

Calciothermic Reduction of Titanium Oxide Compounds

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Abstract—The reduction of TiO₂ and CaTiO₃ in a mixture with calcium has been studied in an argon atmosphere and vacuum at temperatures in the range 1023–1123 K. The adiabatic temperature of the reduction reactions involved has been calculated as a function of the excess of calcium in the starting mixture and its initial temperature. The presence of a thin CaCl₂ film on calcium particles and the use of calcium titanate as a precursor have been shown to increase the reduction rate. The use of a CaTiO₃ precursor and CaCl₂-activated calcium has made it possible to obtain titanium powders containing 0.5 wt % oxygen and having a specific surface area of 1.2 m²/g via reduction at a temperature of 1073 K for 6 h.

Keywords: titanium, powder, calciothermic reduction, titanium dioxide, calcium titanate, calcium chloride, adiabatic temperature

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INTRODUCTION

Calcium reduction of titanium dioxide follows the exothermic reaction



The reduction process is usually run at temperatures from 1273 to 1473 K. Under such conditions, the oxygen affinity of calcium is about 120 kcal/g-at [1]. However, it should be taken into account that titanium and oxygen form solid solutions in a wide range of oxygen concentrations [2]. The stability of Ti–O solid solutions increases with decreasing oxygen content [3], so there are limited possibilities of obtaining titanium with low oxygen content. At a temperature of 1273 K, the total thermodynamic potential of titanium–oxygen bond formation in a solid solution containing 0.07% oxygen is essentially identical to that in CaO. In practice, a considerable amount of calcium chloride, sufficient for dissolving the forming CaO in its melt, is added to the starting mixture for the reduction process. Removing calcium oxide from the reaction zone helps reduce the oxygen content of the titanium powder.

Kikuchi et al. [4] studied the reduction of titanium dioxide powders differing in particle size. The reduction process was run in molten CaCl₂ at a temperature of 1173 K. According to their results, the process is stepwise and involves the formation of the Ti₂O₃, TiO, Ti₂O, Ti₃O, and Ti₆O lower titanium oxides as reaction intermediates. Besides, in the case of incomplete

reduction the powder may contain CaTiO₃, resulting from chemical interaction of CaO (reaction product) and residual TiO₂. The reduction process was accompanied by a considerable decrease in specific surface area: from 120.3 m²/g in the case of the parent TiO₂ to just 1.794 m²/g in the titanium powder. The oxygen content of the titanium powder was 0.42 wt %.

The reduction of TiO₂ with calcium vapor has been the subject of several studies [5–9]. Samples for reduction had the form of compacted TiO₂ + CaCl₂ mixtures. The 1173 K reduction of TiO₂ compacts with an average particle size of 0.2 μm reached completion in 6 h. The particle size of the resultant titanium was 1–2 μm [6]. Wan et al. [7], Xu et al. [8], and Jia et al. [9] studied the reduction of tablets produced by pressing mixtures of calcium chloride and TiO₂ in different ratios. The process was run in a vacuum of 8–20 Pa at a temperature of 1273 K. The optimal CaCl₂ : TiO₂ weight ratio was 1 : 2. The reaction intermediates identified were the lower titanium oxides and the CaTiO₃ titanate. The titanate was assumed to be easier to reduce than Ti₂O, the last lower oxide before the formation of metallic titanium.

The feasibility of obtaining titanium via reduction of the CaTiO₃ titanate was studied by Lei et al. [10]. The starting materials used to synthesize the titanate were TiO₂ and CaCl₂ · 2H₂O in the molar ratio 2 : 1. The starting mixture was pressed into tablets, which were then dried and sintered in air at a temperature of

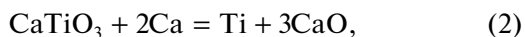
1273 K for 2 h. The green compacts had a porous structure, which facilitated calcium vapor diffusion to the reaction zone. The reduction process was run in a vacuum of 20 Pa at a temperature of 1273 K for 6 h. The oxygen content of the resultant Ti powder was not specified.

