ISSN 1070-4272, Russian Journal of Applied Chemistry, 2007, Vol. 80, No. 9, pp. 1491–1497. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © V.A. Lebedev, V.I. Sal'nikov, M.V. Tarabaev, I.A. Sizikov, D.A. Rymkevich, 2007, published in Zhurnal Prikladnoi Khimii, 2007, Vol. 80, No. 9, pp. 1455–1461.

APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Compatibility of TiO_2 with a $CaO–CaCl_2$ Melt

V. A. Lebedev, V. I. Sal'nikov, M. V. Tarabaev, I. A. Sizikov, and D. A. Rymkevich

Ural State Technical University, State Educational Institution for Higher Professional Education, Yekaterinburg, Russia
AVISMA Titanium and Magnesium Combine, Open Joint-Stock Company, Berezniki, Perm krai, Russia

Received September 16, 2006; in final form, February 2007

Abstract—Interaction of TiO_2 with a $CaO–CaCl_2$ melt was studied to determine whether electrolytic production of titanium from oxide raw materials is possible.

DOI: 10.1134/S1070427207090108

Titanium is among the most widely occurring metals and possesses a unique combination of properties. Its wide and efficient use in various fields of national economy is hindered by the high cost of the metal, which is due to the multistage and batch nature of the Kroll process employed in modern titanium industry. Numerous attempts to develop a continuous electrolytic technique for manufacture of titanium from titanium tetrachloride have failed to produce a widely used industrial technique because of the difficulties associated with the polyvalent nature of the metal, its high vapor pressure, and susceptibility of the tetrachloride to hydrolysis.

In recent years, a considerable interest has been observed in the possibility of electrolytic production of titanium from oxide raw materials. It has been found that understoichiometric titanium dioxide has high electrical conductivity and can serve as a cathode both in reduction of titanium oxides to the metal and in removal of dissolved oxygen from titanium.

It was suggested by Chen et al. [1, 2] to perform direct electrochemical reduction of TiO_2 to titanium in molten $CaCl_2$, which is the so-called FFC process. It was shown on laboratory scale that the reduction reaction occurs at 950°C on a cathode made of solid TiO_2, with oxygen anions oxidized on a graphite anode to give CO_2. Pure calcium chloride $CaCl_2$ was chosen as a molten salt electrode because of the high solubility of calcium oxide in this compound.

Ono and Suzuki [3] studied the high-temperature calcium reduction of TiO_2 and developed a process for continuous production of titanium. The electrolysis was performed at a voltage that was higher than the decomposition voltage of CaO, but lower than that of $CaCl_2$. Ca^{2+} ions were reduced at the cathode to Ca; oxygen evolved at the anode reacted with carbon to give CO and CO_2. A cell for continuous manufacture of titanium was developed and the possibility of using inert anode was discussed.

In [4], a TiO_2 powder or a preform was placed in a holder, and a Ca + 18 wt % Ni alloy, onto the electrolyzer bottom. The reduction was carried out without a current, with the electrochemical circuit formed between the TiO_2 cathode and the calcium alloy. In the process, TiO_2 was reduced and calcium ions were deposited at the anode. The alloy was replenished with calcium at regular intervals of time.

It seems that the FFC process is the best developed and ready for implementation [1, 2, 5, 6].

In view of the possible use of CaO as the main component in electrolytic reduction of TiO_2, it is necessary to substantiate the optimal CaO content and to analyze the oxidation kinetics of O^{2-} ions in relation to temperature and CaO concentration. It remains unclear whether TiO_2 is compatible with the $CaCl_2$–CaO melt.

The rich experience of the electrometallurgy of aluminum indicates that the main reason for a decrease in the current efficiency is the reverse reaction of the electrolysis products (aluminum and CO_2), which may lead to contamination of the metal by carbon via formation of carbides. This issue has not been studied for the materials under consideration. Possibly, it is necessary to choose a stable porous diaphragm for separating the cathode and anode spaces in electrolysis. The aim of this study was to elucidate these issues.

