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INVESTIGATIONS INTO TITANIUM DISTRIBUTION BETWEEN METAL AND SLAG IN LIQUID PHASES

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ABSTRACT

In Polish polymetallic iron ores, titanium occurs in the form of ilmenite and titanomagnetite. After vanadium removal and enrichment, a concentrate with about 60% Fe and 3% TiO_2 is obtained. The concentrate can be used in the production of iron sinters. In the present work, laboratory investigations into titanium distribution between slag and metal have been carried out in conditions similar to those in the blast furnace. Five-component slags of the CaO–SiO_2–Al_2O_3–MgO–TiO_2 system, saturated with carbon, were used in the investigations. The lengths of the experiments were 1, 2, 3, 4, 5 and 6 hours at temperatures of 1723, 1773 and 1823 K. The amounts of titanium (wt.%) transferred to the metal and dissolved in the metal were determined. On the basis of the data obtained, equations for the transfer coefficient and the solubility coefficient of titanium in metal as functions of temperature, TiO_2 content in slag and reaction time, were derived employing statistical methods.

INTRODUCTION

In minerals containing iron oxides, titanium compounds such as ilmenite $FeO \cdot TiO_2$, titanomagnetites, e.g. $TiO_2 \cdot Fe_3O_4$ and $FeO \cdot TiO_2 \cdot Fe_3O_4$ or, more rarely, rutile TiO_2 may also occur. Ores and concentrates containing, in addition to iron compounds significant amounts of titanium compounds are more and more frequently employed in industrial practices.

In polymetallic ores, titanium occurs in the form of ilmenite or titanomagnetite; these minerals usually also contain considerable amounts of vanadium compounds. After enrichment and vanadium removal, the titanomagnetite fraction containing about 60% mass of Fe may be used as a blast furnace charge in the form of ore sinter. A characteristic feature of the concentrate which has an important influence on the sintering and then the reduction in the blast furnace, is its 3% TiO_2 content.

It is known from the literature [1–5] that introduction of titanomagnetite concentrate as a component of the ore sinter may cause changes in the running of the blast furnace. The changes may be advantageous because

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nitrogen may be partially removed from the pig iron produced and, apart from this, a protective layer of infusible titanium carbidonitrides may form in the lower part of the blast furnace thus extending its exploitation. The negative consequences are: the appearance of the high melting carbidonitride phase which increases the density of both pig iron and slag, and causes excessive growth of the infusible layer; the growth of the infusible layer in the output channels and the excessively slow flow of pig iron and slag from the tapping holes; and a more difficult reduction and desulphurization process in the liquid phases.

Exhaustive investigations into the reduction of titanium oxides from blast furnace-type slags by the authors have aimed at a better understanding of these complex phenomena. One of the basic aims of the investigations has been the determination of a hypothetical titanium oxide reduction in liquid metal–slag phases.

METHOD AND RESULTS

Investigations into the reduction of titanium oxides from slag and titanium transfer to the metal was carried out in laboratory conditions using graphite crucibles.

Blast furnace-type 5-component slags of the $CaO–SiO_2–MgO–Al_2O_3–TiO_2$ system with constant Al_2O_3 content (about 7% mass%) and MgO content (about 5 mass% in the first series and 7 mass% in the second) were

TABLE 1

Chemical composition of investigated synthetic slags

No. of slag	Chemical composition (mass%)					
	MgO	TiO_2	Al_2O_3	CaO	SiO_2	$\frac{\%CaO}{\%SiO_2}$
1	5.08	0.53	7.05	46.01	50.60	1.13
2	5.48	1.50	7.10	46.62	39.18	1.16
3	5.02	2.51	7.09	45.39	38.80	1.13
4	4.55	5.04	6.71	43.84	40.94	1.09
5	5.09	9.01	6.86	42.30	36.56	1.15
6	5.24	14.87	7.12	38.82	33.40	1.16
7	6.94	0.55	6.82	45.08	40.40	1.11
8	7.11	1.56	7.12	43.97	39.84	1.10
9	7.12	2.59	7.11	43.54	39.40	1.10
10	6.72	4.81	6.64	43.02	38.76	1.10
11	7.24	8.96	6.83	41.68	35.16	1.16
12	6.86	14.56	6.71	38.29	33.06	1.15

used in the investigations. The concentration of hypothetical TiO_2 in the slag was variable: 0.5, 1.5, 2.5, 5, 9 and 15 mass% in each series. The chemical composition of the slags is shown in Table 1. The metal used in the investigations was obtained by carbonization with graphite of analytically pure iron (Riedel de Haen). Carbonization of the iron was carried out up to the saturation state at the given temperatures. The maximum carbon content