In the above studies, reduction was carried out at temperatures from 1173 to 1273 K. However, it follows from the relationship between the Gibbs energies of formation of the lower titanium oxides, solid solutions of oxygen in titanium, and calcium oxide [3] that lowering the process temperature helps obtain titanium with a lower oxygen content. In the case of the calcium reduction of titanium oxides, equilibrium oxygen content is 0.1 wt % at a temperature of 1273 K and 0.03 wt % at 927 K [1].

The purpose of this work was to study the feasibility of obtaining titanium powder via calcium reduction of titanium dioxide and the CaTiO_3 titanate at a temperature below 1073 K. A high degree of reduction of zirconium dioxide and the CaZrO_3 zirconate with calcium under such conditions was demonstrated previously [11].

EXPERIMENTAL

The adiabatic temperature (T_{ad}) of reaction (1) and that of the reduction of the CaTiO_3 titanate,



were determined as functions of the temperature of the starting mixture (T_0) and the excess of the reducing agent (Δm_{Ca}) using the TERRA software suite for modeling chemical and phase equilibria [12]. The thermodynamic modeling procedure was described in detail previously [13].

The starting materials for the reduction process were pure-grade titanium dioxide powder (Russian Federation Purity Standard TU 6-09-2166-77) with a specific surface area of 7 m²/g and CaTiO_3 titanate powder with a specific surface area of 1.5 m²/g. The latter was synthesized via solid-state sintering of pure-grade titanium dioxide and calcium carbonate at a temperature of 1573 K for 2 h and then ground to a particle size under 400 μm. The reducing agent used was calcium in the form of granules ranging in particle size from 0.04 to 2.0 mm (Russian Federation Purity Standard TU 083.5.290-92), fabricated at AO Chepetsk Mechanical Plant. Calcium was used as-received or after activation via wetting with a saturated CaCl_2 solution in ethanol, followed by drying in air [11]. The amount of CaCl_2 added with the solution was 10–20 g for 100 g of calcium, which was considerably smaller than the amount of CaCl_2 in the above-mentioned studies.

A weighed amount of TiO_2 (8 g) or CaTiO_3 (10 g) as a titanium precursor was mixed with calcium in a 25 or 50% excess relative to the stoichiometry of reactions (1) and (2). The resultant mixture was loaded into a 23-mm-diameter cylindrical niobium container. The height of the loaded powder was 30–40 mm. To improve contact between the reactants, the starting mixture was densified.

The reduction process was run in the range 1023–1123 K either under dynamic vacuum produced in the reactor by a 2NVR-5DM roughing pump or in an argon atmosphere (at a pressure of 110 kPa). The holding time was varied from 1 to 6 h. To remove the excess calcium and the CaO formed, the reaction products were leached twice with a 10% hydrochloric acid solution. The resultant titanium powder was washed with distilled water until neutral solution pH was reached and then dried at a temperature of 323 K.

The phase composition of the synthesis products was determined by X-ray diffraction on a Shimadzu XRD-6000 X-ray diffractometer ($\text{CuK}\alpha$ radiation) using ICDD PDF-2 diffractometry data. The specific surface area of the powders was determined by static BET adsorption measurements on a Micromeritics TriStar II 3020 analyzer. Oxygen concentration in the powders was determined by gas adsorption chromatography in combination with pulsed heating on a K-671 analyzer. The particle size distribution was determined using an FSKh-6K photometric sedimentometer (OOO LabNauchPribor).

RESULTS AND DISCUSSION

At the stoichiometric amount of calcium, the calculated adiabatic temperature of reaction (1) is 2285 K. This value is similar to the adiabatic temperature calculated by Nersisyan et al. [14] using Termo software (Merzhanov Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences), 2470 K, which attests to adequacy of the method. This should be emphasized because the adiabatic temperature obtained by us for reaction (2), 1580 K, is considerably lower than that reported by Lei et al. [10]: 2740 K. The latter value should be regarded as overestimated because heat release in reaction (2) is much smaller than that in reaction (1). Figure 1 illustrates the influence of the Ca excess in the starting mixture and its initial temperature on the adiabatic temperature of the two reactions. Under the experimental conditions of this study, it is either lower or slightly above the boiling point of calcium. This means that the explosive character of the reaction due to the high pressure of its vapor presents no hazard.

