}) at chosen temperature T_c determined by the method of double calorimetry from one sample equals (except of the sign) the sum of the enthalpy change on cooling the sample of melt from T_c to 298 K (measured in a drop calorimeter) and of the heat of solution of the products of cooling of the melt in a mixture of inorganic acids at 298 K (measured in a solution calorimeter). The necessity to measure the heat of solution of products of cooling of the melt is due to the poorly reproducible state of the products of cooling. Cooling of the silicate melt in a drop calorimeter can be accompanied by an incomplete vitrification or crystallization. When using the method of inverse drop calorimetry the relative enthalpy value of the silicate melt at T_c is equal to the measured change of enthalpy on heating the sample of crystalline phase or the mixture of crystalline phases from 298 K to T_c . At this temperature the melt is formed directly in the calorimeter. The reference states used in both these methods are different. In the first case it is the state of solution of the products of cooling of the melt in the mixture of aqueous solutions of hydrofluoric and hydrochloric acids at 298 K and in the second case it is the state of the mixture of crystalline phases at 298 K.

The mutual consistency of relative enthalpies of melts in the $\text{CS—C}_2\text{S—C}_2\text{AS}$ system determined by these two methods is the prerequisite for their utilization in enthalpic analysis of this system. Therefore, it was necessary to calculate the values of relative enthalpies determined by the second method to the reference state corresponding to the first method, using the measured heats of solution of some crystalline phases.

The aim of the present work is to determine the temperature—composition dependence of the consistent values of relative enthalpy of melts of the $\text{CS—C}_2\text{S—C}_2\text{AS}$ system and to determine the values of enthalpy of mixing on formation of the melts of this system from the melts of pure components at 1873 K.

EXPERIMENTAL

The values of the relative enthalpy of the ternary eutectic melt in the $\text{C}_3\text{S}_2\text{—CS—C}_2\text{AS}$ system and those of the ternary peritectic melt in the $\text{CS—C}_2\text{S—C}_2\text{AS}$ system related to the reference state of the mechanical mixtures of crystalline phases of $\gamma\text{-C}_2\text{S}$, CS , C_2AS and $\beta\text{-C}_2\text{S}$, CS , C_2AS , respectively, at temperature 298 K were measured in previous works [6, 7] by the method of inverse drop calorimetry. The mechanical mixtures of crystalline phases were prepared in the ratio necessary for formation of eutectic or peritectic melt.

Because the values of the heats of solution of crystalline phases of CS (pseudowollastonite) and C_2AS (gehlenite) have already been determined [2, 5], it was necessary to measure only the heats of solution of crys-

talline phases γ -C₂S and β -C₂S at temperature 298 K on the solution calorimeter. The purity of both crystalline phases (OZNC, Podolsk, Russia) was verified by X-ray diffraction analysis. The aqueous solution of hydrofluoric acid ($w(\text{HF}) = 40\%$) and hydrochloric acid (1 volume part of HCl ($w(\text{HCl}) = 35\text{--}38\%$) and 1 volume part of H₂O) in the volume ratio 2 : 1, saturated with CaF₂ ($\rho(\text{CaCO}_3 \text{ in dissolving mixture}) = 150 \text{ mg dm}^{-3}$) was used as the solvent.

RESULTS AND DISCUSSION

Determination of the Temperature—Composition Dependence of Relative Enthalpy of Melts in the CS—C₂S—C₂AS System

The values of relative enthalpy of seven melts in the CS—C₂S—C₂AS system (its phase diagram is in [8]) determined with the exception of one composition at five temperatures are given in Table 1 and the compositions of pertinent melts are in Fig. 2 marked by circles. The composition of the melts is expressed in mole fractions of CS and C₂AS ($x(\text{CS})$, $x(\text{C}_2\text{AS})$) and the values of molar relative enthalpy of melts are related to 1 mol of the CS—C₂S—C₂AS system. To calculate the values of molar relative enthalpy of the melts 2, 3, 5, and 6 from the measured values of their specific relative enthalpy, it was necessary to know their molar masses $M(\text{CS—C}_2\text{S—C}_2\text{AS})$. These were obtained from the relation

Table 1. Database for Calculation of Regression Function $H_{\text{rel}}(\text{CS—C}_2\text{S—C}_2\text{AS}) = f(x(\text{CS}), x(\text{C}_2\text{AS}), T)$