Table 1. Gibbs energy of formation of calcium and titanium oxides and chlorides

Substance	$-\Delta G^0$, cal mol^{-1}, at indicated T, K, according to indicated reference					
	[10]			[11]		
	1100	1200	1300	1100	1200	1300
CaO	124 700	122 400	119 900	125 348	122 782	120 218
$CaCl_2$	152 800	150 308	147 700	153 134	150 416	147 788
TiO	98 900	96 700	94 500	109 990	107 824	105 611
Ti_2O_3	290 600	284 350	278 550	295 847	289 112	282 433
Ti_3O_5	471 050	460 850	450 500	–	–	–
TiO_2	178 000	173 890	169 550	171 410	167 205	163 011
$TiCl_2$	85 100	81 850	78 650	–	–	–
$TiCl_3$	115 600	110 750	105 900	–	–	–
$TiCl_4$	150 050	147 100	144 150	141 529	138 763	136 013

The previously published reports have virtually disregarded the mechanism, and presented no results of analysis, of the reaction between TiO_2 of varied origin with $CaCl_2$–CaO melts of various compositions. At the same time, the possible formation of $TiOCl_2$, $CaO \cdot TiO_2$, and $2CaO \cdot TiO_2$ can strongly affect the parameters and results of the electrolysis.

The solubility of TiO_2 in molten $CaCl_2$ is low, and that of metallic titanium reaches 0.5 wt % at 850°C [7].

The authors of [8] attributed the high residual currents in cathodic deoxidation of titanium in molten calcium chloride to the noticeable solubility of lower titanium oxides in $CaCl_2$.

It has been suggested [9], in an analysis of voltammetric data for oxidized titanium in a molten calcium chloride, that fast oxidation of oxygen ions from the oxide phase causes supersaturation of the $CaCl_2$ melt in CaO, which can react with partly reduced titanium oxide to give titanates of variable composition. The suggestions made in the studies mentioned above have not been directly confirmed.

To elucidate these issues, we made a thermodynamic assessment of the possibility of occurrence of various reactions in the system TiO_2–CaO–$CaCl_2$ and carried out chemical and X-ray phase analyses of the reaction products.

Table 1 lists the standard Gibbs energy of formation of calcium and titanium oxides and chlorides at 1100, 1200, and 1300 K according to [10, 11].

The values recommended by the authors are in reasonable agreement. To determine whether a reaction between titanium oxides and molten $CaCl_2$ is possible, we calculated, using the data in Table 1, the Gibbs energy of the corresponding reactions, ΔG_r^0. The results of these calculations for the temperatures of 1100, 1200, and 1300 K are listed in Table 2.

According to two references, the calculated results virtually coincide. The high positive values of ΔG_r^0 indicate that there is no interaction in the systems under standard conditions. Judging from the decreasing value of ΔG_r^0, calculated per gram-atom of titanium, the probability of a reaction with the $CaCl_2$ melt increases in the order TiO_2, Ti_3O_5, Ti_2O_3, and TiO, in qualitative agreement with the suggestions made in [8].

In the system under consideration, perovskite $CaTiO_3$ can be formed in accordance with the equation

$$3TiO_2 + 2CaCl_2 = 2CaTiO_3 + TiCl_4. \qquad (1)$$

Table 3 list thermodynamic parameters of the substances involved in reaction (1), according to the reference book [12].

The enthalpy of reaction (1) can be found using the equation

$$\Delta H^0_{r,298} = 2\Delta H^0_{CaTiO_3,298} + \Delta H^0_{TiCl_4,298} - 3\Delta H^0_{TiO_2,298} - 2\Delta H^0_{CaCl_2,298} = 2 \times 1661.7 - 805.96 + 3 \times 944 + 2 \times 797.17 = 297 \text{ kJ mol}^{-1}. \qquad (2)$$

The value of ΔH_r^0 at a temperature T is given by

$$\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^{T} \Delta C_p \, dT, \qquad (3)$$