Our results on the state of the starting mixture and reduction conditions demonstrate that, during heating

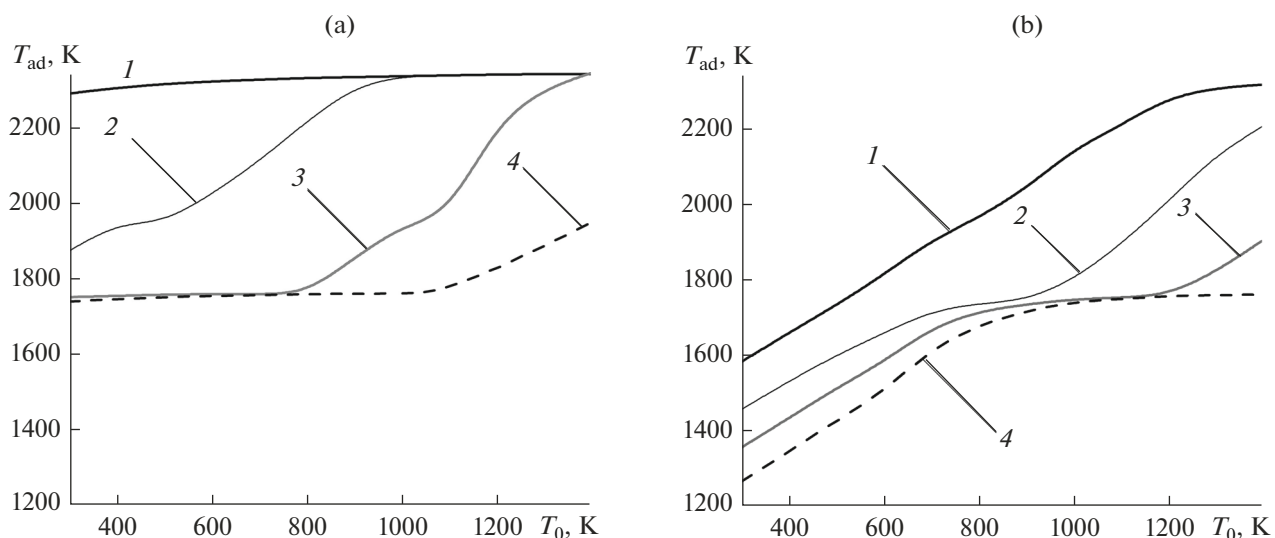


Fig. 1. Adiabatic temperature as a function of starting-mixture temperature for the reduction process in the (a) TiO_2 -Ca and (b) CaTiO_3 -Ca systems: (1) stoichiometric amount of calcium; (2) 25, (3) 50, and (4) 75% excess Ca.

of the mixture of TiO_2 with as-received calcium in argon, an increase in temperature, indicative of the reduction reaction onset, was observed at 1060–1080 K (Fig. 2, curve 1). The use of a starting mixture containing calcium wetted with calcium chloride led to a decrease in reaction onset temperature to 1020–1030 K (Fig. 2, curve 2). During heating in vacuum, reaction between TiO_2 and calcium began at a temperature as low as 960–980 K (Fig. 2, curve 4). Even though consisting of larger particles, the titanate powder was more reactive than TiO_2 : it began to react with activated calcium in an argon atmosphere at a temperature near 1000 K (Fig. 2, curve 3).

