

EQUILIBRIUM OF REDUCTION OF TITANIUM OXIDES FROM BLAST-FURNACE-TYPE SLAGS OF THE CaO–MgO–SiO₂–Al₂O₃–TiO₂ SYSTEM IN LIQUID PHASES

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ABSTRACT

Experiments on the reduction of hypothetical TiO₂ from the 5-component slag of the CaO–MgO–SiO₂–Al₂O₃–TiO₂ system and on titanium transfer to metal saturated with carbon were carried out up to the equilibrium state which was reached after 6 hours at temperatures of 1723, 1773 and 1823 K. On the basis of the experimental data, the free enthalpy and equilibrium constants of reduction of hypothetical TiO₂ from slag with simultaneous dissolution of Ti in metal, as well as the activities and activity coefficients of Ti dissolved in metal and TiO₂ in slag in equilibrium conditions, were determined.

INTRODUCTION

The behaviour of titanium in the blast furnace, its distribution between metal and slag, as well as the basic thermodynamic functions have been quite adequately described in the literature. Investigations into the distribution of titanium between metal and slag were carried out under conditions more or less imitating those in the blast furnace with differences in the composition of the blast furnace slags and metals. Phenomenological thermodynamics, however, resulting from these experiments usually consider pure oxides. Only the present authors [1–5,8] have carried out their experiments under practical or laboratory conditions accurately imitating those of the blast furnace process.

In these experiments, synthetic multicomponent slags or those obtained by melting pre-reduced ore sinters were used, as in Łędzki's work [2]. From the experiments, it was found that the presence of titanium in pig iron resulted from several reactions following titanium transfer from slag to metal [6,7]. The results obtained by the present authors regarding the reduction of TiO₂ from slag displayed more or less significant differences.

Also taking into account the practical importance of the problem, (titano-magnetite concentrates of Polish polymetallic ores are being consid-

ered as future components of sinters) an extensive examination of the behaviour of titanium in the blast furnace has been undertaken. In the present paper, which is part of planned investigations, the authors examined the reduction of hypothetical TiO_2 from synthetic, blast-furnace-type slag and determined the reduction equilibrium of TiO_2 in the liquid phases under conditions corresponding to those in the blast furnace.

EXPERIMENTAL

Experiments were carried out in a Tamman furnace, type LEW, in a graphite crucible. The chemical compositions of the synthetic slags used in the $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2$ system are shown in Table 1. Metals used in experiments were obtained by carbonization of pure iron (Riedel de Haen) with graphite up to saturation states at temperatures of 1723, 1773 and 1823 K. Carbon concentration $[\text{C}]_{\text{max}}$ at these temperatures amounted to 5.02, 5.15 and 5.28 mass%, respectively. Experiments on reduction of hypothetical TiO_2 from slag and Ti transfer to metal were carried out at the same temperatures, i.e. 1723, 1773 and 1823 K. During the preliminary investigations, the time taken for the system to reach equilibrium was determined; it amounted to 6 hours. After that time the Ti and C contents did not vary within the limits of chemical analysis error. After each experiment, the crucible containing slag and metal was cooled in an atmosphere of argon. Samples of metal were analysed for Ti, Si and Fe contents, both spectrometrically and chemically, and the carbon concentration in the

TABLE 1

Chemical composition of synthetic, blast-furnace-type slags of the $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2$ system used in the investigations

Slag no.	Chemical composition (mass%)					
	CaO	MgO	SiO_2	Al_2O_3	TiO_2	CaO/ SiO_2
1	46.01	5.08	40.6	7.05	0.53	1.13
2	46.62	5.48	39.18	7.1	1.5	1.16
3	45.39	5.02	38.8	7.09	2.51	1.13
4	43.84	4.55	40.04	6.71	5.04	1.09
5	42.3	5.09	36.56	6.86	9.01	1.15
6	38.82	5.24	33.4	7.12	14.87	1.16
7	45.08	6.49	40.4	6.82	0.55	1.11
8	43.97	7.11	39.84	7.12	1.56	1.10
9	43.54	7.12	39.4	7.11	2.59	1.10
10	43.02	6.72	38.76	6.64	4.81	1.10
11	41.68	7.24	35.16	6.83	8.96	1.16
12	38.29	6.85	33.06	6.71	14.56	1.15

TABLE 2

Results of chemical analyses of slags 1-6 and corresponding metals after experiments

Slag	Temp. (K)	Chemical composition (mass%)								
		Slag					Metal			
		CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂	Si	C	Ti _{tot}	Ti _s
1	1723	48.54	38.2	5.37	7.3	0.45	1.01	5.19	0.05	0.04
2		49.75	36.15	5.3	7.05	1.3	1.05	5.29	0.09	0.08
3		48.25	36.03	5.83	7.26	2.13	1.15	5.21	0.15	0.1
4		45.52	38.0	4.79	6.92	4.4	0.79	5.3	0.26	0.14
5		45.08	34.6	5.39	6.89	8.10	0.82	5.33	0.42	0.18
6		41.6	31.34	5.64	7.16	13.46	0.88	5.35	0.54	0.19
1	1773	49.03	37.83	5.4	7.15	0.41	1.51	5.15	0.07	0.05
2		50.9	36.0	5.32	7.42	1.32	1.38	5.19	0.11	0.08
3		48.52	35.37	5.43	7.4	2.11	1.34	5.25	0.18	0.12
4		46.38	37.29	4.6	7.11	4.35	1.18	5.27	0.3	0.17
5		44.28	34.0	5.79	6.79	7.98	0.95	5.2	0.45	0.21
6		43.01	31.02	5.35	7.25	13.11	1.03	5.32	0.57	0.24
1	1823	52.6	36.6	5.45	6.99	0.35	2.82	5.01	0.11	0.08
2		53.55	32.66	5.31	7.4	1.15	2.65	5.11	0.14	0.11
3		51.87	32.46	5.83	7.4	1.85	2.68	5.15	0.24	0.15
4		46.2	35.74	5.18	6.99	4.15	1.89	5.15	0.36	0.21
5		44.8	33.0	6.01	6.89	7.8	1.54	5.11	0.53	0.26
6		44.05	29.67	6.08	7.36	12.05	1.55	5.21	0.68	0.32

metal was determined by burning. The slag components were analysed spectrometrically. The results of these analyses are shown in Tables 2 and 3.

