

Distribution of sulfur between liquid iron and the system CaO—MgO—Al₂O₃

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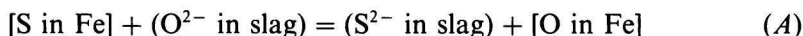
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The standard reaction Gibbs energies of the distribution of sulfur between Fe(l) and the system CaO—Al₂O₃ were determined by means of the electrochemical measurement of the oxygen activity in the metal and of the FeO activity in the ionic melt at the temperature of 1600 °C. The distribution coefficient of sulfur $L(S, \text{exp})$ is in agreement with the calculated one on the basis of the oxygen activity in the metal and of the optical basicity of the system CaO—MgO—Al₂O₃. The agreement of $L(S, \text{exp})$ and $L(S, \text{calc})$ shows an ideal behaviour of sulfur in the metal. The activity coefficient $\gamma(\text{CaS})$ does not change with the composition.

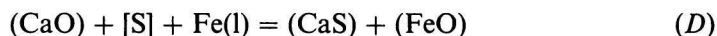
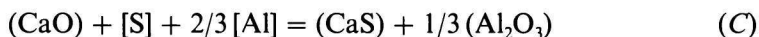
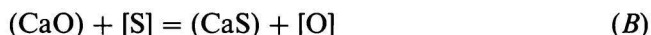
The basis of a number of metallurgical processes is the distribution of components between two immiscible melts — the ionic and metallic ones. Among the most important reactions belongs the distribution of oxygen, aluminium, and sulfur [1—4].

The exchange reaction at the phase boundary can be expressed in the ionic form



where the angular brackets denote the component in the metal and the round ones in the melt. From the reaction (A) it is obvious that the distribution of sulfur depends on the activity of ions O^{2-} , e.g. the acid-base character of the melt, and on the oxygen activity in the metal.

With regard to the fact that the activity of ions in the concentrated solutions cannot be determined, it is convenient in the case of a thermodynamic approach to express the desulfurization using the CaO-based ionic melts in the molecular form



It is also necessary to express the basicity in a different way, not by means of

the O^{2-} activity. The basicity may be expressed for example as the sulfide capacity or by means of the optical basicity. The sulfide capacity is defined in the reaction slag—gas with the following relation [5]

$$C_s = 10^2 w(S) [p(O_2)/p(S_2)]^{1/2} \quad (I)$$

where $w(S)$ is the mass fraction of sulfur in the slag and $p(O_2)$ and $p(S_2)$ is the partial pressure of oxygen and sulfur in the gaseous phase, respectively. The C_s value may be determined also by means of the reaction slag—metal [1].

The optical basicity was defined on the basis of the $d^{10}s^2$ ions spectra shift in the UV region in [6, 7] and for the oxide systems it can be calculated from the composition.

The aim of the present work was to describe the distribution of sulfur on the basis of the electrochemical measurement of the oxygen activity in the metal [Fe—O—Al—S] and of the oxidation potential of the melt (CaO—Al₂O₃) and (CaO—MgO—Al₂O₃) at the temperature of 1600 °C and to look for the relation between the acid-base character of the ionic melt, the oxygen activity in the metal deoxidized with aluminium, and the sulfide capacity of the slag. Iron(II) oxide was not added to the melt. However, after blowing the system with argon it was formed in the ionic melt and therefore the reaction (D) had to be also considered.

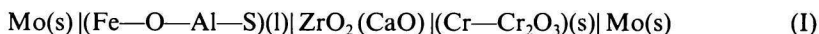
Experimental

The samples were prepared in a high-frequency furnace GV-22. The iron melt was adjusted by adding of iron(II) sulfide to a sulfur content of 0.035—0.045 mass % and deoxidized with aluminium to an oxygen content of *ca.* 0.001 mass %.

The ionic melt was prepared by mixing of the individual anal. grade purity oxides and by melting in a PtRh crucible.

The measurements were carried out in a Tammann resistance furnace. The experimental device used is shown in Fig. 1. The temperature was measured using a PtRh30—PtRh6 thermocouple immersed directly in the melt. To provide a faster equilibrium constitution the system was blown with argon (the flow rate was *ca.* $2 \times 10^{-3} \text{ dm}^3 \text{ s}^{-1}$) through a double corundum capillary during 10 min.

For the measurement of the partial oxygen pressure in the metal the galvanic cell



was used. The activity of FeO in the ionic melt was determined using the galvanic cell



The oxygen electrode consisted of a reference mixture (Cr—Cr₂O₃) and of a ZrO₂ solid electrolyte. The electrode was immersed both in the metallic (cell I) as well as in the ionic

melt (cell II). Details on the measurement in both liquid phases and the determination of oxygen activity in the metal and of the FeO activity in the ionic melt are given in [8]. The Fe_2O_3 content due to its very low value was neglected and the measured component was not expressed as Fe_tO , but as FeO.