Table 1 presents characteristics of the materials obtained by reducing titanium dioxide in an argon atmosphere. The powders prepared using as-received calcium as a reducing agent contained not only metallic Ti (ICDD card no. 89-5009) but also CaTiO_3 (ICDD card no. 89-0056) and Ti_3O (ICDD card no. 76-1644) (Fig. 3, scan 1). Raising the calcium excess in the starting mixture from 25 to 50% enabled a decrease in oxygen content from 2.7 to 1.8 wt %. Under the same conditions, using activated calcium as a reducing agent we obtained a material containing just 1 wt % oxygen. Increasing the reaction time to 6 h led to a more complete reduction: oxygen content decreased to 0.7 wt %. According to X-ray diffraction data, the titanium powders contained no by-products even after reduction at a temperature below the melting point of calcium (Table 1, powder 3; Fig. 3, scan 2).

Running the process in vacuum lowered the reaction onset temperature, but without raising the degree

of reduction of titanium dioxide. Moreover, the degree of reduction dropped considerably. The powders obtained by reducing the starting mixture containing as-received calcium for 1–3 h in the range 1073–1123 K contained 9–10 wt % oxygen. The use of activated calcium in the starting mixture allowed us to slightly improve process parameters. Figure 4 shows the oxygen content of titanium as a function of reduction temperature at calcium excesses of 25 and 50 wt % in the starting mixture and holding times of 1 and 3 h. With increasing process temperature, the percentage of oxygen decreases and the effect of the holding time becomes weaker. All of the powders in this series, except for those obtained by reducing the starting mix-

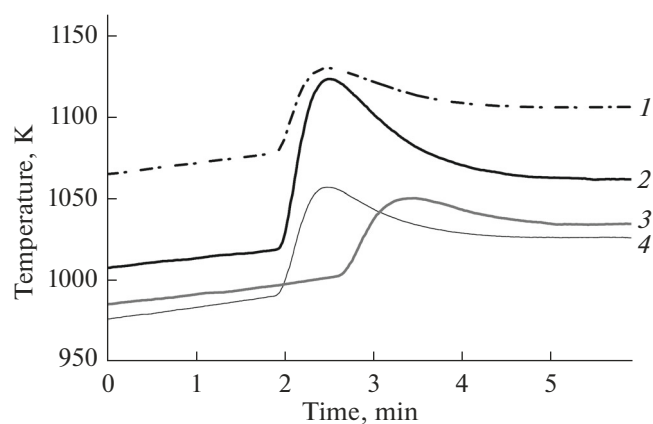


Fig. 2. Variation of temperature during the reduction of TiO_2 in argon (1, 2) and vacuum (4) and CaTiO_3 in argon (3): (1, 4) as-received calcium, (2, 3) calcium wetted with calcium chloride.

Table 1. Characteristics of the powders prepared by reducing titanium dioxide in an argon atmosphere

No.	$\Delta m_{\text{Ca}}, \%$	T, K	τ, h	Phase composition	$S, \text{m}^2/\text{g}$	wt % O_2
As-received Ca						
1	25	1123	3	Ti, CaTiO_3 , Ti_3O	0.7	2.7
2	50			Ti, CaTiO_3 , Ti_3O	1.0	1.8
CaCl ₂ -activated Ca						
3	50	1073	6	Ti	0.7	0.9
4	50	1123	3	Ti, CaTiO_3^* , Ti_3O^*	0.6	1.0
5			6	Ti	0.5	0.7

S is the specific surface area of the powders and wt % O_2 is oxygen concentration in the powders.

* Trace amount.

Table 2. Characteristics of the powders prepared by reducing CaTiO_3 in an argon atmosphere

No.	$\Delta m_{\text{Ca}}, \%$	T, K	τ, h	Phase composition	$S, \text{m}^2/\text{g}$	wt % O_2
As-received Ca						
1	50	1123	1	Ti, CaTiO_3 , $\text{TiO}_{0.89}$	3.2	3.2
2			3	Ti	1.8	2.6
CaCl ₂ -activated Ca						
3	50	1073	6	Ti	1.2	0.5
4	50	1123	1	Ti	1.0	0.4
5			3	Ti	0.8	0.4

ture containing 50 wt % excess calcium at a temperature of 1123 K, contained, in addition to the Ti and CaTiO_3 phases, the titanium oxide Ti_3O (ICDD card no. 76-1644).