EQUILIBRIUM OF REDUCTION OF HYPOTHETICAL TiO₂ FROM SLAG IN LIQUID PHASES

On the basis of the experimental data obtained, the following functions were calculated: the free enthalpy of reduction of hypothetical TiO₂ from slag, with simultaneous dissolution of Ti in metal; the solubility of nitrogen in liquid metal; the activity coefficients of Ti dissolved in metal and of TiO₂ in slag under equilibrium conditions; and the chemical activity of Ti dissolved in metal and of TiO₂ in slag under equilibrium conditions. For calculation of the free enthalpy of reduction of TiO₂ from slags proceeding in the experimental conditions, two types of reaction were proposed



and



TABLE 3

Results of chemical analyses of slags 7–12 and corresponding metals after experiments

Slag	Temp. (K)	Chemical composition (mass%)								
		Slag					Metal			
		CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂	Si	C	Ti _{tot}	Ti _s
7	1723	46.38	39.17	7.34	7.02	0.5	0.58	5.21	0.06	0.06
8		46.18	38.29	7.28	7.2	1.39	0.77	5.3	0.11	0.08
9		45.02	38.09	7.27	7.19	2.3	0.85	5.32	0.18	0.11
10		44.19	37.58	7.06	6.84	4.26	0.82	5.38	0.32	0.18
11		44.1	33.49	7.46	7.11	7.95	0.79	5.4	0.53	0.22
12		42.07	31.4	7.0	6.92	12.91	0.86	5.43	0.81	0.23
7	1773	47.62	37.47	7.38	7.23	0.41	1.36	5.09	0.08	0.06
8		47.36	67.68	7.29	7.35	1.3	1.38	5.17	0.14	0.1
9		45.59	37.24	7.3	7.22	2.21	1.13	5.26	0.22	0.13
10		45.39	35.34	7.18	7.02	4.02	1.18	5.27	0.39	0.21
11		45.52	33.21	7.48	7.1	7.85	0.95	5.3	0.57	0.24
12		43.04	30.92	7.18	6.98	12.18	0.92	5.28	0.86	0.29
7	1823	48.41	34.89	7.65	7.49	0.33	2.59	5.02	0.13	0.08
8		48.31	34.81	7.45	7.39	1.12	2.35	5.06	0.2	0.13
9		48.19	35.01	7.41	7.36	1.91	2.14	5.11	0.31	0.17
10		46.96	34.72	7.13	7.11	3.8	1.86	5.09	0.45	0.24
11		45.63	31.8	7.53	7.11	7.44	1.51	5.23	0.68	0.29
12		44.55	28.96	7.37	7.0	11.62	1.5	5.28	1.01	0.34

where $TiO_{2(s)}$ is the TiO_2 in the slag (solid state), $[C]$ is the carbon in the metal, $[Ti]_s$ is the Ti dissolved in the metal and $[C]_{(graph)}$ is graphite.

In reactions (1) and (2), TiO_2 transfer to slag according to eqn. (3)



was not considered because of lack of data.

For reaction (1), positive values for the free enthalpies and values for the equilibrium constants which were less than unity were obtained. Consequently, one should state that reaction (1) cannot proceed under the present experimental conditions. For reaction (2), the free enthalpy was calculated taking into account the following reactions



The sum of these reactions gives reaction (2), and enthalpies of these reactions for the temperatures of the experiments were calculated from the following dependences

$$\Delta G_{T(4)}^\circ = (223300 - 41.55 \times T) \times 4.187, \text{ J mol}^{-1}, \text{ after Phelke [9]} \quad (7)$$

$$\Delta G_{T(5)}^{\ominus} = (-13100 - 10.7 \times T) \times 4.187, \text{ J mol}^{-1}, \text{ after Narita et al. [10]} \quad (8)$$

$$\Delta G_{T(6)}^{\ominus} = (-53400 - 41.9 \times T) \times 4.187, \text{ J mol}^{-1}, \text{ after Mamro [11]} \quad (9)$$

Summation of eqns. (7)–(9) gave the functional dependence of the free enthalpy of reaction (2) on temperature in the form

$$\Delta G_{T(2)}^{\ominus} = (156800 - 94.15 \times T) \times 4.187 \text{ J mol}^{-1}$$

The calculated free enthalpy values and the equilibrium constants for reaction (2) at the particular temperatures of the experiments were:

$$\Delta G_{1723}^{\ominus} = -22690.21, \text{ J mol}^{-1}; K_{1723} = 4.8695$$

$$\Delta G_{1773}^{\ominus} = -42395.81, \text{ J mol}^{-1}; K_{1773} = 17.7145$$

and

$$\Delta G_{1823}^{\ominus} = -62100.4, \text{ J mol}^{-1}; K_{1823} = 60.0336$$

These values for ΔG_T^{\ominus} and K show that such a reaction course is thermodynamically the most probable.