No.	$x(\text{CS})$	$x(\text{C}_2\text{AS})$	T	$H_{\text{rel}}(\text{CS—C}_2\text{S—C}_2\text{AS})$
			K	kJ mol ⁻¹
1	1.0	0.0	1830	550.8
			1850	553.9
			1875	557.6
			1900	561.3
			1950	568.9
2	0.8751	0.1249	1707	619.7 ± 2.2
			1745	627.7 ± 3.1
			1768	630.2 ± 1.2
			1798	638.0 ± 2.9
			1819	642.8 ± 2.3
3	0.8078	0.1922	1622	651.7 ± 5.1
			1667	663.5 ± 5.4
			1724	673.2 ± 2.6
			1767	684.1 ± 3.6
			1823	696.7 ± 4.1
4	0.0	1.0	1873	1482.2 ± 16.1
			1888	1487.1 ± 9.6
			1908	1501.5 ± 16.0
			1932	1513.6 ± 14.8
			1948	1519.1 ± 7.1
5	0.7559	0.1707	1653	670.2 ± 5.2
			1675	676.8 ± 4.9
			1701	684.2 ± 6.9
			1722	689.2 ± 5.4
			1748	693.5 ± 5.7
6	0.6682	0.1777	1773	703.2 ± 5.7
			1624	681.7 ± 8.0
			1654	690.1 ± 7.8
			1684	698.6 ± 7.6
			1714	706.8 ± 7.5
7	0.0	0.0	1775	723.8 ± 7.5
			1600	829.9
			1700	850.8
			1800	871.7
			1900	892.6
			2000	913.6

Table 2. The Values of the Heat of Solution of γ -C₂S and β -C₂S and the Values of their Arithmetic Mean

X_k	$-\Delta_{\text{sol}}h(X_k; 298 \text{ K})$							$-\Delta_{\text{sol},\Phi}h(X_k; 298 \text{ K})$
	J g ⁻¹							J g ⁻¹
γ -C ₂ S	2956	2900	2933	2903	2911	2945	2950	2928 ± 22
β -C ₂ S	2908	2902	2885	2874	2909	2864		2890 ± 20

$$M(\text{CS—C}_2\text{S—C}_2\text{AS}) = x(\text{CS}) M(\text{CS}) + x(\text{C}_2\text{S}) M(\text{C}_2\text{S}) + x(\text{C}_2\text{AS}) M(\text{C}_2\text{AS}) \quad (1)$$

where x and M are mole fractions and molar masses of pure components CS, C₂S, and C₂AS in the pertinent mixtures, respectively.

The relation between the mole fractions $x(\text{CS})$, $x(\text{C}_2\text{S})$, and $x(\text{C}_2\text{AS})$ and the mole fractions of oxides $x(\text{C})$ and $x(\text{A})$ is expressed by the equations

$$x(\text{CS}) = \frac{2 - 3x(\text{C}) - 2x(\text{A})}{1 - x(\text{C}) - x(\text{A})} \quad (2a)$$

$$x(\text{C}_2\text{S}) = \frac{2x(\text{C}) - 1}{1 - x(\text{C}) - x(\text{A})} \quad (2b)$$

$$x(\text{C}_2\text{AS}) = \frac{x(\text{A})}{1 - x(\text{C}) - x(\text{A})} \quad (2c)$$

The molar relative enthalpies of the melts 1—4 were determined on the basis of enthalpic data measured by the method of double calorimetry from one sample in works [1—5]. The relative enthalpies of 1 (melt CS), determined from the enthalpic data in [1, 2], were taken from [3], the relative enthalpies of 2 from [3], 3 from [4], and 4 from [5]. To calculate the error of their determination, only the error of the arithmetic mean of the heat of solution, corrected by the Student's coefficient on the level of reliability 0.95, has been considered. The error of one measurement of heat of cooling was in most cases several times smaller than the error of the determination of arithmetic mean of the heat of solution and, therefore, it was neglected.

The values of molar relative enthalpy of melts 5 (the ternary eutectic melt) and 6 (the ternary peritectic melt) at temperature T were determined on the basis of the relation

$$H_{\text{rel}}(\text{melt}, T) = M(\text{CS—C}_2\text{S—C}_2\text{AS}) \cdot \left[\sum_{k=1}^3 w(X_k)(-\Delta_{\text{sol},\Phi}h(X_k, 298 \text{ K})) + h_{\text{rel},1}(\text{melt}, T) \right] \quad (3)$$

where $w(X_k)$ are the pertinent mass fractions of crystalline phases γ -C₂S, CS, and C₂AS and β -C₂S, CS, and C₂AS in mechanical mixtures needed for the formation of melts 5 and 6 [6, 7], $\Delta_{\text{sol},\Phi}h(X_k, 298 \text{ K})$ are the values of arithmetic mean of the specific heat of solution of the pertinent crystalline phases at temperature 298 K, and $h_{\text{rel},1}(\text{melt}, T)$ are the specific relative enthalpy values of melt 5 or 6 at temperature T related to the reference state of the pertinent mixture of

crystalline phases at temperature 298 K, determined by the inverse drop calorimetry method (SETARAM HTC 1800 K) in [6, 7]. The measured values of heat of solution of γ -C₂S and β -C₂S at temperature 298 K as well as the values of their arithmetic means are given in Table 2.