The specific surface area of the powders with the lowest oxygen content prepared by reducing titanium dioxide with activated calcium in an argon atmosphere and vacuum is 0.5–0.7 and 0.9–1.2 m^2/g , respectively. This is considerably smaller than the specific surface area of the precursor (7.0 m^2/g). A similar effect, namely, a decrease in the specific surface area of powders relative to their precursor, was reported by Kikuchi et al. [4].

Table 2 presents characteristics of the powders prepared by reducing calcium titanate in an argon atmosphere. These results confirm previously reported data

[10] demonstrating the feasibility of using this precursor. The rise in temperature accompanying the reaction onset during heating of the starting mixture containing as-received Ca was observed at 1123 K; that is, it corresponded to the reduction temperature used in this study. After holding for 1 h at this temperature in an argon atmosphere, we obtained titanium powders containing 3.2 wt % oxygen, which however contained impurity phases as well: CaTiO_3 titanate and Ti_3O oxide (Fig. 3, scan 3). Increasing the holding time to 3 h allowed us to obtain single-phase titanium powder according to X-ray diffraction data (Table 2, powder 2).

The use of a starting mixture containing calcium wetted with a calcium chloride solution markedly activated the reduction process. The reaction onset temperature was about 1000 K (Fig. 2, curve 3). The only phase in the powders was titanium. Powders 3–5