Table 2. Gibbs energy of reactions of titanium oxides with $CaCl_2$

Reaction	$-\Delta G_r^0$, cal mol^{-1} (cal at.$^{-1}$ Ti), at indicated T, K, according to indicated reference					
	[10]			[11]		
	1100	1200	1300	1100	1200	1300
$TiO_2 + 2CaCl_2 = 2CaO + TiCl_4$ (I)	84 150 (84 150)	82 600 (82 606)	81 000 (81 000)	85 453 (85 453)	83 710 (83 710)	82 138 (82 138)
$Ti_3O_5 + 5CaCl_2 = 5CaO + 2TiCl_4 + TiCl_2$ (II)	226 350 (73450)	224 340 (74780)	222 550 (74183)	–	–	–
$Ti_2O_3 + 3CaCl_2 = 3CaO + TiCl_4 + TiCl_2$ (III)	139 750 (69 879)	139 124 (69 562)	139 150 (69 575)	–	–	–
$Ti_2O_3 + 3CaCl_2 = 3CaO + 2TiCl_3$ (IV)	143 700 (71 850)	146 574 (73 287)	150 150 (75 075)	–	–	–
$TiO + CaCl_2 = CaO + TiCl_2$ (V)	41 900 (41 900)	42 758 (42 758)	43 650 (43 650)	–	–	–

Table 3. Thermodynamic parameters of substances involved in reaction (1)

Substance	$-\Delta H^0_{298}$, kJ mol^{-1}	S^0_{298}, J mol^{-1} K^{-1}	$C_p = a + b \times 10^{-3}T + c \times 10^5 T^{-2}$, J mol^{-1} K^{-1}		
			a	b	c
TiO_2	944.0	50.28	75.24	1.17	–18.21
$CaCl_2$	799.17	113.9	71.93	12.73	–2.51
$CaTiO_3$	1661.7	93.8	127.57	5.68	–28.01
$TiCl_4$	805.96	252.9	106.55	1.0	–9.88

where ΔC_p is the difference between the heat capacitiess of the reaction products and starting substances, taken with their stoichiometric coefficients,

$$\Delta C_p = -7.89 - 16.61 \times 10^{-3}T - 6.25 \times 10^5 T^{-2}. \quad (4)$$

Integrating this equation, we obtain

$$\int_0^T \Delta C_p \mathrm{d}T = -7.89T - 8.305 \times 10^{-3}T^2 + 6.25 \times 10^5 T^{-1}. \quad (5)$$

For 298, 100, 1100, and 1200 K, the values of the integral are –991, –15 570, –18 160, and –20 906 J mol^{-1}, respectively. The differences at 1000, 1100, and 1200 K are –14 580, –17 169, and –19 915 J mol^{-1}, respectively. Substituting these values and the enthalpy given by (2) into Eq. (3), we obtain $\Delta H^0_{1000} = -282.42$, $\Delta H^0_{1100} = -279.83$, and $\Delta H^0_{1200} = -277.09$ kJ mol^{-1}.

We calculate the entropy of reaction (1) at 298 K by the equation

$$\Delta S^0_{298} = 2S^0_{CaTiO_3,298} + S^0_{TiCl_4,298} - 3S^0_{TiO_2,298} - S^0_{CaCl_2,298}$$

$$= 2 \times 93.8 + 252.9 - 3 \times 50.28 - 2 \times 113.9$$

$$= 61.86 \text{ J mol}^{-1} \text{ K}^{-1} \quad (6)$$

We find ΔS^0_T as

$$\Delta S^0_T = \Delta S^0_{298} + \int_{298}^T (\Delta C_p/T)\mathrm{d}T. \quad (7)$$

Taking into account Eq. (4), we can write

$$\int_0^T (\Delta C_p/T)\mathrm{d}T = -7.89 \ln T - 16.61 \times 10^{-3}T + 3.125 \times 10^5 T^{-2}.$$

For 298, 1000, 1200, and 1300 K, we obtain –46.38, –70.80, –73.26, and –75.63 J mol^{-1} K^{-1}.

The differences of the integral at a temperature T and at 298 K give values of the integral $\int_{298}^T (\Delta C_p/T)\mathrm{d}T$ at T(K), equal to –24.42, –26.88, and –29.25 J mol^{-1} K^{-1} for 1000, 1100, and 1200 K, respectively. Substituting these values and the entropy given by (6) into Eq. (7), we obtain ΔS_T^0 equal to 37.44, 34.98, and 32.61 J mol^{-1} K^{-1} at 1000, 1100, and 1200 K, respectively.

We find the Gibbs energy of reaction (1) using the equation

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0. \tag{8}$$

At 1000, 1100, and 1200 K, the values of ΔG_T^0 are, respectively, 244 980, 241 352, and 237 958 J mol^{-1}, or 58 552, 57 689, and 56 873 cal mol^{-1}. It can be seen that these values are markedly (by a factor of nearly 2) lower than the respective values for reaction (I) in Table 2.