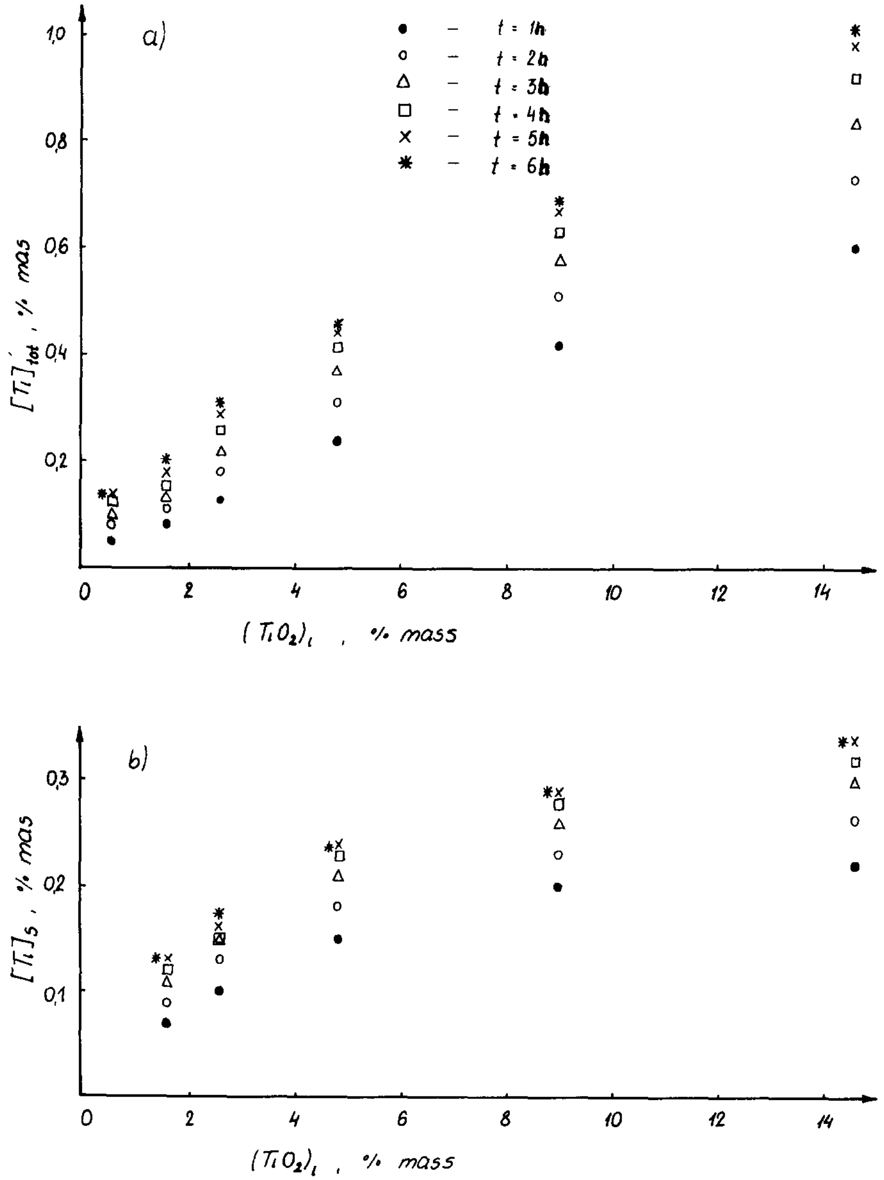

Fig. 1. (a) Ti_{tot} and (b) Ti_S contents in metal after reaction time of 1–6 hours. Slags 1–6 (Table 1) (MgO = 5 mass%). Temperature 1723 K.

at 1723, 1773 and 1823 K amounted to 5.02, 5.15 and 5.28 mass%, respectively.

TiO_2 reduction from slag and Ti transfer to metal were investigated in a Tamann furnace, type LEW, at 1723, 1773 and 1823 K and at times of 1, 2, 3, 4, 5 and 6 hours. For slags and metals with the lowest and highest TiO_2