With regard to relatively high errors of the measurement of the heats of solution, the difference between the values of the arithmetic mean of heat of solution of γ -C₂S and β -C₂S is not significant. From the physical point of view, the enthalpy of β -C₂S is higher than that of γ -C₂S. The values of the enthalpy of formation of β -C₂S and γ -C₂S at 298 K confirm this fact. However, these values are similar and, thus, the enthalpy of transformation of β -C₂S to γ -C₂S at 298 K, calculated from the data of enthalpy of formation of these phases according to [9], is relatively small ($-10.4 \text{ kJ mol}^{-1}$). Errors of determination of relative enthalpy of melts 5 and 6 were calculated using the Gauss law of spreading of errors considering the Student's coefficient on the reliability level 0.95.

The values of relative enthalpy of the undercooled melt C₂S in the temperature interval 1600—2000 K have been calculated according to the relation

$$H_{\text{rel}}(\text{C}_2\text{S, melt}; T) = M(\text{C}_2\text{S})(-\Delta_{\text{sol},\Phi}h(\gamma\text{-C}_2\text{S}; 298 \text{ K})) + \Delta_f H(\text{C}_2\text{S, melt}; T_{\text{fus}}) + \int_{T_{\text{fus}}}^T C_p(\text{C}_2\text{S, melt}; T) dT - \Delta_f H(\gamma\text{-C}_2\text{S}; 298 \text{ K}) \quad (4)$$

on the basis of the measured specific heat of solution of γ -C₂S at 298 K and the data of molar enthalpy of formation of γ -C₂S at 298 K ($\Delta_f H(\gamma\text{-C}_2\text{S}; 298 \text{ K})$), molar enthalpy of formation of the C₂S melt at temperature of its fusion ($\Delta_f H(\text{C}_2\text{S, melt}; T_{\text{fus}})$), and molar heat capacity of the C₂S melt ($C_p(\text{C}_2\text{S, melt}; T)$) taken from [9]. The database of relative enthalpies of melts of the CS—C₂S—C₂AS system was thus completed, besides the values for the CS melt (1) and C₂AS melt (4), with the values for the third component of the studied system (the melt 7).

The molar relative enthalpies of melts in the CS—C₂S—C₂AS system presented in Table 1 were processed by multilinear regressive analysis based on the least-squares method. By comparison of statistical parameters several models of regression dependence $H_{\text{rel}}(\text{CS—C}_2\text{S—C}_2\text{AS}) = f(x(\text{CS}), x(\text{C}_2\text{AS}), T)$ in

Table 3. Exponents a_i , b_i , c_i and Coefficients B_i for Individual Mixed Terms of Regression Polynomial $H_{\text{rel}}(\text{CS}-\text{C}_2\text{S}-\text{C}_2\text{AS}) = \sum_i B_i(x(\text{CS}))^{a_i}(x(\text{C}_2\text{AS}))^{b_i}T^{c_i}$

	a_i	b_i	c_i	B_i	$\sigma(B_i)$
				$\text{kJ mol}^{-1} \text{K}^{-c_i}$	$\text{kJ mol}^{-1} \text{K}^{-c_i}$
1	0	0	0	461.8403	7.9717
2	2	0	0	-232.0578	18.8824
3	0	0	1	0.2273	0.0044
4	1	0	1	-0.1767	0.0027
5	2	0	1	0.1241	0.0103
6	0	2	1	0.3167	0.0010
7	1	1	1	0.2361	0.0044

the form of polynomial $H_{\text{rel}}(\text{CS}-\text{C}_2\text{S}-\text{C}_2\text{AS}) = \sum_i B_i(x(\text{CS}))^{a_i}(x(\text{C}_2\text{AS}))^{b_i}T^{c_i}$ were tested. The exponents a_i , b_i were chosen as integer values ≤ 3 and the exponent $c_i \leq 1$.