All the calculations were made for the standard conditions (component activities equal to unity, vapor pressure of 1 atm). The real activities and component concentrations, especially those of products of reaction (1), markedly differ from unity. According to experimental estimates, the concentrations of CaO and $TiCl_4$ in the final melt are lower than 0.01 mol %. Taking into account that the solubility limit of CaO in $CaCl_2$ at the temperature under consideration is close to 20 mol %, we can estimate the shift of ΔG_{CaO} to negative values by the equation

$$\Delta G_{CaO} = RT\ln(0.01/20) = 8.314T(-7.60) = -63.187T. \tag{9}$$

For 1000, 1100, and 1200 K, ΔG_T is $-63\,187$, $-69\,513$, and $-75\,833$ J mol^{-1}, respectively.

The shift of ΔG_{TiCl_4} to negative values was estimated using the equation

$$\Delta G_{TiCl_4} = RT\ln(0.01/20) = 8.314T(-9.21) = -76.57T. \tag{10}$$

For 1000, 1100, and 1200 K, ΔG_{TiCl_4} is $-76\,570$, $-84\,229$, and $-91\,886$ J mol^{-1}, respectively. The shift of the Gibbs energy of reaction (1) for 1000, 1100, and 1200 K is $-202\,944$, $-223\,555$, and $-243\,550$ J mol^{-1}, respectively.

It can be seen that the values obtained become equal to, and even exceed in magnitude the positive standard values of ΔG_r^0, which indicates that, in principle, reaction (1) is possible.

For reaction (I) in Table 2, ΔG_r^0 is 352 084, 345 624, and 338 904 J mol^{-1} at 1100, 1200, and 1300 K, respectively, and the negative shift of the Gibbs energy, calculated by the equation

$$\Delta G_r = 2\Delta G_{CaO} + \Delta G_{TiCl_4}, \tag{11}$$

is obviously insufficient for compensating the positive values of ΔG_r^0. This means that this reaction is thermodynamically impossible.

Unfortunately, we could not find in reference literature any evidence about thermodynamic properties of the compound $TiOCl_2$. However, at temperatures above 300°C it can decompose to give TiO_2 and $TiCl_4$, and, with account of this circumstance, a thermodynamic analysis of reactions that involve this compound is similar to that of reactions involving $TiCl_4$.

EXPERIMENTAL

The aim of our experimental study was to examine the reaction of titanium dioxide TiO_2 with calcium chloride to elucidate the process mechanism and identify the products formed. We used as starting substances titanium dioxide and calcium chloride of chemically pure grade, subjected to preliminary dehydration.

Being an element of the secondary subgroup of Group IV, titanium is the most stable in the tetravalent state. All soluble compounds of Ti^{4+} are easily hydrolyzed, to TiO_2 upon complete hydrolysis, and to $TiOCl_2$ upon incomplete hydrolysis. According to Bol'shakov's data [13], $TiOCl_2$ decomposes at 300°C, whereas in an oxidizing atmosphere (O_2, H_2O) it can be formed at higher temperatures. Zelikman reported [14] that $TiOCl_2$ soluble in the chlorinator melt can be formed as an intermediate product of TiO_2 chlorination.

Titanium tends to form with alkali (M) and alkaline-earth metals (Me) titanates of the types M_2TiO_3, $M_2Ti_2O_5$, $MeTiO_3$, Me_2TiO_4, and Me_3TiO_5, which can be readily obtained by fusion of TiO_2 with carbonates of the respective metals. These properties of titanium suggest that the interaction of TiO_2 with $CaCl_2$ at temperatures above 800°C may involve reactions (I) (Table 2), (1), and

$$CaCl_2 + 2TiO_2 = CaTiO_3 + TiOCl_2. \tag{12}$$

Experiments were carried out in an electrically heated furnace, with the temperature controlled to within ±5°C. Portions of $CaCl_2$ and TiO_2, weighed with an accuracy as good as 1 mg, were placed in a beryllium oxide crucible and heated to 800°C, at which $CaCl_2$ was in the liquid state. The overheating of the melt over the melting point of $CaCl_2$ was 50°C. Preliminary experiments at a TiO_2 content of the stock equal to 25–30% demonstrated that the melting