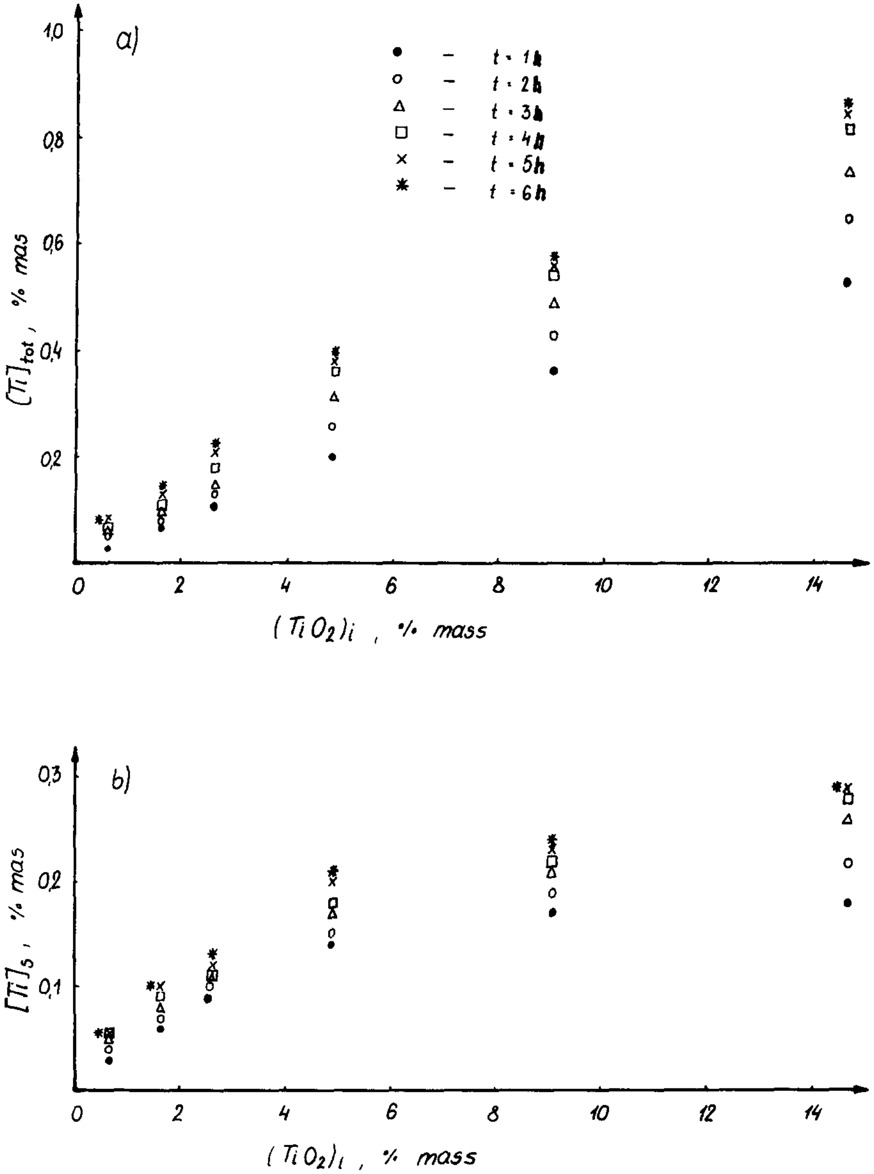

Fig. 2. (a) Ti_{tot} and (b) Ti_S contents in metal after reaction time of 1–6 hours. Slags 1–6 (Table 1) (MgO = 5 mass%). Temperature 1773 K.

and Ti concentrations, additional investigations into the Ti transfer from slag to metal were carried out at times of 7 and 8 hours.

On the basis of these experiments it was found that reduction of TiO_2 from slag reached equilibrium after 6 hours because concentrations of Ti_{tot} and C in metal did not vary after this time (within the limits of the analytical error).

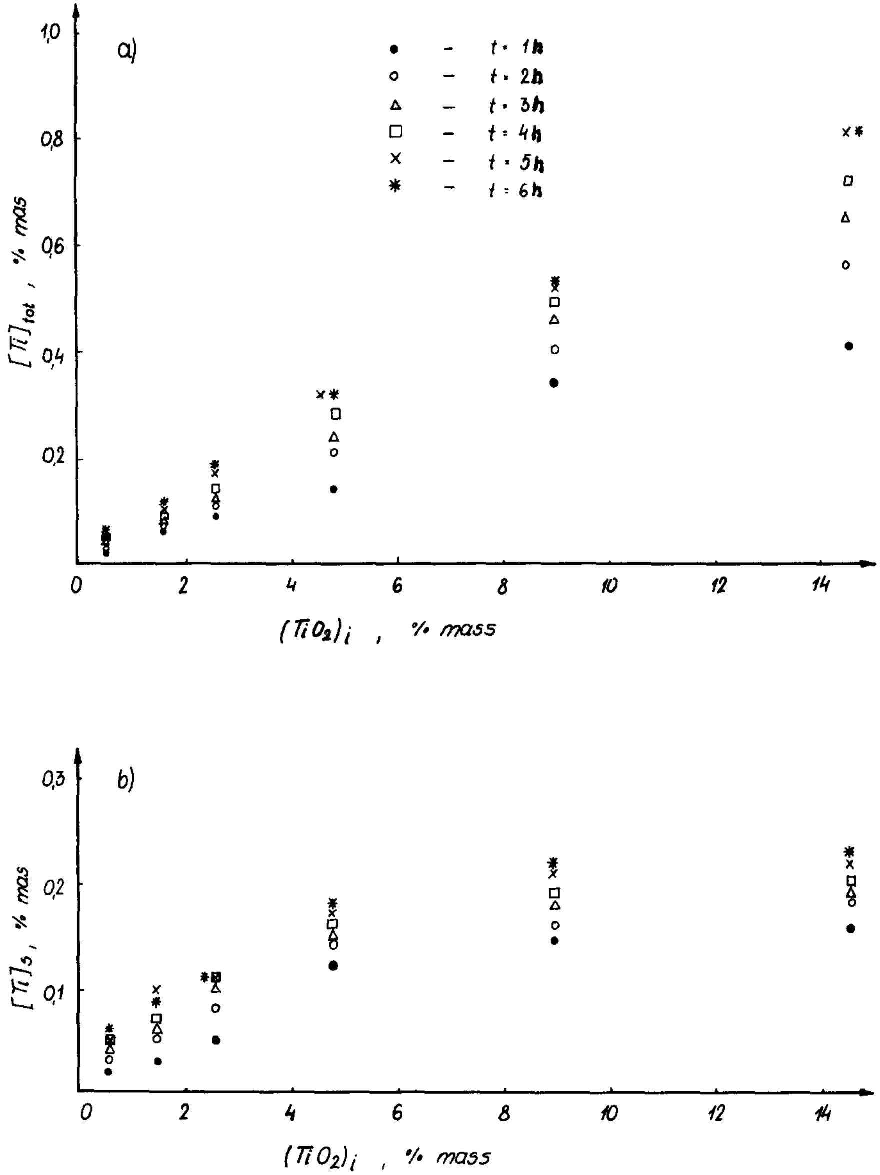

Fig. 3. (a) Ti_{tot} and (b) Ti_S contents in metal after reaction time of 1–6 hours. Slags 1–6 (Table 1) (MgO = 5 mass%). Temperature 1823 K.

After each experiment, the crucible containing the sample was cooled in an atmosphere of argon. The Ti, Si and Fe concentrations in the metal were determined both spectrometrically and chemically, and the carbon concentration in the metal was determined by burning. The total concentration of Ti in the metal was determined spectrometrically, whereas Ti dissolved in the metal was determined chemically.