The equilibrium constant K for that reaction can be written

$$K_{T(2)} = \frac{a_{[\text{Ti}]_s} \times p_{\text{CO}}^2}{a_{\text{TiO}_2} \times a_c^2} \quad (10)$$

For pure graphite, it can be assumed that $a_c = 1$ and the pressure of the CO generated, according to reaction (6), is

$$P_{\text{CO}} = 2p_{\text{O}_2} = 2 \times 0.21 = 0.42 \text{ atm} \quad (11)$$

which leads to the final form for the expression of the equilibrium constant of reaction (2)

$$K_{T(2)} = \frac{a_{[\text{Ti}]_s} \times 0.42^2}{a_{\text{TiO}_2(s)}} \quad (12)$$

Considering the time of the experiments and the gas atmosphere employed, it was assumed that the nitrogen in the metal is in the saturation state. Consequently, nitrogen of saturation concentration was calculated according to the equation given by Mamro and Pytel [12]

$$\lg(\%N_T) = \left(\frac{189}{T} - 1,252 \right) - \lg f_{\text{N},T}^{(i)} \quad (13)$$

where $f_{\text{N},T}^{(i)}$ is the activity coefficient of nitrogen in a multicomponent iron melt, calculated after Henry from the following dependence

$$\lg f_{\text{N},T}^{(i)} = \left(-0,75 + \frac{3280}{T} \right) \times \lg f_{\text{N},1873}^{(i)} \quad (14)$$

TABLE 4
 Calculated values of thermodynamic functions of Ti and N dissolved in metals and TiO₂ in slags 1-6 (MgO 5 mass%)

Slag ^a	Metal ^a	T (K)	f[N]	[%N] × 10 ⁻³	X[Ti] × 10 ⁻³	X(TiO ₂)	a'[Ti] × 10 ⁻²	f[Ti]	a[Ti] × 10 ⁻⁶	Ti × 10 ⁻³	a(TiO ₂) × 10 ⁻⁸	(TiO ₂) × 10 ⁻⁶	a'(TiO ₂) × 10 ⁻⁴	f(TiO ₂) × 10 ⁻⁴
1	1M	1723	6.88	6.32	0.39	5.2E-3	0.351	8.78E-2	0.376	0.966	1.36	2.61	1.27	2.83
2	2M	1723	6.66	6.52	0.78	1.48E-2	0.673	8.41E-2	0.719	0.925	2.61	1.76	2.44	1.87
3	3M	1723	6.31	6.89	0.97	2.42E-2	0.872	8.72E-2	0.931	0.959	3.27	1.4	3.16	1.48
4	4M	1723	5.73	7.58	1.36	5.23E-2	1.17	8.36E-2	1.251	0.919	4.53	0.87	4.24	0.96
5	5M	1723	5.39	8.06	1.75	9.16E-2	1.485	8.25E-2	1.592	0.907	5.76	0.63	5.38	0.66
6	6M	1723	5.38	8.08	1.85	0.1504	1.554	8.18E-2	1.666	0.9	6.03	0.4	5.63	0.42
1	1M	1773	6.54	6.69	0.49	4.7E-3	0.469	9.37E-2	0.502	1.031	0.5	1.05	0.47	1.14
2	2M	1773	6.17	7.1	0.78	1.46E-2	0.736	9.2E-2	0.791	1.013	0.79	0.538	0.733	0.56
3	3M	1773	5.82	7.52	1.17	2.4E-2	1.077	9E-2	1.151	0.987	1.15	0.477	1.07	0.51
4	4M	1773	5.09	8.59	1.66	5.11E-2	1.508	8.87E-2	1.598	0.976	1.66	0.325	1.55	0.36
5	5M	1773	4.65	9.42	2.05	9.08E-2	1.837	8.75E-2	1.974	0.963	2.01	0.221	1.88	0.24
6	6M	1773	4.4	9.95	2.35	0.1446	2.078	8.66E-2	2.237	0.952	2.34	0.162	2.18	0.17
1	1M	1823	6.53	6.75	0.77	3.8E-3	0.837	0.1046	0.89	1.151	0.26	0.684	0.246	0.7
2	2M	1823	6.26	7.04	1.06	1.23E-2	1.102	0.1002	1.169	1.102	0.34	0.281	0.324	0.28
3	3M	1823	5.95	7.42	1.45	1.99E-2	1.479	9.86E-2	0.567	1.085	0.46	0.232	0.435	0.235
4	4M	1823	4.78	9.22	2.04	4.84E-2	2.063	9.82E-2	2.2	1.08	0.65	0.134	0.606	0.15
5	5M	1823	4.11	10.73	2.54	8.77E-2	2.591	9.96E-2	2.782	1.096	0.82	9.3E-2	0.761	9.8E-2
6	6M	1823	3.83	11.5	3.11	0.1301	3.056	9.55E-2	3.266	1.05	0.96	7.4E-2	8.98E-2	0.898

^a Compositions listed in Table 2.

TABLE 5

Calculated values of thermodynamic functions of Ti and N dissolved in metals and TiO₂ in slags 7-12 (MgO 7 mass%)