However, the values of relative enthalpy in the binary CS—C₂S system calculated according to these formal models were unreal and led to considerably high values of enthalpy of mixing in the region of composition of melts close to that of C₃S₂ (crystalline phase of this composition is rankinite). This was inconsistent with the fact that the value of enthalpy of reaction at formation of rankinite from pseudowollastonite and γ -C₂S at temperature 298 K, determined from their enthalpies of formation according to [9], was small. The enthalpy of reaction at formation of rankinite from minerals makes only approximately 0.5 % of the value of enthalpy of formation of rankinite from elements so that the enthalpy of reaction at formation of rankinite from pseudowollastonite and γ -C₂S is neglected. Because on formation of rankinite from pseudowollastonite and γ -C₂S reorganization of bonds is more extensive than on formation of C₃S₂ melt from the melts of CS and C₂S, it can be assumed that also the heat effect of mixing of melts CS and C₂S will be negligible and the melts in the CS—C₂S system can be taken for athermal solutions. On the basis of this consideration the database of relative enthalpies of melts in the CS—C₂S—C₂AS system has been completed with relative enthalpies of another nine melts on the connecting line CS—C₂S with the mole fraction CS $x(\text{CS}) = 0.1, \dots, 0.9$. The relative enthalpy values of these melts at pertinent temperature (for each melt five temperatures were considered) have been calculated from the values of relative enthalpy of melts CS and C₂S according to the relation

$$H_{\text{rel}}(\text{CS}-\text{C}_2\text{S}, \text{melt}; T) = x(\text{CS}) H_{\text{rel}}(\text{CS}, \text{melt}; T) + (1 - x(\text{CS})) H_{\text{rel}}(\text{C}_2\text{S}, \text{melt}; T) \quad (5)$$

and with regard to the relation (7), they led to zero values of the enthalpy of mixing on the CS—C₂S straight line (model for athermal solutions).

From this extended database the values of relative enthalpy of the melts in the CS—C₂S—C₂AS system

were processed again by multilinear regressive analysis. It was shown that the most convenient polynomial for temperature—composition dependence of relative enthalpy of melts in the CS—C₂S—C₂AS system is the model "2213" where the figures in the order 2,2,1,3 designate the highest powers of variables $x(\text{CS})$, $x(\text{C}_2\text{S})$, T and the maximum total degree ($a_i + b_i + c_i$) at mixed terms of regression polynomial. The exponents a_i , b_i , c_i , the found coefficients B_i , and the standard deviations of these coefficients $\sigma(B_i)$ for individual terms of the regression model "2213" are given in Table 3.

Differentiating the temperature—composition regression dependence of molar relative enthalpy of melts in the CS—C₂S—C₂AS system with respect to temperature the composition dependence of the molar heat capacity of melts of this system has been obtained

$$C_p(\text{CS}-\text{C}_2\text{S}-\text{C}_2\text{AS}, \text{melt})/(\text{kJ mol}^{-1} \text{K}^{-1}) = 0.2273 - 0.1767 x(\text{CS}) + 0.1241 (x(\text{CS}))^2 + 0.3167 (x(\text{C}_2\text{AS}))^2 + 0.2361 x(\text{CS}) x(\text{C}_2\text{AS}) \quad (6)$$

The composition dependence of the values of molar heat capacity of melts in the binary C₂AS—CS system calculated according to the relation (6) (solid line) and that obtained on the basis of the heat capacity data taken from [10] (dashed line) are illustrated in Fig. 1. In work [10] the heat capacity data of the melts in the binary C₂AS—CS system are included in the heat capacity data of the melts in the ternary CS—CAS₂—C₂AS system. The agreement between both composition dependences of molar heat capacity of melts in the C₂AS—CS system was found to be relatively good, although the values of molar heat capacity of melts in the C₂AS—CS system calculated according to (6) were greater than those obtained from [10].

Enthalpy of Mixing on Formation of the Melts in the CS—C₂S—C₂AS System

The temperature—composition dependence of the molar relative enthalpy of the melts in the CS—C₂S—C₂AS system makes possible to calculate the enthalpy of mixing on the formation of melts in this system from

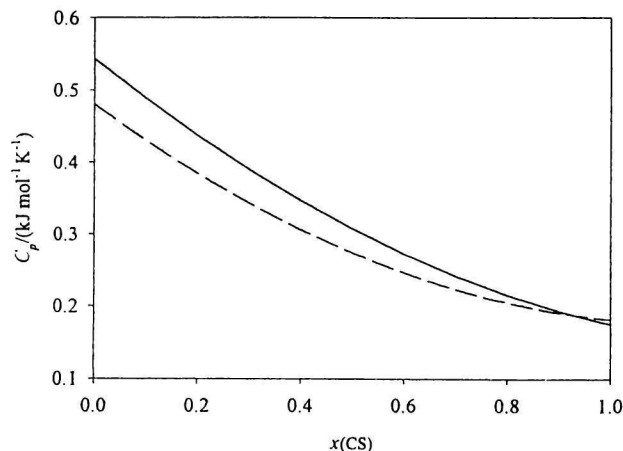


Fig. 1. The composition dependence of the molar heat capacity of the melts in the C_2AS — CS system calculated according to relation (6) (—); calculated according to [10] (---).