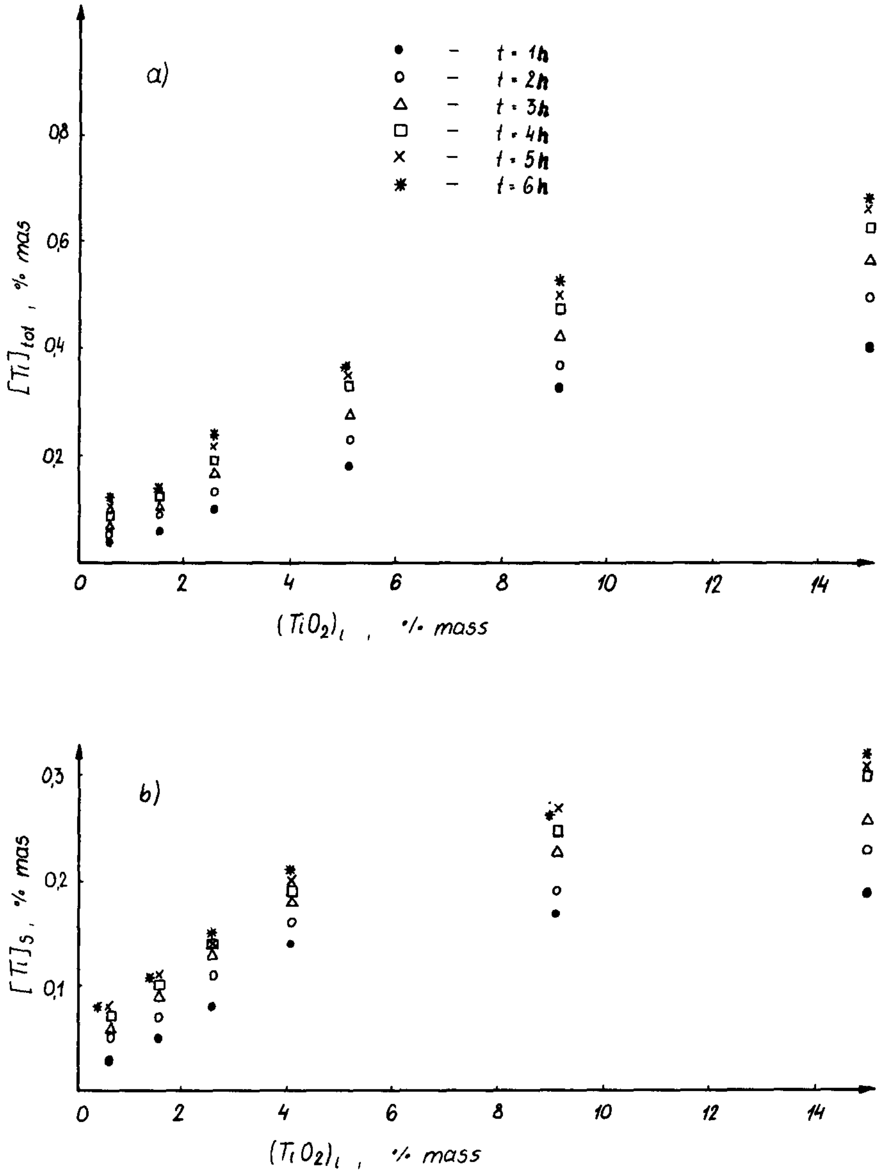

Fig. 4. (a) Ti_{tot} and (b) Ti_S contents in metal after reaction time of 1–6 hours. Slags 7–12 (Table 1) (MgO = 7 mass%). Temperature 1723 K.