Slag ^a	Metal ^a	T (K)	f[N]	[%N] × 10 ⁻³	X[Ti] × 10 ⁻³	X(TiO ₂) × 10 ⁻²	a'[Ti] × 10 ⁻²	f[Ti]	a[Ti] × 10 ⁻⁶	Ti × 10 ⁻³	a(TiO ₂) × 10 ⁻⁸	(TiO ₂) × 10 ⁻⁶	a'(TiO ₂) × 10 ⁻⁴	f(TiO ₂) × 10 ⁻⁴
7	7M	1723	6.26	6.95	0.59	5.8E-3	0.521	8.68E-2	0.564	0.955	2.04	3.54	1.89	3.77
8	8M	1723	6.42	6.78	0.78	1.59E-2	0.668	8.36E-2	0.717	0.919	2.6	1.63	2.42	1.74
9	9M	1723	6.18	7.04	1.07	2.66E-2	0.912	8.29E-2	0.973	0.912	3.52	1.33	3.3	1.44
10	10M	1723	5.5	7.91	1.75	4.92E-2	1.452	8.07E-2	1.549	0.887	5.61	1.14	5.26	1.23
11	11M	1723	5.11	8.51	2.14	8.72E-2	1.758	7.99E-2	1.879	0.879	6.81	0.78	6.37	0.8
12	12M	1723	5.12	8.49	2.24	0.1401	1.815	7.89E-2	1.941	0.868	7.03	0.502	6.57	0.51
7	7M	1773	6.15	7.12	0.59	4.6E-3	0.576	9.61E-2	0.622	1.057	0.62	1.34	0.574	1.401
8	8M	1773	5.9	7.42	0.98	1.46E-2	0.929	9.29E-2	0.992	1.022	0.99	0.676	0.925	0.712
9	9M	1773	5.57	7.86	1.26	2.53E-2	1.16	8.92E-2	1.238	0.981	1.23	0.486	1.155	0.523
10	10M	1773	4.75	9.22	2.04	4.6E-2	1.185	8.88E-2	1.991	0.976	2.04	0.443	1.907	0.469
11	11M	1773	4.24	10.33	2.35	8.56E-2	2.093	8.72E-2	2.253	0.959	2.41	0.282	2.241	0.286
12	12M	1773	3.91	11.22	2.84	0.1307	2.488	8.58E-2	2.681	0.944	2.87	0.219	2.658	0.218
7	7M	1823	6.35	6.93	0.77	3.7E-3	0.836	0.1045	0.889	1.15	0.26	0.715	0.246	0.744
8	8M	1823	5.69	7.75	1.26	1.24E-2	1.329	0.1022	1.413	1.125	0.42	0.335	0.391	0.349
9	9M	1823	5.24	8.42	1.64	2.1E-2	1.7	0.1	1.808	1.1	0.53	0.253	0.5	0.261
10	10M	1823	4.42	9.98	2.33	4.2E-2	2.419	0.1008	2.581	1.108	0.76	0.181	0.711	0.187
11	11M	1823	4.05	10.89	2.81	8E-2	2.746	9.47E-2	2.928	1.041	0.86	0.107	0.807	0.108
12	12M	1823	3.77	11.71	3.3	0.1221	3.15	9.26E-2	3.365	1.019	0.99	8.1E-2	0.925	8E-2

^a Compositions listed in Table 2.

while for $f_{N,1873}^{(i)}$

$$\lg f_{1873}^{(i)} = 0.123 \times \sum_{i=1}^n K_N^{(i)} \times (\%i) + 0.00225 \times \sum_{i=1}^n K_N^{(i)} \times (\%i)^2 \quad (15)$$

where $K_N^{(i)}$ is the equivalent coefficient of the i th component interaction on nitrogen activity (after Henry) in this melt. The values of $K_N^{(i)}$ adopted after Mamro and Pytel [12] were as follows: for C, $K_N^{(C)} = 1.0$; for Ti, $K_N^{(Ti)} = -5.88$; and for Si, $K_N^{(Si)} = 0.444$.

Calculated according to relations (13) and (14), the concentration of nitrogen of saturation and the coefficients of nitrogen activity in Fe–Si–C–N melts are shown in Tables 4 and 5, respectively. Using the known, simplified form of the Wagner–Chipman equation, the activity coefficients of titanium dissolved in metal (after Henry) were calculated for the particular temperatures of the experiments

$$\lg f_{[Ti]_s} = e_{Ti}^{(Ti)} \times [\%Ti]_s + e_{Ti}^{(C)} \times [C] + e_{Ti}^{(N)} \times [\%N] \quad (16)$$

where $e_{Ti}^{(Ti)}$, $e_{Ti}^{(C)}$ and $e_{Ti}^{(N)}$ are the interaction coefficients of the components of the metal (Ti, C, N, respectively) on the activity of titanium dissolved in the melt. The value of the coefficient $e_{Ti}^{(Ti)} = 0.042$ was adopted after Mamro and Yun [11,13]. The value of $e_{Ti}^{(C)}$ was calculated by means of the relation given by Sumito et al. [14]

$$e_{Ti}^{(C)} = -\frac{221}{T} - 0.072$$

and the value of $e_{Ti}^{(N)}$ from the relation

$$e_{Ti}^{(N)} = -\frac{19502}{T} + 8.372$$

given by Morita and Kunisada [15].

The term $e_{Ti}^{(Si)}$, the interaction coefficient of Si on titanium, was neglected in equation (16) because of lack of literature data.

The activities, after Henry, were calculated from the relation

$$a'_{[Ti]_s} = f_{[Ti]_s} \times [\%Ti]_s \quad (17)$$

and from the mole fractions of titanium dissolved in the metal and of TiO_2 in the slag at equilibrium. Using the well-known relations of Henry and Raoult, the activities of titanium dissolved in metal and TiO_2 in slag were determined.

The results of these calculations are shown in Tables 3 and 4 and Figs. 1–4.

The dependence of the activity of Ti dissolved in metal, under experimental conditions, on the Ti mole fraction or Ti mass% was calculated by statistical methods.