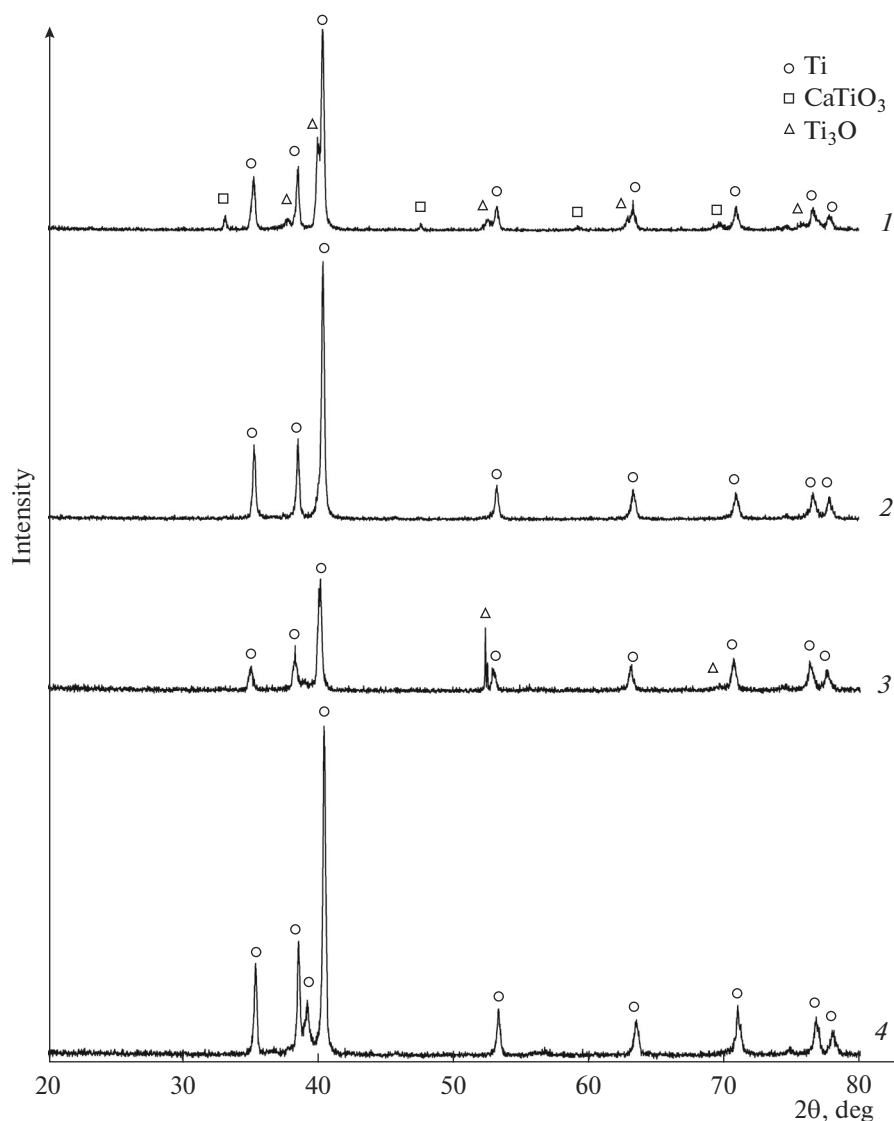


Fig. 3. X-ray diffraction patterns of the powders prepared by reducing (1, 2) TiO_2 and (3, 4) CaTiO_3 using (1, 3) as-received calcium and (2, 4) calcium wetted with CaCl_2 .

(Table 2) had a factor of 1.7 larger specific surface area but contained half as much oxygen as the powders prepared by reducing TiO_2 under the same conditions (Table 1, powders 4, 5).

During reduction in vacuum, reaction began at the same temperature as in an argon atmosphere. The oxygen content of the powders prepared using the starting mixture containing 25 wt % excess calcium was at a level of 8 wt %. The powders prepared using the starting mixture containing 50 wt % excess calcium (Fig. 5) contained a factor of 1.5 to 3 less oxygen than the powders prepared under the same conditions using titanium dioxide. Note that oxygen content decreases with decreasing reduction temperature, in accordance

with the relationship identified for the reduction of zirconium oxide compounds [11].

The fact that, in the case of the reduction of titanium dioxide, the oxygen content of the powder did not decrease with decreasing reduction temperature (Fig. 4), in contrast to what was observed previously [11], can be accounted for as follows. As distinct from the reduction of zirconium dioxide, the reduction of titanium dioxide is a stepwise process involving the formation of lower oxides as reaction intermediates. After the formation of lower titanium oxide particles, further decrease in oxygen content is due to oxygen diffusion from the bulk to the surface in contact with calcium. The diffusion rate rises with increasing tem-

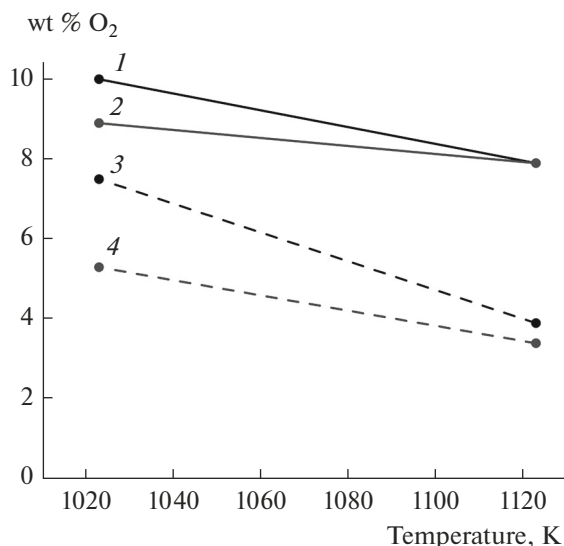


Fig. 4. Effect of reduction temperature on the oxygen content of the titanium powders prepared by reducing TiO_2 in vacuum at Ca excesses of (1, 2) 25 and (3, 4) 50 wt % and holding times of (1, 3) 1 and (2, 4) 3 h using calcium wetted with CaCl_2 .