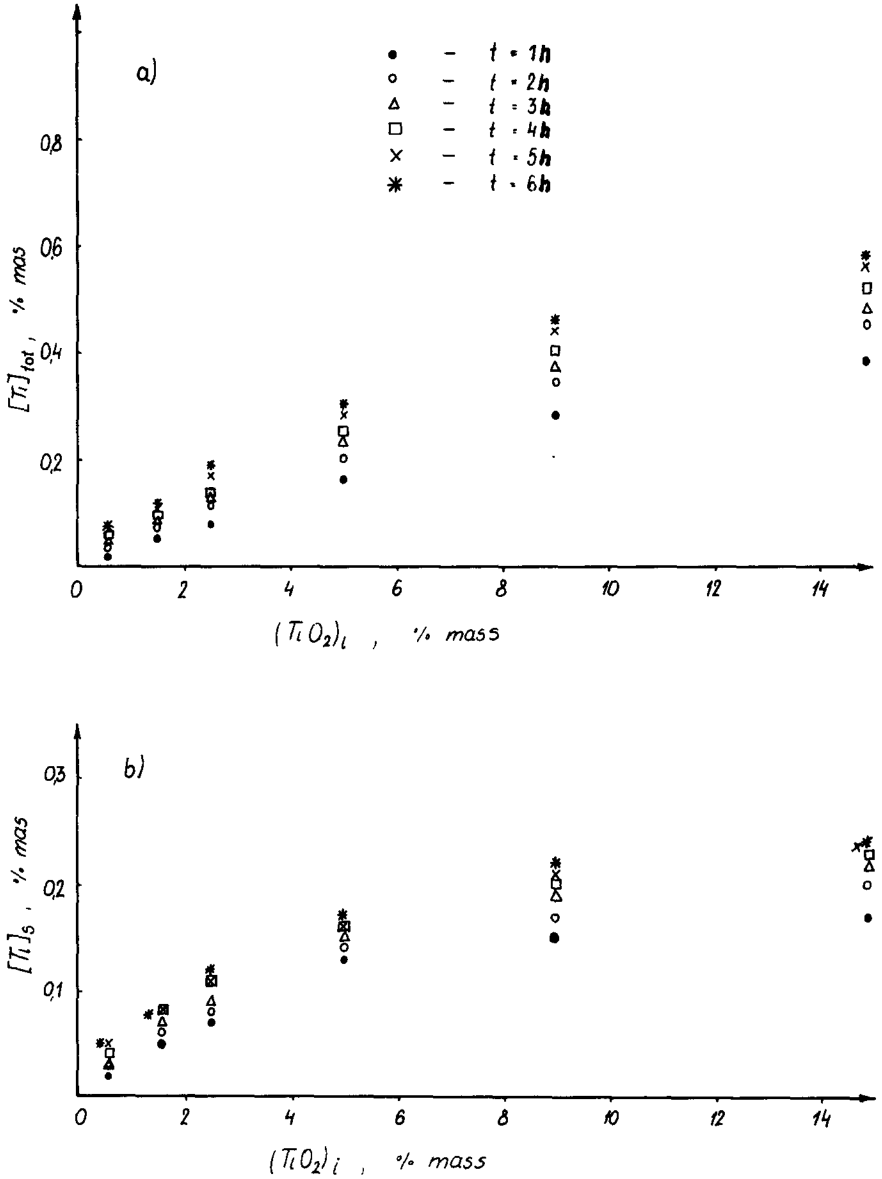

Fig. 5. (a) Ti_{tot} and (b) Ti_S contents in metal after reaction time of 1–6 hours. Slags 7–12 (Table 1) (MgO = 7 mass%). Temperature 1773 K.

Finally, the components of the slags were determined spectrometrically. The results of the investigations into the reduction of hypothetical TiO_2 from slag and Ti transfer to metal are shown graphically in Figs. 1–6.

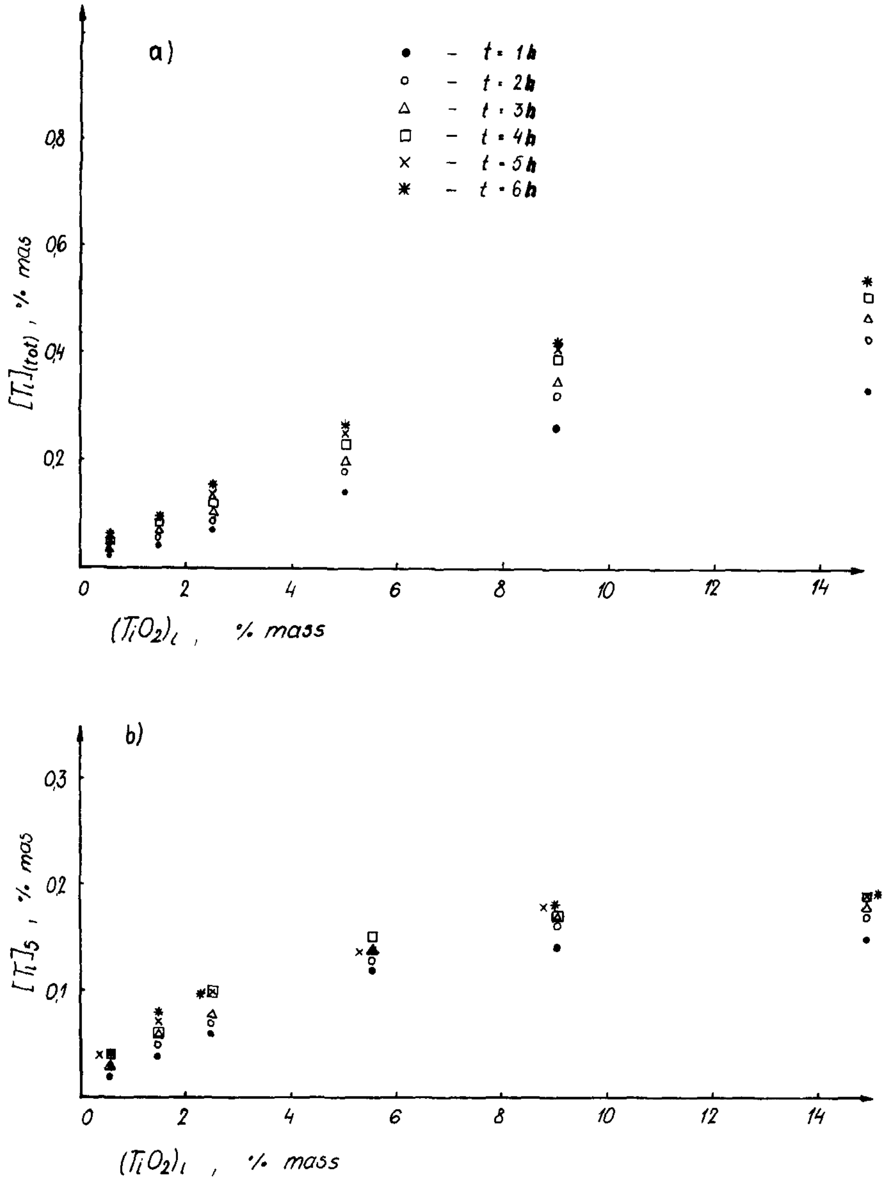

Fig. 6. (a) Ti_{tot} and (b) Ti_S contents in metal after reaction time of 1–6 hours. Slags 7–12 (Table 1) (MgO = 7 mass%). Temperature 1823 K.