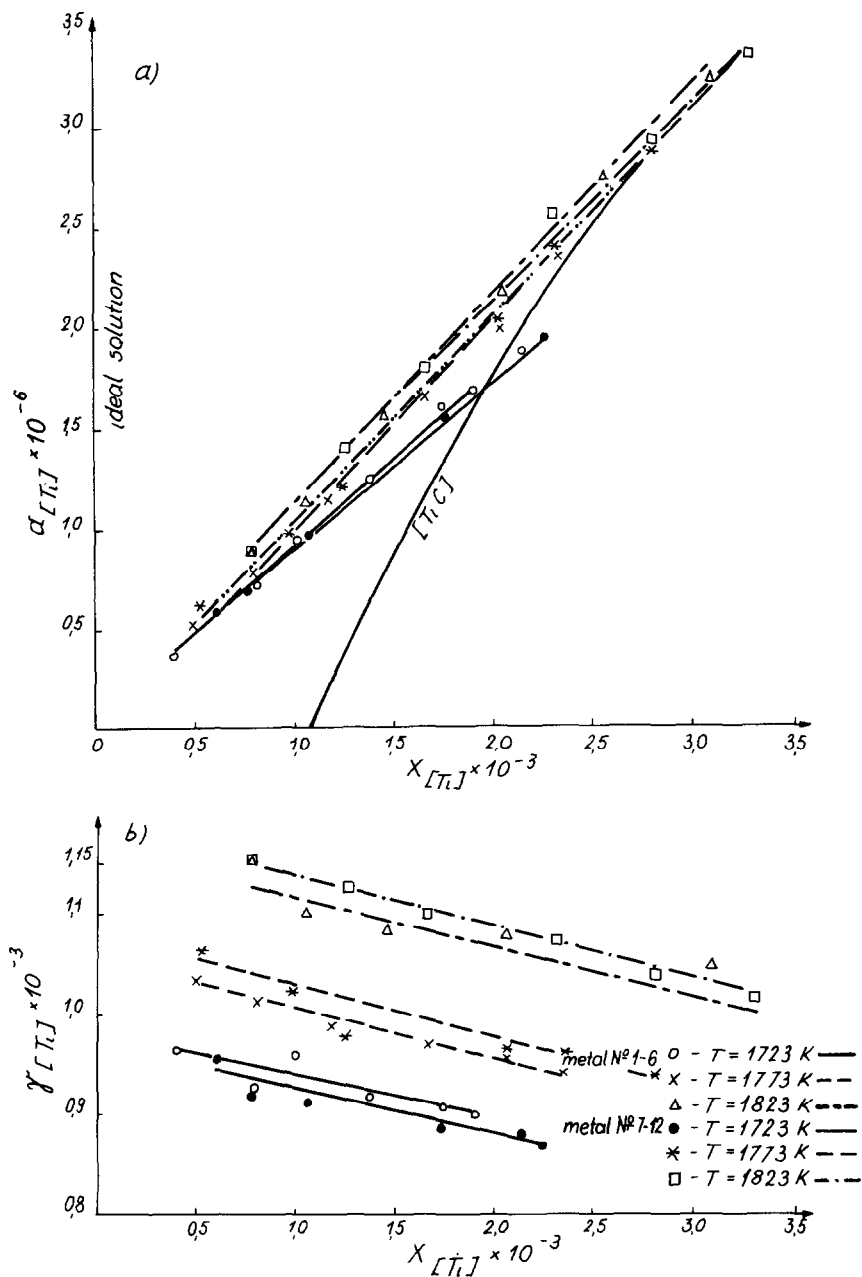


Fig. 1. Dependences of (a) activity and (b) activity coefficient of Ti on Ti atom fraction of Ti dissolved in metal, after Raoult.

These relations, according to Raoult and Henry, have the following forms

$$a_{[Ti]_s} = 2.12649 \times 10^{-5} + 3.13231 \times 10^{-6} \times \ln X_{[Ti]_s} \quad (18)$$