Table 4. Conditions and results of interaction in the $CaCl_2–TiO_2$ system

Run no.	Initial weight, g (%)			Gain in TiO_2 weight, g	Weight and content of $TiOCl_2$ in the electrolyte, counting on TiO_2		Completeness of reaction (12) in terms of TiO_2, %
	$CaCl_2$	TiO_2	CaO		g	%	
1	18.731	3.268 (14.9)	–	0.156	0.224	1.30	13.3
2	14.582	2.610 (15.2)	–	0.198	0.285	1.93	21.6
3	14.008	1.920 (11.8)	0.283	0.147	0.211	1.70	22.0

of the components is accompanied by a substantial increase in the viscosity of the melt. This fact suggests a chemical reaction between the components to give low-mobile complex groups. Further, the content of TiO_2 in the stock was lowered to 12–15%. A melt of this composition had relatively low viscosity at 820°C.

The time of contact between $CaCl_2$ and TiO_2 after the melting was 1.5 h, after which the crucible was cooled, together with the melt, to room temperature and weighed. To evaluate the reaction completeness, the fusion cake was dissolved in water. The precipitate was filtered off on an ash-free paper filter. After washing, the precipitate was dried at 100–120°C, calcined to complete burning-out of the filter at 700°C, and weighed. The calcium chloride solution was analyzed for the presence of CaO and titanium ions.

Titanium was determined in the filtrate by photocolorimetry with diantipyrylmethane, which forms with titanium ions a soluble yellow compound with the light absorption maximum at 380 nm. Variation of acidity in the range 0.5–4 N HCl has no effect on the optical density of solutions. The detection limit of titanium is 0.01 $\mu g\ ml^{-1}$, and its molar extinction coefficient, 1.80×10^4. The coloration develops in 45 min and is stable during several months. The optical density of the solutions is proportional to the titanium concentration in a wide range of concentrations.

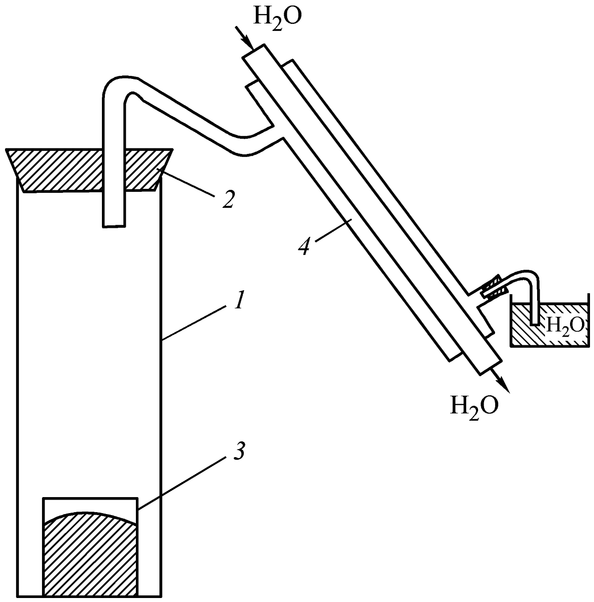
Titanium ions were not found in any of the samples we analyzed. The solutions exhibited a weakly acidic reaction, which confirms the occurrence of hydrolysis.

The mass of the precipitate exceeded that of the starting portion of TiO_2, which indicates that it reacts with $CaCl_2$ to give water-insoluble chemical compounds. The gain in the precipitate weight in run no. 1 (Table 4) was 156 mg (4.8%). Judging from the ratio of the molecular weights, the increase in the precipitate weight is possibly due to the occurrence of a reaction to give $TiCl_4$ and reaction (12) to give $TiOCl_2$. Reaction (I) (Table 2) leads to a decrease in the precipitate weight, because CaO is soluble in water and $TiCl_4$ volatilizes.

To experimentally verify the possibility of titanium tetrachloride formation, we carried out additional experiments (Table 4, run no. 2) in a hermetically sealed cell with a $TiCl_4$ condensation unit (see figure).

A beryllium oxide crucible with the starting substances, $CaCl_2$ and TiO_2, was placed in a hermetic steel cell closed with a rubber plug. After preliminary evacuation at 300–500°C to remove traces of moisture, the stock was heated to 840°C and kept at this temperature for 2.5 h. The condensation unit was cooled with flowing water having a temperature of 15°C.