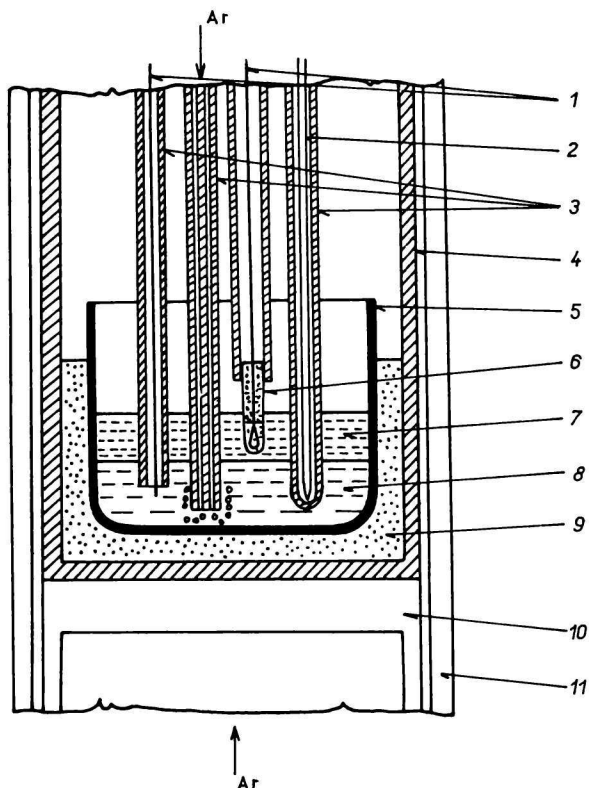


Fig. 1. Scheme of the experimental device.

1. Contact; 2. thermocouple; 3. protecting Al_2O_3 tube; 4. corundum cylinder; 5. Al_2O_3 or MgO crucible; 6. oxygen electrode; 7. slag melt; 8. metallic melt; 9. Al_2O_3 isolation; 10. ceramic basis; 11. heating graphite tube.

The measurement was realized at the temperature of $(1600 \pm 10)^\circ\text{C}$. The EMF values and the temperatures were registered using an SE 463 GOERZ recorder.

After the measurements over, the samples of the ionic melt were removed using a corundum stick and the metal samples using an evacuated silica tube.

The sulfur content in the metallic and nonmetallic phase was determined by means of the LECO CS-244 analyzer, the analysis of individual elements was realized using the AAS method.

Results and discussion

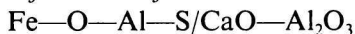
The results of the equilibrium distribution of components in the system metal—ionic melt are given in Table 1. In the table the SiO₂ content is not given; it attains the value of *ca.* 1 mass %.

Samples 1—7 represent the system CaO—Al₂O₃ measured in a corundum crucible. Samples 8—20 represent the system CaO—MgO—Al₂O₃ measured in a magnesia crucible. Samples 17—20 represent composition of the melt in which 5 mass % MgO was added.

Table 1
The equilibrium composition of the slag and the metal

Sample	Slag w _i /%					Metal w _i /%		a[O] 10 ⁴
	CaO	Al ₂ O ₃	FeO	CaS	MgO	S	Al	
1	42.33	56.53	0.06	0.25	—	0.0045	0.010	9
2	42.16	56.28	0.08	0.41	—	0.0080	0.006	8
3	40.63	56.81	0.14	0.27	—	0.0107	0.007	23
4	38.20	59.35	0.10	0.23	—	0.0110	0.006	23
5	38.46	58.32	0.15	0.19	—	0.0095	0.007	12
6	40.12	57.92	0.14	0.24	—	0.0051	0.009	6
7	39.74	56.76	0.11	0.24	—	0.0055	0.007	9
8	45.15	45.59	0.09	0.25	7.14	0.0075	0.001	21
9	36.50	50.68	0.11	0.18	9.83	0.0062	0.001	13
10	41.25	48.12	0.15	0.26	8.62	0.0044	0.008	10
11	38.10	49.11	0.12	0.18	9.65	0.0058	0.001	14
12	35.74	52.09	0.07	0.19	10.51	0.0035	0.019	6
13	36.76	50.88	0.04	0.20	9.89	0.0027	0.005	6
14	39.14	50.17	0.06	0.23	9.80	0.0026	0.045	11
15	34.85	50.84	0.13	0.19	10.00	0.0053	0.003	10
16	34.82	52.45	0.06	0.21	11.05	0.0048	0.008	12
17	36.39	54.71	0.22	0.45	7.40	0.0077	0.076	5
18	40.24	50.20	0.21	0.47	7.97	0.0033	0.053	5
19	42.96	48.37	0.17	0.44	7.32	0.0020	0.029	6
20	50.02	42.07	0.13	0.44	6.52	0.0018	0.059	7

From the values in Table 1 it is obvious that after attaining the equilibrium, in samples 8—20 an increase of the MgO content to the values of 8—12 mass % occurs. This fact is in agreement with the phase diagram of the system CaO—MgO—Al₂O₃ and with other experimental results at the same temperature [3].