$$a'_{[Ti]_s} = 0.063178 + 0.029295 \times \ln [\%Ti]_s \quad (19)$$

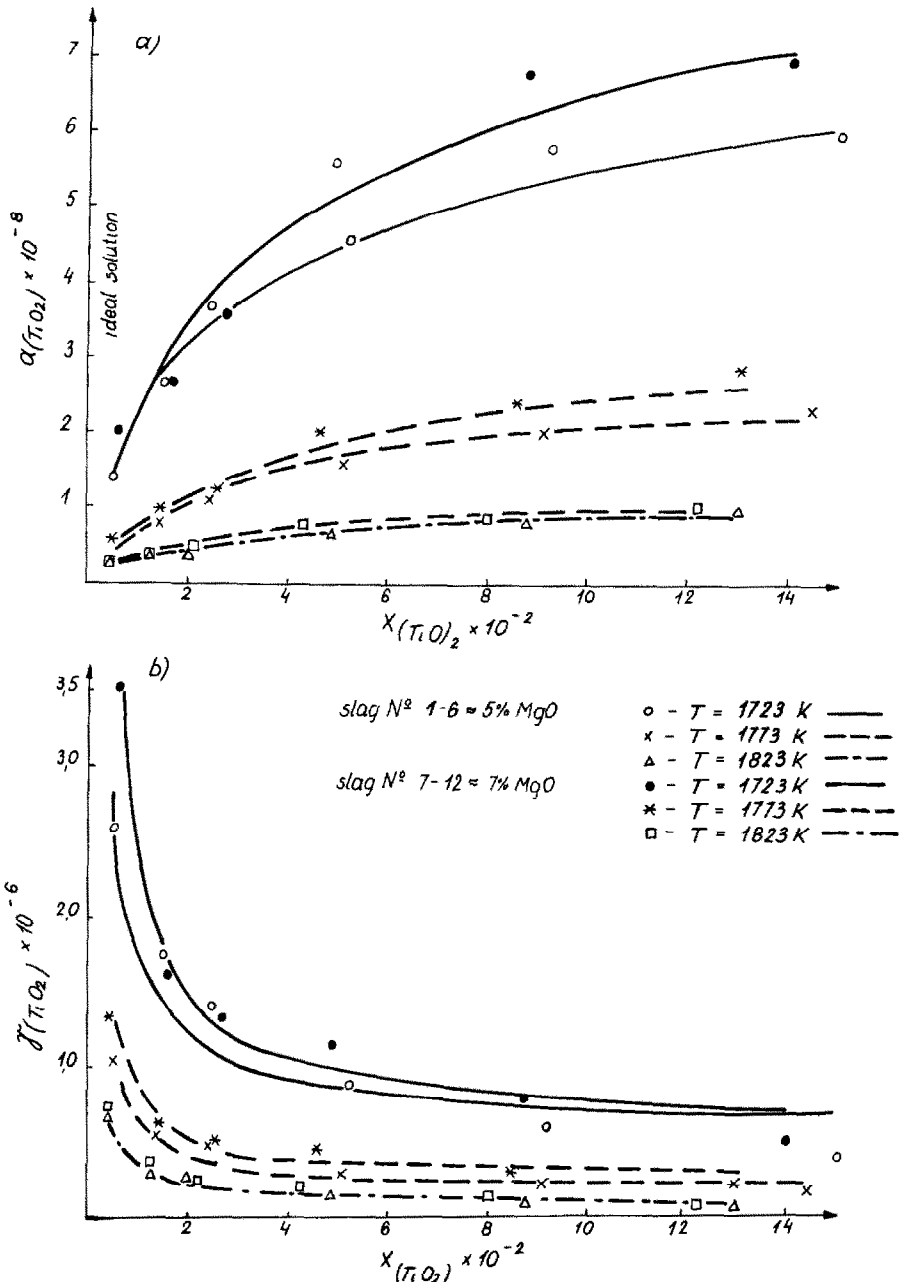


Fig. 2. Dependences of (a) activity and (b) activity coefficient of TiO_2 in slag on mole fraction of TiO_2 , after Raoult.

at standard deviations 1.0489×10^{-7} and 9.82659×10^{-4} for equations (18) and (19), respectively, with the root-mean-square error being $\pm 10\%$.

The results obtained regarding the contents of titanium dissolved in the

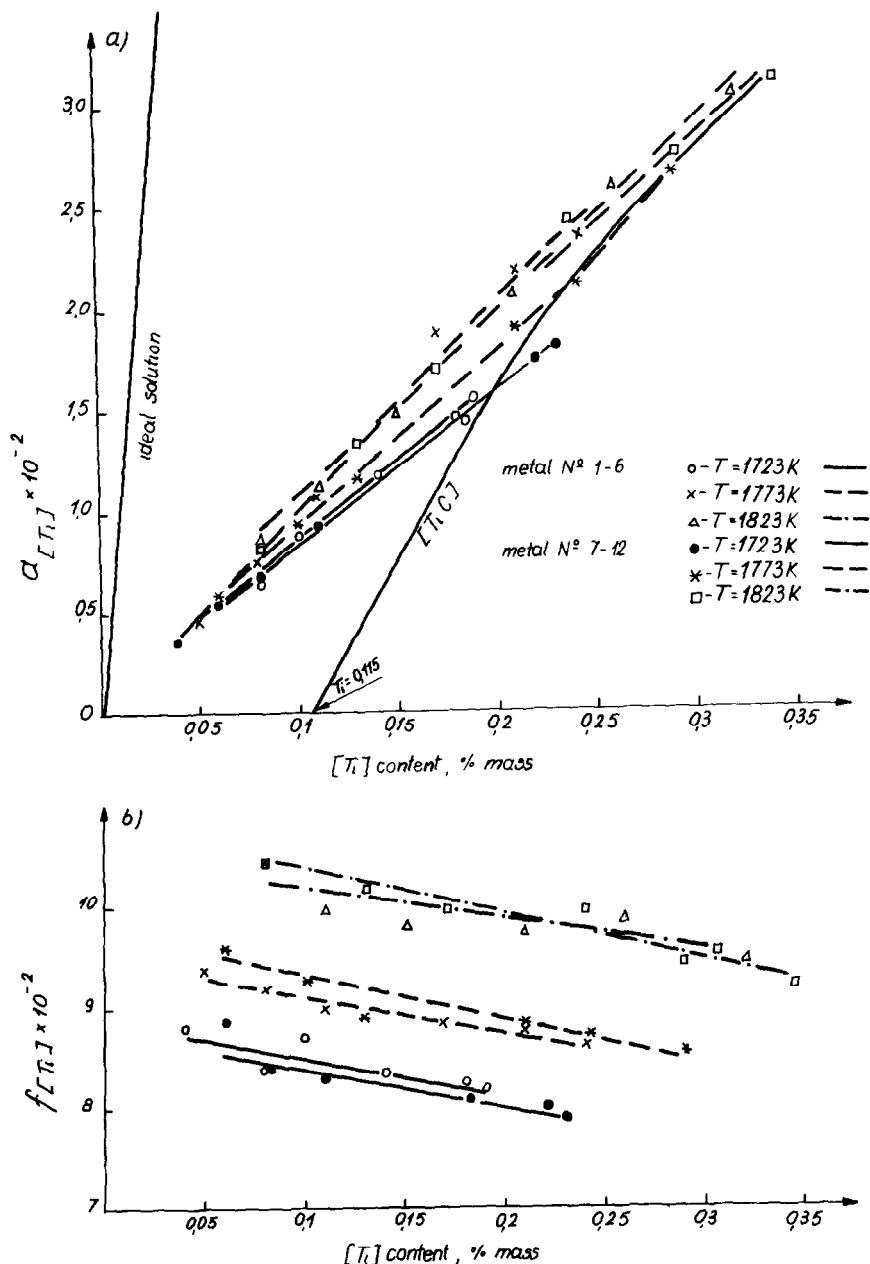


Fig. 3. Dependences of (a) activity and (b) activity coefficient of Ti on content of Ti dissolved in metal, after Henry.