The $TiCl_4$ vapor pressure is 5.5 mm Hg at 10°C and 10 mm Hg at 20°C. These conditions allow efficient condensation of $TiCl_4$. The end tube of the condensation unit was dipped into water to catch $TiCl_4$ in the case of its breakthrough. In the process, a gel-



Schematic of the installation: (*1*) steel cell, (*2*) rubber plug, (*3*) crucible with a stock, and (*4*) vapor condenser.

like precipitate is to be formed. A visual monitoring of the cell demonstrated that $TiCl_4$ was not formed at all. This compound was found neither in the condensation unit, nor in the final aqueous solution. This indicates that reactions (1) and (I) (Table 2) do not occur. At the same time, the weight of the precipitate that was washed, filtered off, and calcined at 700°C increased by 0.198 g (7.6%). The increase in weight, compared with the first run, was 1.5 times larger. Calculation of the increase in the precipitate weight in terms of reaction (12) demonstrates that obtaining a weight gain equal to 0.198 g requires a TiO_2 expenditure of 0.287 g. The extent of reaction in terms of TiO_2 was 21.6%.

The increase in the precipitate weight is due to the formation of calcium titanate $CaTiO_3$, which can be yielded by two reactions, (1) and (12). Calculation in terms of reaction (1) shows that 1.134 g of TiO_2 should remain in the precipitate ($m^{\text{in}}_{\text{TiO}_2} - m^{\text{react}}_{\text{TiO}_2} = 2.61 - 1.476 = 1.134$) and 1.674 g of $CaTiO_3$ and 1.169 g of $TiCl_4$ should be formed. In this case, the TiO_2 content of the precipitate will be 40.4% and that of $CaTiO_3$, 59.6%. An X-ray phase analysis of the precipitate demonstrated that the content of rutile (TiO_2) was 88.3%, and that of calcium titanate ($CaTiO_3$), 11.7%.[1] Such a significant discrepancy between the results obtained by the calculation of the composition of the precipitate and by its X-ray phase analysis, as well as the absence of a condensate, do not confirm the occurrence of reaction (1).

Calculation in terms of reaction (12) shows that 2.327 g of TiO_2 should remain in the precipitate and 0.481 g of $CaTiO_3$ should be formed. The content of TiO_2 will be 90.5%, and that of $CaTiO_3$, 9.5%. In this case, the calculated increase in the precipitate weight is very close to that furnished by X-ray phase analysis. This suggests that $CaCl_2$ interacts with TiO_2 by reaction (12) to give calcium titanate and titanium oxychloride, which dissolves in the molten salt.

In dissolution of the solidified fusion cake in water, $TiOCl_2$ is hydrolyzed by the reaction

$$TiOCl_2 + H_2O = TiO(OH)Cl + HCl \qquad (13)$$

and precipitates. In calcination of the precipitate at 700–800°C, titanium oxychloride hydrate decomposes to TiO_2:

$$TiO(OH)Cl \rightarrow TiO_2 + HCl. \qquad (14)$$

The results of run no. 3, performed at 860°C in the course of 3 h, show that a higher temperature and a longer keeping time favor more complete course of the reaction between $CaCl_2$ and TiO_2. The filtrate obtained on washing the precipitate was also analyzed for the content of free calcium oxide and titanium ions, and the calcined precipitate was weighed.

In run no. 3 (Table 4), we tested the effect of calcium oxide addition to the $CaCl_2$ melt on the reaction between TiO_2 and the salt melt. The content of CaO in the electrolyte was 2 wt % (about 4 mol %). The experiment was performed at a higher temperature (870°C), with stock keeping for 1 h. The increase in the weight of the precipitate after its washing to remove $CaCl_2$, filtration, and calcination was 0.147 g (7.7%), which virtually coincides in percentage with the results of run no. 2 (7.6%). This may indicate that the equilibrium state is attained by the system $CaCl_2$–TiO_2–$CaTiO_3$–$TiOCl_2$. The weight of $TiOCl_2$ in the electrolyte in run nos. 2 and 3 was, counting on TiO_2, 285 and 211 mg, respectively, and its content, about 1.9 and 1.7 wt %. The calculated extents of reaction between TiO_2 and $CaCl_2$ in run nos. 2 and 3 are virtually the same (21.6–22.0%).