DISTRIBUTION OF TITANIUM BETWEEN METAL AND SLAG

On the basis of the results obtained, the balance of titanium in its reduction and its transfer coefficients from slag to metal were determined according to the following relations

— the final mass of metal sample

$$M_{\mathrm{fm}} = \frac{M_{\mathrm{im}}}{\left[1 - \left(\mathrm{Si} + \mathrm{C} + \mathrm{Ti}_{\mathrm{tot}} - \mathrm{C}_{\mathrm{max}_{\mathrm{Fe-C}}}\right)\right] \times 0.01} \tag{1}$$

— the initial mass of Ti in slag

$$M_{(\mathrm{Ti})_\mathrm{i}} = M_{\mathrm{sl,i}} \times (\%\mathrm{TiO_2})_\mathrm{i} \times 0.5985 \times 0.01 \tag{2}$$

— the total mass of Ti in metal

$$M_{[\mathrm{Ti}]_{\mathrm{tot}}} = M_{\mathrm{fm}} \times [\mathrm{Ti}]_{\mathrm{tot}} \times 0.01 \tag{3}$$

— the mass of Ti dissolved in metal

$$M_{[\mathrm{Ti}]_\mathrm{S}} = M_{\mathrm{fm}} \times [\mathrm{Ti}]_\mathrm{S} \times 0.01 \tag{4}$$

— the coefficient of transfer of Ti (total amount) to metal

$$K_{[\mathrm{Ti}]_{\mathrm{tot}}} = \frac{M_{[\mathrm{Ti}]_{\mathrm{tot}}}}{M_{(\mathrm{Ti})_\mathrm{i}}} \times 100\% \tag{5}$$

— the coefficient of transfer of Ti to metal solution (Ti dissolving in the metal)

$$K_{[\mathrm{Ti}]_\mathrm{S}} = \frac{M_{[\mathrm{Ti}]_\mathrm{S}}}{M_{(\mathrm{Ti})_\mathrm{i}}} \times 100\% \tag{6}$$

TABLE 2

Values of titanium transfer to metal solution coefficients $K_{[\mathrm{Ti}]_\mathrm{S}}$ (%) from slags 1–6 (Table 1) (MgO = 5%)

Temperature (K)	No. of slag	Time of reaction (h)					
		1	2	3	4	5	6
1723	1	6.62	9.98	10.02	13.4	13.39	13.42
	2	4.71	5.91	7.1	7.12	8.30	9.5
	3	4.22	4.95	5.07	7.1	7.1	7.09
	4	4.21	5.57	4.93	5.29	4.93	4.93
	5	2.75	3.14	3.35	3.35	3.35	3.55
	6	1.79	2.03	2.15	2.27	2.27	2.27
1773	1	6.65	8.88	10.04	13.44	16.63	16.85
	2	5.9	7.09	8.31	9.51	9.51	9.52
	3	4.93	5.67	6.39	7.82	7.81	8.54
	4	4.56	4.94	5.3	5.65	5.66	6.01
	5	2.95	3.35	3.74	3.94	4.14	4.14
	6	2.03	2.39	2.63	2.74	2.87	2.87
1823	1	9.99	16.79	20.37	23.28	27.28	27.31
	2	5.9	8.3	10.83	12.06	13.26	13.26
	3	5.63	7.8	9.36	10.08	10.1	10.81
	4	4.92	5.66	6.4	6.77	7.2	7.47
	5	3.34	3.76	4.56	4.96	5.36	5.15
	6	2.26	2.76	3.12	3.6	3.76	3.86

TABLE 3

Values of titanium transfer to metal solution coefficients $K_{[\mathrm{Ti}]_\mathrm{S}}$ (%) from slags 7–12 (Table 1) (MgO = 7%)

Temperature (K)	No. of slag	Time of reaction (h)					
		1	2	3	4	5	6
1723	7	6.62	9.98	10.02	13.4	13.39	13.42
	8	4.71	5.91	7.1	7.12	8.30	9.5
	9	4.22	4.95	5.07	7.1	7.1	7.09
	10	4.21	5.57	4.93	5.29	4.93	4.93
	11	2.75	3.14	3.35	3.35	3.35	3.55
	12	1.79	2.03	2.15	2.27	2.27	2.27
1773	7	6.65	8.88	10.04	13.44	16.63	16.85
	8	5.9	7.09	8.31	9.51	9.51	9.52
	9	4.93	5.67	6.39	7.82	7.81	8.54
	10	4.56	4.94	5.3	5.65	5.66	6.01
	11	2.95	3.35	3.74	3.94	4.14	4.14
	12	2.03	2.39	2.63	2.75	2.87	2.87
1823	7	9.99	16.79	20.37	23.28	27.28	27.31
	8	5.9	8.3	10.83	12.06	13.26	13.26
	9	5.63	7.8	9.36	10.08	10.1	10.81
	10	4.92	5.66	6.4	6.77	7.2	7.47
	11	3.34	3.76	4.56	4.96	5.36	5.15
	12	2.26	2.76	3.12	3.6	3.76	3.86

where M_{im} is the initial mass of metal sample (kg); $M_{\mathrm{sl,i}}$ is the initial mass of slag sample = 0.05 kg; [Si], [C], $[\mathrm{Ti}]_{\mathrm{tot}}$ and $[\mathrm{Ti}]_\mathrm{S}$ are the concentrations of Si, C, Ti total and Ti dissolved in metal, respectively (mass%); $[\mathrm{C}]_{\mathrm{max}_{\mathrm{Fe-C}}}$ is the maximum C content in metal samples used to investigate Ti distribution in $\mathrm{Fe{-}C_{sat}}$ (mass%); and $(\%\mathrm{TiO_2})_\mathrm{i}$ is the initial content of $\mathrm{TiO_2}$ in synthetic slag according to Table 1.

Values of $K_{[\mathrm{Ti}]_{\mathrm{tot}}}$ and $K_{[\mathrm{Ti}]_\mathrm{S}}$ coefficients and their variation with time and temperature are shown in Tables 2–5.