metal enable the determination of its maximum solubility as a function of temperature, in the experimental conditions employed

$$[Ti]_s = 1.2 \times 10^{-3} \times T - 1.85927 \quad (20)$$

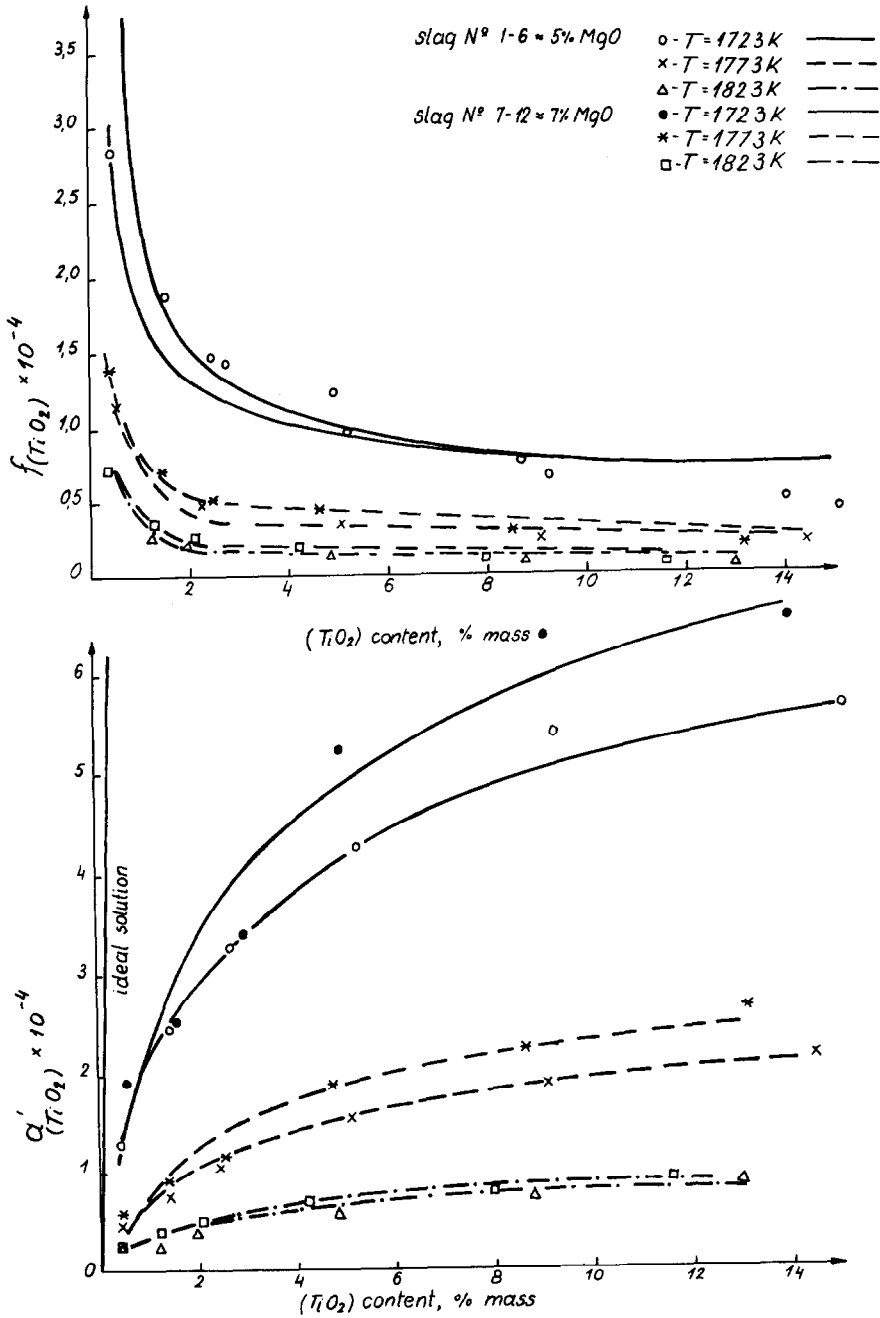


Fig. 4. Dependences of (a) activity and (b) activity coefficient of TiO_2 in slag on content of TiO_2 in slag, after Henry.

at correlation coefficients $R = 0.92905$ and $R_{\text{crit}} = 0.917$, corresponding to a significance level of 0.01.