To determine the content of CaO, the filtrate from run nos. 1–3, exhibiting an alkaline reaction, was titrated with solutions of hydrochloric and nitric acids in the presence of an indicator. The results of analysis of run nos. 1 and 2 point to the complete absence of free CaO in the filtrate. Consequently, the whole amount of calcium oxide formed in the reaction of $CaCl_2$ and TiO_2 passes into the precipitate as calcium titanates as a result of its reaction with excess titanium dioxide [reaction (12)]. In run no. 3, we found in solution 15 mg of CaO, which constituted 5.3% of the amount we charged. The incomplete conversion of calcium oxide to perovskite is presumably due to kinetic limitations.

CONCLUSIONS

(1) Thermodynamic calculations demonstrated that, in principle, titanium dioxide can react with a $CaCl_2$ melt to give perovskite $CaTiO_3$ and $TiCl_4$ or $TiOCl_2$.

(2) Experiments were performed to analyze the reaction of TiO_2 with molten $CaCl_2$ and $CaCl_2$–CaO at 820–870°C. The increase in the weight of the filtered-off and calcined precipitate and its quantitative X-ray phase analysis confirm that there occur reactions of TiO_2 with molten $CaCl_2$ to give perovskite. The extent of the reaction increases with temperature, keeping time, and CaO content of the starting melt.

---

[1] The X-ray phase analysis was made at the Institute of Solids, Ural Division, Russian Academy of Sciences.

The most probable pathway of the reaction of TiO_2 with the $CaCl_2$ melt is that described by Eq. (12).

(3) The binding of TiO_2 into calcium titanates markedly complicates the electrolytic production of titanium from oxide raw materials. This is so because the activity of TiO_2 in the titanates is substantially lower and it is difficult for CaO to pass from TiO_2 pellets into the $CaCl_2$ melt.

REFERENCES

1. Chen, G.Z. and Fray, D.J., *Progress in Molten Salt Chemistry 1: Prof. N.J. Bjerrum Special Volume*, Berg, R.W. and Hjuler, H.A., Eds., Elsevier, 2000, pp. 157–161.
2. Chen, G.Z., Fray, D.J., and Farthing, T.W., *Nature*, 2000, September, vol. 407, pp. 361–364.
3. Ono, K. and Suzuki, R.O., *J. Met.*, 2002, February, pp. 59–61.
4. Abiko, T., Park, I., and Okabe, T.H., Abstracts of Papers, *10th World Conf. on Titanium*, Hamburg (Germany), July 15, 2003.
5. Stresov, L., Ratchev, I., et al., Patent WO 03/016594 A1, February 27, 2003.
6. JPN Patent Appl. 2005-194554 (P2005-194554A).
7. Sibert, M.E., McKenna, Q.H., Steinberg, M.A., and Wainer, E., *J. Electrochem. Soc.*, 1955, vol. 102, pp. 252–260.
8. Chen, G.Z., Fray, D.J., and Farthing, T.W., *Metall. Mater. Trans.*, 2001, vol. 32B, pp. 1041–1051.
9. Chen, G.Z. and Fray, D.J., *J. Electrochem. Soc.*, 2002, vol. 149, no. 11, pp. 455–467.
10. Wicks, C.E., and Block, F.E., *Thermodynamic Properties of 65 Elements, Their Oxides, Halides, Carbides, and Nitrides*, Washington: US Government, 1963.
11. Kubashevski, O. and Evans, E.L., *Metallurgical Thermochemistry*, London, 1951.
12. *Termodinamicheskie svoistva neorganicheskikh veshchestv: Spravochnik* (Thermodynamic Properties of Inorganic Substances: Reference Book), Zefirov, A.P., Ed., Moscow: Atomizdat, 1965, pp. 86, 118, 132.
13. *Khimiya i tekhnologiya redkikh i rasseyannykh elementov* (Chemistry and Technology of Rare and Trace Elements), Bol'shakov, K.A., Ed., Moscow: Vysshaya shkola, 1976, part 2.
14. Zelikman, A.N., *Metallurgiya tugoplavkikh redkikh metallov* (Metallurgy of Rare Refractory Metals), Moscow: Metallurgiya, 1986.