For metallurgical purposes, it is necessary to anticipate Ti transfer from slag to metal taking into account the influences of such parameters as the initial concentration of Ti in the slag, the Ti reduction time and the temperature of this reaction. Employing statistical methods, the equations of the $K_{[\mathrm{Ti}]_{\mathrm{tot}}}$ and $K_{[\mathrm{Ti}]_\mathrm{S}}$ coefficients were derived as functions of three variables: the initial $\mathrm{TiO_2}$ content in the slag, the time of $\mathrm{TiO_2}$ reduction with simultaneous Ti transfer to metal, and the temperature of $\mathrm{TiO_2}$ reduction from the slag.

Such an approach to the Ti transfer problem, also taking into account the time function, gives an approximate evaluation of the dynamics of the process. The Ti transfer coefficients, calculated as a function of $\mathrm{TiO_2}$ content

TABLE 4

Values of total titanium transfer to metal coefficients $K_{[\mathrm{Ti}]_{\mathrm{tot}}}$ (%) from slags 1–6 (Table 1) (MgO = 5%)

Temperature (K)	No. of slag	Time of reaction (h)					
		1	2	3	4	5	6
1723	1	6.62	6.98	10.2	13.4	13.39	16.77
	2	4.77	7.09	8.28	9.49	10.67	10.69
	3	4.93	6.36	7.09	8.52	9.94	10.64
	4	4.92	6.33	7.04	8.11	8.81	9.16
	5	5.11	6.29	6.89	7.69	8.08	8.29
	6	3.94	5.13	5.61	6.09	6.46	6.46
1773	1	6.65	10.4	13.38	16.81	20.02	23.6
	2	5.9	8.27	9.5	10.7	11.89	13.09
	3	5.63	7.8	9.24	9.95	12.08	12.81
	4	5.62	7.95	8.13	8.84	9.9	10.61
	5	5.7	6.7	7.29	7.89	8.68	8.88
	6	4.53	5.38	5.73	6.22	6.69	6.82
1823	1	13.33	16.79	23.77	30.63	34.1	37.56
	2	7.08	10.67	12.03	14.47	15.67	16.87
	3	7.04	9.22	12.24	13.69	15.87	17.03
	4	6.33	8.14	9.96	11.75	12.46	12.81
	5	6.48	7.32	8.52	9.53	10.12	10.51
	6	4.89	6.0	6.85	7.57	8.06	8.18

in the slag, time and temperature, were defined by the authors as dynamic Ti transfer coefficients (in contradiction to the above-mentioned coefficients of Ti transfer from slag to metal).

The general form of these relations can be written as follows

$$K_{\mathrm{d}_{[\mathrm{Ti}]_{\mathrm{tot}}}} = f\left[(\%\mathrm{TiO_2})_{\mathrm{i}},\ t,\ T\right] \text{ at 5 and 7 mass\% MgO} \tag{7}$$

and

$$K_{\mathrm{d}_{[\mathrm{Ti}]_{\mathrm{S}}}} = f\left[(\%\mathrm{TiO_2})_{\mathrm{i}},\ t,\ T\right] \text{ at 5 and 7 mass\% MgO} \tag{8}$$

where $K_{\mathrm{d}_{[\mathrm{Ti}]_{\mathrm{tot}}}}$ is the dynamic total Ti transfer from slag to metal coefficient (at 5 and 7% MgO in slag), $K_{\mathrm{d}_{[\mathrm{Ti}]_{\mathrm{S}}}}$ is the dynamic Ti transfer to metal solution coefficient (at 5 and 7% MgO in slag), $(\%\mathrm{TiO_2})_{\mathrm{i}}$ is the initial $\mathrm{TiO_2}$ concentration in slag according to Table 1 (mass%), t is the reaction time (time of experiment) (h) and T is the reaction temperature (K).

These functions for particular dynamic Ti transfer coefficients determined by means of the stochastic approximation method can be expressed as

TABLE 5

Values of total titanium transfer to metal coefficients $K_{[Ti]_{tot}}$ (%) from slags 7–12 (Table 1) (MgO = 7%)

Temperature (K)	No. of slag	Time of reaction (h)					
		1	2	3	4	5	6
1723	7	6.62	9.98	10.02	13.4	13.39	13.42
	8	4.71	5.91	7.1	7.12	8.30	9.5
	9	4.22	4.95	5.07	7.1	7.1	7.09
	10	4.21	5.57	4.93	5.29	4.93	4.93
	11	2.75	3.14	3.35	3.35	3.35	3.35
	12	1.79	2.03	2.15	2.27	2.27	2.27
1773	7	6.65	8.88	10.4	13.44	16.63	16.85
	8	5.9	7.09	8.31	9.51	9.51	9.52
	9	4.93	5.67	6.39	7.82	8.81	8.54
	10	4.56	4.94	5.3	5.65	5.66	6.01
	11	2.95	3.35	3.74	3.94	4.14	4.14
	12	2.03	2.39	2.63	2.75	2.87	2.87
1823	7	9.99	16.79	20.37	23.28	27.28	27.31
	8	5.9	8.3	10.83	12.06	13.26	13.26
	9	5.63	7.8	9.36	10.08	10.1	10.81
	10	4.92	5.66	6.4	6.77	7.2	7.47
	11	3.34	3.76	4.56	4.96	5.36	5.15
	12	2.26	2.76	3.12	3.6	3.76	3.86