In Fig. 5 literature data [3, 8, 10, 14] on the solubility of Ti in metal as a

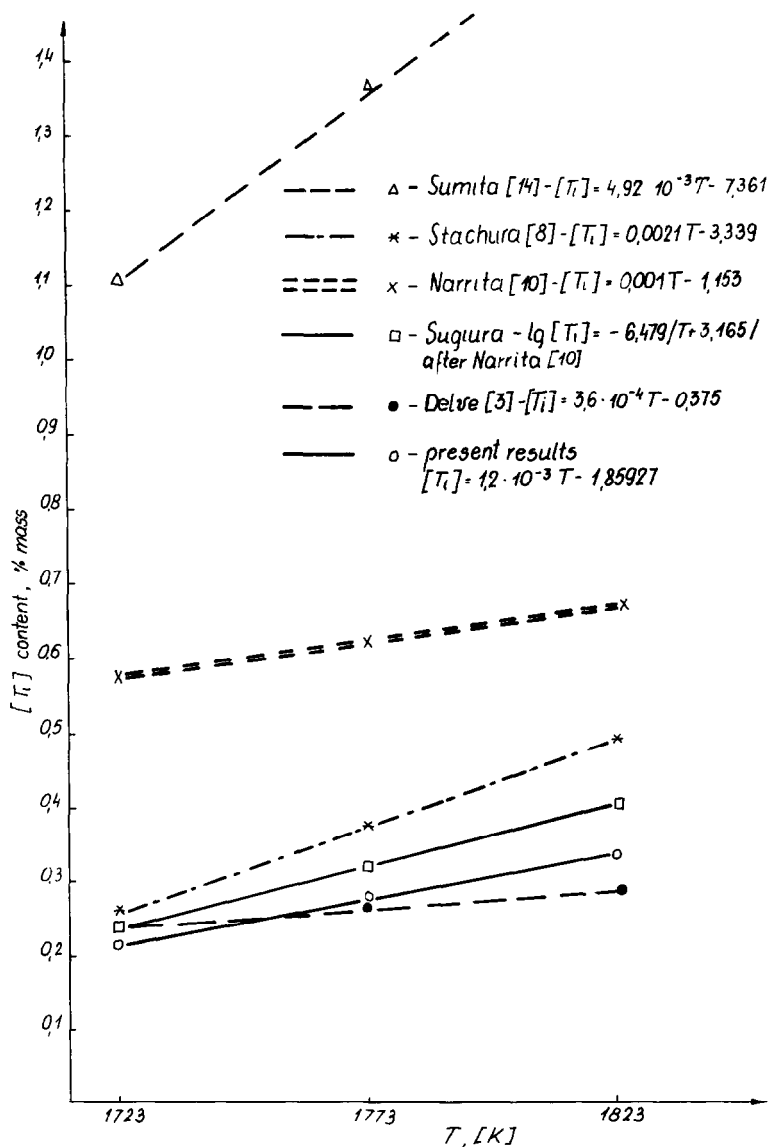


Fig. 5. Solubility of titanium in liquid iron in the temperature range 1723–1823 K. Comparison of present results with those of the quoted authors.

function of temperature are compared with the results of the present work. As can be seen, the present results are consistent with those of Delve [3] and Suigura (quoted by Narita and Maekawa [10]). Delve [3] and Stachura [8] also investigated the transfer of titanium to the metal from TiO_2 contained in the slag, as did the present authors. In refs. 10 and 14, the transfer of titanium to metal from pure TiO_2 was investigated (Fig. 5). It should be noted that these quoted authors employed different gas atmospheres.

SUMMARY

The experiments showed that, in the investigated liquid metal–liquid slag system, after 6 hours at constant temperature and pressure, no analytically detectable changes in the chemical compositions of the reacting phases occurred. It was assumed that the system was close to the thermodynamic equilibrium state.

The calculated values of the free enthalpies of reduction of hypothetical TiO_2 from slag and of the titanium transfer to metal indicated the endothermic character of the TiO_2 reduction.

The calculated values of the free enthalpies and the equilibrium constants suggest that temperatures of pig iron and slag in the blast furnace should not exceed 1723 K, in order to limit the reduction of TiO_2 .

The values of the activities and activity coefficients obtained in the present work are consistent with those of Narita and Maekawa [10], Sumito et al. [14] and Stachura [8], particularly the values of $a'_{(\text{TiO}_2)}$ and $f_{(\text{TiO}_2)}$ as well as those of $a_{[\text{Ti}]_s}$ and $\gamma_{[\text{Ti}]_s}$.

The activities of titanium in metal (after Raoult and Henry) in its solubility conditions were determined in the present work by statistical methods using relations (18) and (19).

In the course of the present work, values of the titanium solubility (calculated from eqn. (20) were determined and are consistent with results reported previously [3, 8, 10] within the limits of experimental error.

Reduced titanium is dissolved in the metal in only a limited amount. The remaining titanium reacts with carbon and nitrogen forming titanium carbide nitrides.

On the basis of the results of the present work, the authors intend to quantitatively determine, in forthcoming papers, the formation of titanium carbide nitrides as a result of the reduction of TiO_2 from slag in liquid phase, as well as the thermochemical conditions of both reactions.

REFERENCES

- 1 R. Benesch, M. Wyderko-Delekta and A. Łędzki, *Hutn. Listy*, 8 (1987) 533.
- 2 A. Łędzki, *Hutnik*, 4 (1986) 95.
- 3 F.D. Delve, *A Study of the Physical Chemistry of Titanium in the Blast Furnace*, Metallurgical Society of AJME, New York, 1961, pp. 1111.
- 4 W. Hess and S. Mayer, *Stahl Eisen*, 93 (1973) 107.
- 5 A.W. Szawrin and G.G. Paszkiew., *Stal* 5 (1966) 392.
- 6 J.N. Zacharow, S.W. Szawrin and E.U. Zajcew, *Miery*, 4 (1967) 14.
- 7 A. Poos, and R. Widal, *Slag Volume and Composition for Optimal Blast Furnace Operation*, McMaster Symposium, May 1984, no. 12, pp. 67–93.
- 8 R. Stachura, *Badania rozdziału tytanu między surówką i żużel w zależności od warunków cieplnych gaRu wielkiego pieca*, Praca doktorska, AGH Kraków, 1985.
- 9 R.D. Phelke, *Unit Process of Extractive Metallurgy*, American Elsevier, New York, 1973.

- 10 K. Narita and M. Maekawa, *Trans. Iron Steel Inst. Jpn.*, 17 (8) (1977) 459.
- 11 K. Mamro, *Tablice parametrów oddziaływania w wieloskładnikowych stopach żelaza*, AGH, Kraków, 1985.
- 12 K. Mamro and K. Pytel, *Hutnik*, 10 (1977) 485.
- 13 Yun Zixang, *Stahl Eisen*, 17 (4) (1973) 779.
- 14 M. Sumito, N. Tsuchiya, K. Okabe and K. Saunbongi, *Trans. Iron Steel Inst. Jpn.*, 21 (6) (1981) 414.
- 15 Z. Morita and K. Kunisada, *Trans. Iron Steel Inst. Jpn.*, 18 (1978) 648.