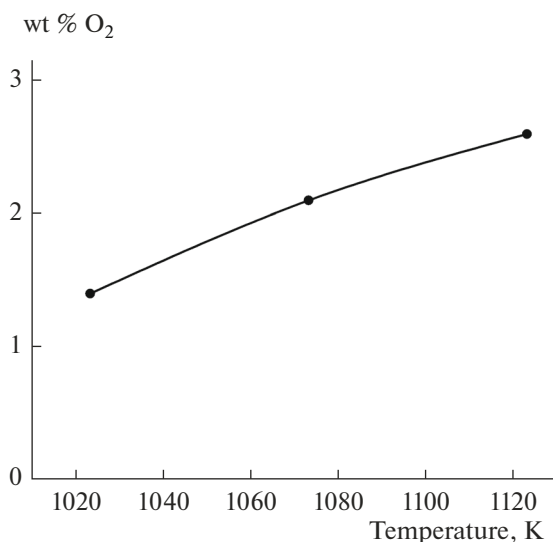


Fig. 5. Effect of reduction temperature on the oxygen content of the titanium powder prepared by reducing CaTiO_3 in vacuum at a Ca excess of 50 wt % and a holding time of 3 h using calcium wetted with CaCl_2 .

perature and, accordingly, oxygen is removed more rapidly and the degree of reduction rises. Another limiting factor influencing the rate of oxygen removal is the particle size.

Figure 6 shows particle size distributions in the powders. In the powder prepared by reducing TiO_2 ,

the fraction of particles less than $10\ \mu\text{m}$ in size is about 40% and that of particles less than $5\ \mu\text{m}$ in size is about 30% (Fig. 6a). The powder particles obtained by reducing CaTiO_3 are considerably smaller: about 95% of the particles are less than $10\ \mu\text{m}$ in size, and the fraction of particles less than $5\ \mu\text{m}$ in size is about 75% (Fig. 6b). Therefore, the oxygen diffusion path to the surface in this powder is considerably shorter, and the amount of oxygen decreases more rapidly. It seems likely that the substantial decrease in the particle size of the powder prepared using CaTiO_3 as a precursor enabled a decrease in the oxygen content of the titanium with decreasing reduction temperature, as suggested by the thermodynamics of the process.

The specific surface area of the powders prepared by reducing calcium titanate exceeds that of the powders prepared using TiO_2 as a precursor, but the difference is smaller than that observed in the case of the reduction of simple and double oxides of the Group V (Nb and Ta) and VI (Mo and W) refractory rare metals [15–17]. This lends support to the assumption made previously that a different mechanism is responsible for the formation of metal particles during the reduction of Group IV metal oxide compounds [11]. The larger specific surface area of the powders prepared by reducing calcium titanate is due to the lower degree of aggregation of primary titanium particles during the reduction process.

The observed decrease in the degree of reduction when the process was run in vacuum is an anomalous effect and further research is needed to understand it.

CONCLUSIONS

The adiabatic temperature of reactions underlying the calcium reduction of TiO_2 and CaTiO_3 has been calculated as a function of the excess of the reducing agent and the initial temperature of the reactants. At an initial temperature of 1100 K and calcium excess of 50 wt % relative to stoichiometry, the adiabatic temperature is 1970 K for the reduction of TiO_2 and 1750 K for the reduction of CaTiO_3 . This suggests that the reaction in the reactant mixture proceeds smoothly, without ejection of its components by calcium vapor.

The onset temperature for reaction of calcium with TiO_2 is 1070 K, and that for reaction with CaTiO_3 is 1123 K. If calcium activated by applying a small amount of CaCl_2 to its surface (10–20 g of CaCl_2 for 100 g of Ca) is used as a reducing agent, the reaction onset temperature is lower by 50 and 100 K, respectively, and a more complete reduction is possible. Under identical conditions, the degree of reduction of titanium is higher if CaTiO_3 is used as a precursor. The use of activated calcium in the starting mixture