follows

$$\begin{aligned} K_{d_{[Ti]S}} &= f\left[(\%TiO_2)_i,\ t,\ T\right] \\ &= \left[77.87\times10^{-3}(\%TiO_2)_i^2\right] - \left[1.4782(\%TiO_2)_i\right] \\ &\quad - \left[99.34\times10^{-3}(\%TiO_2)_i\times t\right] - \left[72.94\times10^{-3}\times t^3\right] \\ &\quad + \left[0.6385\times t^2\right] + \left[33.6914\times10^{-3}T\right] - 50.496 \end{aligned}$$

at standard deviation = 2.617, and

$$\begin{aligned} K_{d_{[Ti]S}} &= f\left[(\%TiO_2)_i,\ t,\ T\right]_{MgO=7\%} \\ &= +\left[109.243\times10^{-3}(\%TiO_2)_i^2\right] - \left[198.65\times10^{-2}(\%TiO_2)_i\right] \\ &\quad - \left[113.665\times10^{-3}(\%TiO_2)_i\times t\right] - \left[84.35\times10^{-3}\times t^3\right] \\ &\quad + \left[72.228\times10^{-2}\times t^2\right] + \left[36.13\times10^{-3}\times T\right] - 53.228 \end{aligned}$$

at standard deviation = 2.533, and

$$\begin{aligned} K_{d_{[Ti]tot}} &= f\left[(\%TiO_2)_i,\ t,\ T\right]_{MgO=5\%} \\ &= \left[71.775\times10^{-3}(\%TiO_2)_i^2\right] - \left[115.893\times10^{-2}(\%TiO_2)_i\right] \\ &\quad - \left[140.639\times10^{-3}(\%TiO_2)_i\times t\right] - \left[87.036\times10^{-3}\times t^3\right] \\ &\quad + \left[839.531\times10^{-2}\times t^2\right] + \left[48.828\times10^{-3}\times T\right] - 77.078 \end{aligned}$$

at standard deviation = 3.2, and

$$K_{d_{[Ti]_{tot}}} = f\left[(\%TiO_2)_i,\ t,\ T\right]_{MgO=7\%}$$
$$= \left[101.102\times10^{-3}(\%TiO_2)_i^2\right] - \left[162.37\times10^{-2}(\%TiO_2)_i\right]$$
$$-\left[141.334\times10^{-3}(\%TiO_2)_i\times t\right] - \left[118.53\times10^{-3}\times t^3\right]$$
$$+\left[107.109\times10^{-2}\times t^2\right] + \left[70.312\times10^{-3}\times T\right] + 113.648$$

at standard deviation = 3.98.

Determined in this way, the coefficient of titanium transfer from slag to metal can be useful in practice for the prediction of a TiO_2 reduction run. Thus, criteria can be defined concerning charge and slag, avoiding excessive titanium reduction in the blast furnace.

Control of the TiO_2 reduction run under given technological conditions enables the elimination of excessive thickening of pig iron and slag causing technological problems, and controlled protection of the lower part of the blast furnace refractory lining resulting in an extension of its working time.

Reported laboratory investigations into titanium distribution between metal and synthetic slag have also been carried out for slags obtained from fusion of previously reduced ore sinters with enhanced titanium contents. The results of investigations into titanium distribution between metal and slag in semi-industrial conditions have been reported by Łędzki [4]. The values obtained for the titanium concentration in metal and its transfer coefficients under analogous conditions of time and reaction temperature have been consistent within the limits of experimental error.

The results obtained and theoretical analysis lead to the following conclusions.

1. In passing to the metal, titanium partially dissolves in it and partially forms titanium carbido-nitrides in the form of a dispersed solid phase in the metal.
2. The maximum values of the titanium distribution coefficients were obtained when the experiment time was 6 hours, i.e. the assumed time of approaching the equilibrium state. The coefficients for 6-hour experiments, depending on temperature and slag composition, had the following values:

a) for 5% MgO in the slag

$K_{[Ti]_{tot}}$ at 1723 K, 16.7–6.46%,
$K_{[Ti]_{tot}}$ at 1773 K, 23.6–6.82%,
$K_{[Ti]_{tot}}$ at 1823 K, 37.56–8.18%,
$K_{[Ti]_S}$ at 1723 K, 13.24–2.27%,
$K_{[Ti]_S}$, at 1773 K, 16.85–2.87%,
$K_{[Ti]_S}$, at 1823 K, 27.31–3.84%,
at initial TiO_2 contents in slags from 14.87 to 0.53 mass%;

b) for about 7% MgO in the slag
$K_{[Ti]_{tot}}$ at 1723 K, 19.32–9.9%,
$K_{[Ti]_{tot}}$ at 1773 K, 25.93–10.49%,
$K_{[Ti]_{tot}}$ at 1823 K, 42.68–12.41%,
$K_{[Ti]_S}$ at 1723 K, 19.32–2.81 %,
$K_{[Ti]_S}$ at 1773 K, 19.45–3.45%,
$K_{[Ti]_S}$ at 1823 K, 26.26–4.71%,
at initial TiO_2 contents in slags from 14.56 to 0.55 mass%.

3. Titanium transfer to metal $K_{Ti_{tot}}$ and titanium solution in metal $K_{[Ti]_S}$ coefficients increase with increasing initial TiO_2 content in the slag.
4. The derived functional dependences of $K_{[Ti]_{tot}}$ and $K_{[Ti]_S}$ can be useful in predicting the TiO_2 reduction run under conditions imitating those in the blast furnace; they should, however, be verified in experiments under real blast furnace conditions.

The authors intend to report in further papers the results of investigations into the equilibrium of the reduction of titanium oxides from slag in liquid phases and the formation of titanium carbido-nitrides during this reaction.

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