Thermodynamics of the desulfurization reactions in the system

For the study of the ionic system $\text{CaO—Al}_2\text{O}_3$ (in corundum crucibles) those figurative points in the phase diagram [9] were chosen at which the liquid phase at 1600°C was assumed. Using the values of the oxygen activity in the metal and of the FeO activity in the slag, obtained from the experimental data, as well as from the analysis of the metallic and nonmetallic phase the values of the equilibrium constants of the desulfurization reactions ($B—D$) were calculated.

The values of the CaO and Al_2O_3 activities were taken from [2]. For the $a(\text{CaS})$ calculation the value of the activity coefficient $\gamma(\text{CaS}) = 20$ given in [4] was used. According to the equation

$$\Delta G^\circ = -RT \ln K_a \quad (2)$$

the values of the respective standard Gibbs energies were calculated.

Into the relation for the equilibrium constant of the reactions ($B—D$) the values of $w[\text{S}]$ and $w[\text{Al}]$ in % instead of $a[\text{S}]$ and $a[\text{Al}]$ were inserted. This procedure is fully correct. The Henry's activity $a[\text{X}]$ is defined by means of the difference between the chemical potential in the liquid iron, $\mu[\text{X}]$, and that in the hypohetic solution $[\text{Fe} + 1 \text{ mass } \% \text{ X}]$, $\mu^\circ[\text{X}]$. The Henry's activity coefficient $f[\text{X}]$ is in relation to $a[\text{X}]$ according to the equation

$$f[\text{X}] = 10^{-2} a[\text{X}]/w[\text{X}] \quad (3)$$

From the definition it follows

$$\lim_{w[\text{X}] \rightarrow 0} f[\text{X}] = 1 \quad (4)$$

and also

$$\lim_{w[\text{X}] \rightarrow 0.01} a[\text{X}] = 1 \quad (5)$$

The values of $f[\text{S}]$ and $f[\text{Al}]$ at the temperature of 1600°C may be calculated using the interaction parameters of the first order given in [10] and are for the contents of components given in Table 1 equal to one. The measured and calculated parameters are given in Table 2.

The theoretical values of the Gibbs energies of the desulfurization reactions at 1600°C were calculated on the basis of the thermodynamic values [11]: $\Delta G_2^\circ = 56500 \text{ J mol}^{-1}$, $\Delta G_3^\circ = -103200 \text{ J mol}^{-1}$, $\Delta G_4^\circ = 34100 \text{ J mol}^{-1}$. The theoretical values for the reactions ($B—D$) given in the literature are: $\Delta G_2^\circ = 52000 \text{ J mol}^{-1}$ [4], $\Delta G_3^\circ = -105400 \text{ J mol}^{-1}$ [2], and $\Delta G_4^\circ = 27600 \text{ J mol}^{-1}$ [4]. From the experimental data only the value for the reaction (C), $\Delta G_3^\circ =$

= $-107800 \text{ J mol}^{-1}$ [2], obtained using another method than in the present work, is available.

Comparing our experimentally obtained values (Table 2) $\Delta G_2^\circ = (45200 \pm \pm 5000) \text{ J mol}^{-1}$, $\Delta G_3^\circ = (-102200 \pm 3500) \text{ J mol}^{-1}$, and $\Delta G_4^\circ = (33000 \pm \pm 3600) \text{ J mol}^{-1}$ with the theoretical ones, a very good accordance especially for reactions (C) and (D) may be noted. At the ΔG° values the reliability interval on the 0.95 confidence level is given.

Table 2

Thermodynamic data for the system $\text{CaO}-\text{Al}_2\text{O}_3$ at the temperature of 1600°C

Sample	$a(\text{CaO})$	$a(\text{Al}_2\text{O}_3)$	$a(\text{FeO}) \cdot 10^4$	$\frac{\Delta G_2^\circ}{\text{J mol}^{-1}}$	$\frac{\Delta G_3^\circ}{\text{J mol}^{-1}}$	$\frac{\Delta G_4^\circ}{\text{J mol}^{-1}}$
1	0.181	0.160	24	44600	-103000	29200
2	0.186	0.158	24	47900	-106700	30800
3	0.166	0.173	27	36400	-97300	38000
4	0.133	0.234	28	39700	-101200	36700
5	0.141	0.219	35	51500	-96000	35000
6	0.155	0.191	18	51200	-105500	34000
7	0.158	0.186	29	45200	-105900	27100
Mean				45200	-102200	33000

Sulfide capacity and distribution coefficient of sulfur

On the basis of the obtained data given in Table 1 the values of the optical basicity for all measured systems were calculated according to [7].