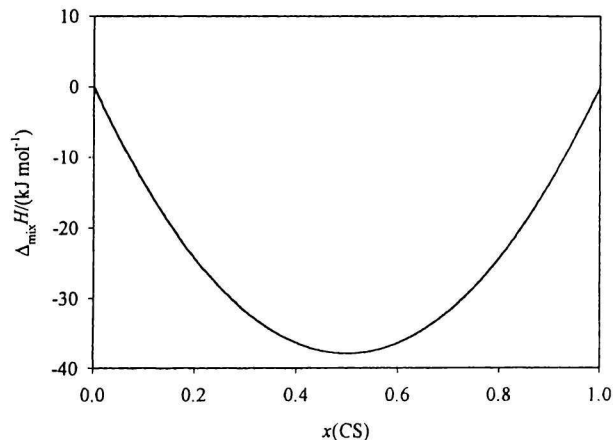


Fig. 3. Enthalpy of mixing in the C_2AS — CS system at temperature 1873 K related to 1 mol of mixture of the CS — C_2S — C_2AS system.

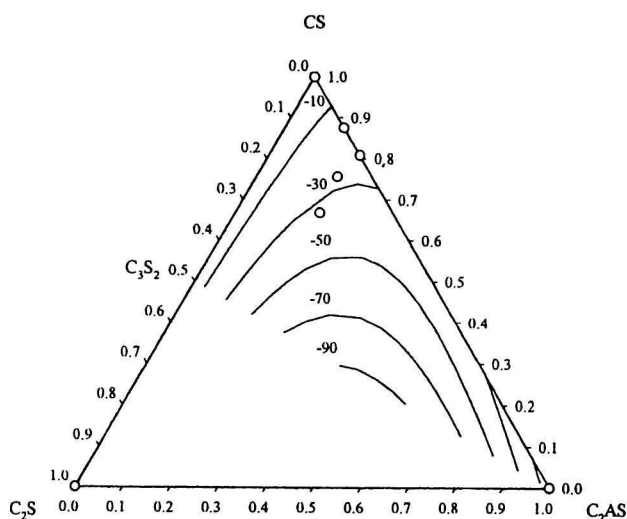


Fig. 2. Enthalpy of mixing in the C_3S_2 — CS — C_2AS system at temperature 1873 K (parameter of curves: $\Delta_{\text{mix}}H(1873 \text{ K})/(\text{kJ mol}^{-1})$) related to 1 mol of mixture of the CS — C_2S — C_2AS system.

the molten pure components. According to the Hess law, for the enthalpy of mixing the following relation is valid

$$\begin{aligned} \Delta_{\text{mix}}H(\text{CS—}C_2\text{S—}C_2\text{AS, melt}) &= \\ &= H_{\text{rel}}(\text{CS—}C_2\text{S—}C_2\text{AS, melt}) - \\ &- \sum_{k=1}^3 x(Y_k) H_{\text{rel}}^0(Y_k, \text{melt}) \end{aligned} \quad (7)$$

where $x(Y_k)$ are the mole fractions of CS , C_2S , and C_2AS in the melt of pertinent composition and $H_{\text{rel}}^0(Y_k, \text{melt})$ are the molar relative enthalpies of melts of pure components CS , C_2S , and C_2AS at chosen temperature T_c .

The enthalpies of mixing in the C_3S_2 — CS — C_2AS

subsystem of the CS — C_2S — C_2AS system at chosen temperature $T_c = 1873 \text{ K}$ are drawn in Fig. 2. The composition dependence of enthalpy of mixing in the binary C_2AS — CS system at the same temperature is illustrated in Fig. 3. As seen from Fig. 2, the enthalpies of mixing on formation of melts in the C_3S_2 — CS — C_2AS subsystem at 1873 K are, except for the straight line C_3S_2 — CS , negative. Consequently, formation of melts of this subsystem from the melts of pure components CS , C_2S , and C_2AS is accompanied by exothermic reaction between their structural particles.

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