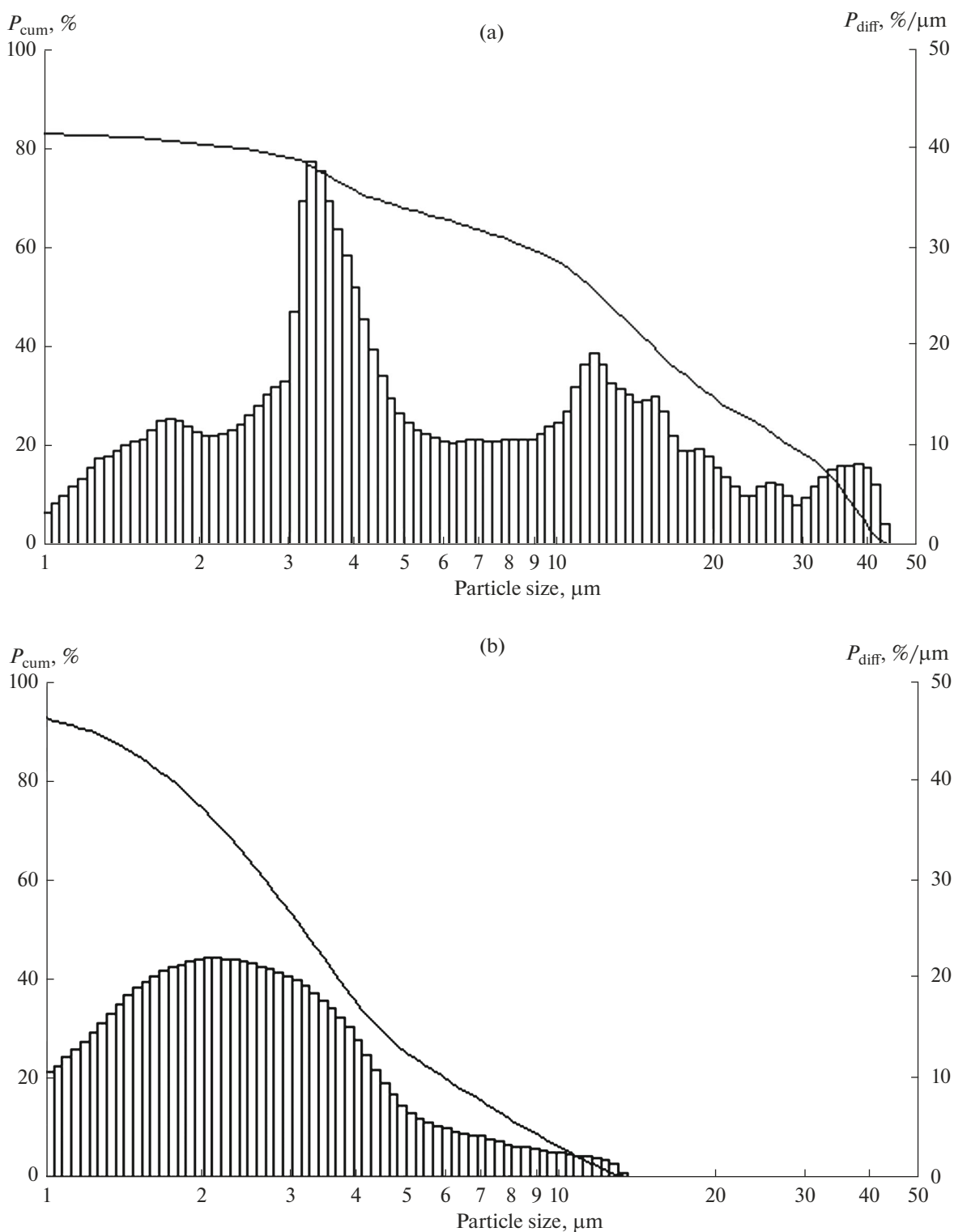


Fig. 6. Particle size distributions in the powders prepared by reducing (a) TiO_2 ($S = 0.9 \text{ m}^2/\text{g}$) and (b) CaTiO_3 ($S = 1.6 \text{ m}^2/\text{g}$) at a temperature of 1123 K.

has made it possible to obtain titanium powders with rather low oxygen content at a temperature of 1073 K and holding time of 6 h: 0.9 (TiO_2 precursor) and 0.5 wt % (CaTiO_3 precursor), with specific sur-

face areas of 0.7 and $1.2 \text{ m}^2/\text{g}$, respectively. The particle size of the forming titanium powder has been shown to influence the degree of reduction.

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