The sulfide capacity C_S was calculated from eqn (6), which was derived from the relation (1) including the reactions of the dissolution of oxygen and sulfur in molten iron

$$\log C_S = \log \left(\frac{a[\text{O}] w(\text{S}) 10^2}{a[\text{S}]} \right) + \frac{936}{T} - 1.375 \quad (6)$$

The dependence of the sulfide capacity on the optical basicity for the measured systems at 1600°C is shown in Fig. 2. A linear dependence of $\log C_S$ on the optical basicity A of the ionic melt was found

$$\log C_S = 13.26 A - 12.22 \quad (7)$$

The correlation coefficient of the calculated straight line (7) $r = 0.86$. Analogical dependences according to [3] and [12] are also shown in Fig. 2.

The distribution coefficient of sulfur $L(S, \text{exp})$ was determined directly from the sulfur content in the metal and in the ionic melt

$$L(S, \text{exp}) = \frac{w(S)}{w[S]} \quad (8)$$

The distribution coefficient $L(S, \text{calc})$, derived from eqns (6) and (7), was calculated from the equation

$$\log L(S, \text{calc}) = 13.26 \Lambda - \log a[\text{O}] - 11.35 \quad (9)$$

The comparison of the $L(S, \text{exp})$ and $L(S, \text{calc})$ values is shown in Fig. 3.

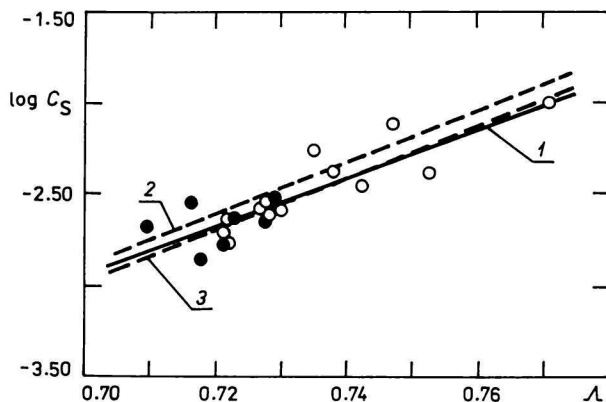


Fig. 2. Dependence of the sulfide capacity on the optical basicity at 1600 °C.

1. Our results; 2. and 3. according to [3] and [12]. ● System $\text{CaO}-\text{Al}_2\text{O}_3$, ○ system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3$.

It may be concluded that a good accordance was found between the sulfide capacity values, obtained by three independent methods:

- fast constitution of equilibrium after gas blowing into the system slag—metal with the electrochemical indication of the oxygen distribution (this paper),

- long-termed constitution of equilibrium in the same system (*ca.* 4 h) presented in [3],

- from dependences taken from [12], determined by the regression analysis of till now published values of the sulfide capacity on the basis of the equilibrium slag—gas.

A relatively good accordance of $L(S, \text{exp})$ and $L(S, \text{calc})$ values shows that at a given composition the sulfur behaves ideally in the metal and the activity coefficient $\gamma(\text{CaS})$ does not change with the composition.

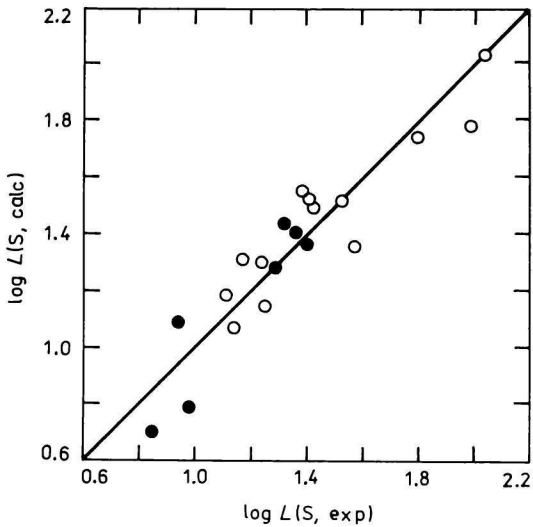


Fig. 3. Dependence of $\log L(S, \text{calc})$ on $\log L(S, \text{exp})$ at 1600 °C.
 ● System CaO—Al₂O₃, ○ system CaO—MgO—Al₂O₃.

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