

Preparation of various titanium suboxide powders by reduction of TiO_2 with silicon

C. HAUF, R. KNIEP

Technical University Darmstadt, Department of Inorganic Chemistry, Eduard-Zintl-Institut, Hochschulstr. 10, 64289 Darmstadt, Germany

G. PFAFF

Merck KGaA, Research & Development, Pigments Division, Frankfurter Str. 250, 64293 Darmstadt, Germany

Various titanium suboxide powders have been produced by solid-state reaction between TiO_2 powders or TiO_2 coated mica and silicon as reducing agent at temperatures below 1000°C in an inert atmosphere. The process leads to blue-grey powders with colour characteristics depending on the composition and the structure of the materials. Titanium suboxides like Ti_2O_3 , $\gamma\text{-Ti}_3\text{O}_5$, Ti_4O_7 , Ti_7O_{13} , Ti_8O_{15} or Ti_9O_{17} are formed during the reduction processes. Calcium chloride as an additive, type of atmosphere as well as temperature have an important influence on the composition and on the colour of the powders. The titanium suboxide powders were characterized by XRD. © 1999 Kluwer Academic Publishers

1. Introduction

The phase diagram of the system Ti-TiO₂ investigated by Gilles and Wahlbeck [1] shows several titanium suboxide compositions besides Ti and TiO₂. Pure titanium exists at normal pressure up to a temperature of 883°C as α -titanium in hexagonal close packing and above this temperature up to the melting point at 1677°C as β -titanium in cubic close packing [1]. Oxygen can be dissolved in the α -modification up to the composition Ti₂O by occupation of octahedral holes of the hexagonal close packed titanium atoms [2]. This Ti₂O phase crystallizes in the anti-CdI₂-type and decomposes at 1800°C incongruently to α -titanium and a melt. There is also a low-temperature modification of Ti₂O known which is not shown in the phase diagram [3]. The phase TiO is formed in a homogeneity region from TiO_{0.65} to TiO_{1.25} [4]. The phase Ti₂O₃ which melts congruently at 1839°C includes a homogeneity region from TiO_{1.49} to TiO_{1.51} [2]. There are two thermodynamically stable phases ($\alpha\text{-Ti}_3\text{O}_5$ and $\beta\text{-Ti}_3\text{O}_5$) and a metastable phase ($\gamma\text{-Ti}_3\text{O}_5$) of different crystal structures for the composition Ti₃O₅. $\beta\text{-Ti}_3\text{O}_5$ melts incongruently at 1774°C and is transformed to the low temperature modification $\alpha\text{-Ti}_3\text{O}_5$ at 120°C [5]. Oxygen rich phases (Magnéli phases) are formed likewise having the composition Ti_nO_{2n-1} ($4 \leq n \leq 9$) [6]. Rutile which melts at 1870°C forms the most oxygen rich phase of the system Ti-TiO₂ [7]. Titanium dioxide exists in four modifications. Besides a high-pressure modification crystallizing in the $\alpha\text{-PbO}_2$ structure, the three titanium dioxide types rutile, anatase and brookite are known. Rutile is at normal pressure the thermodynamic stable TiO₂ modification independent of temperature. There is an equilibrium between rutile and the high-pressure modification. On the other hand, anatase and brookite are transformed

in dependence on pressure and temperature monotropically into one of the thermodynamically stable phases [8]. All TiO₂ modifications have structures consisting of titanium atoms octahedrally coordinated to oxygen, whereas oxygen atoms are threefold coordinated to titanium. The titanium dioxide modifications differ from each other by the linking of the TiO₂ octahedra.

Titanium suboxides have already been synthesized for example by reduction of titanium dioxide [1, 2]. As an example, the preparation of golden yellowish titanium monoxide is possible by the reaction of titanium and titanium dioxide at temperatures of about 1500°C in vacuum. The intensive colour of some of the titanium suboxides make them interesting for use as pigments in form of their powders.

The primary objective of the present paper was the investigation of the synthesis of titanium suboxide powders of various compositions via a solid-state reaction. Rutile and anatase powders as well as rutile and anatase fixed on mica platelets were used together with silicon powder and calcium chloride as starting materials to obtain intensively coloured titanium suboxide powders after reaction [9]. The formation of these products under different conditions and their characterization by XRD measurements are described here.

2. Experimental procedure

The starting components for the formation of the titanium suboxide powders are summarized in Table I. The morphological properties of the pure rutile and anatase powders are very similar (mean particle size of about $0.40\ \mu\text{m}$ for rutile and $0.35\ \mu\text{m}$ for anatase, specific surface area in both cases $7\ \text{m}^2\text{g}^{-1}$). There is a difference in the amounts of impurities consisting of significantly

TABLE I Characterization of the starting materials

Material	Purity (%)	Mean particle size (μm)	Supplier
Rutile	>99	0.40	Bayer AG, Uerdingen
Anatase	>99.5	0.35	Bayer AG, Uerdingen
Rutile on mica	100	7	Merck KGaA, Darmstadt
Rutile on mica	100	15	Merck KGaA, Darmstadt
Rutile on mica	100	30	Merck KGaA, Darmstadt
Anatase on mica	100	7	Merck KGaA, Darmstadt
Anatase on mica	100	15	Merck KGaA, Darmstadt
Anatase on mica	100	30	Merck KGaA, Darmstadt
Silicon	>99	5	Merck KGaA, Darmstadt
CaCl ₂	>97		Merck KGaA, Darmstadt

higher values for Al, Si and organic components for the rutile powder. The particle size of the TiO₂/mica particles was varied in order to study the influence of this parameter. Silicon powder or silicon/calcium chloride powder mixtures were tested as reducing agents. Argon and nitrogen (Messer Griesheim, purity 99.996%) were used alternatively to realize an atmosphere free of oxygen.

The TiO₂ or the TiO₂/mica powders were homogenized under dry conditions together with the silicon powder or the silicon/CaCl₂ powder mixture using a roll bench. The mixtures were filled into quartz glass boats which were placed in the center of a horizontal quartz glass tube. Air in the tube was replaced by argon or nitrogen to get an optimal reducing atmosphere for the reactions. The tube was then installed in an electric tube kiln which was already heated to the desired reaction temperature. The experiments were carried out using stationary or streaming gas atmospheres. Streaming of the gases was controlled by rotameters. After 2 h in case of mica containing materials and 4 or 12 h in case of pure rutile or anatase powders, the hot tube was taken out of the kiln. After cooling down to room temperature, the tube was opened and the products were isolated. In summary, the following parameters were varied during the experiments: Reaction time, temperature, gas atmosphere (argon or nitrogen, stationary or streaming 120 l/h), reducing agent (silicon or silicon/CaCl₂ mixture), and particle size (TiO₂ coated mica). The weight ratios for

the starting compositions were TiO₂ : Si = 100 : 25 and TiO₂ : Si : CaCl₂ = 100 : 8 : 3, respectively. The sample size was 5 g.

Characterization of the synthesized pigments was carried out by X-ray diffraction (CuK α ₁, Debye-Scherrer method, STOE Powder Diffraction System No. 6.11.1 with PSD No. 8.11.1).

3. Results

3.1. Reduction of rutile and anatase powders

Experimental conditions for the reduction of TiO₂ powders are given in Table II. Rutile was reduced at 1000 °C in stationary and streaming argon atmospheres and in a streaming nitrogen atmosphere. After 4 h reaction at streaming gas atmosphere, a blue grey product has been formed. However, exclusively rutile was detected in the X-ray powder patterns. After a longer time of reaction (12 h), titanium suboxides Ti_nO_{2n-1} ($n = 7-9$) were formed (Table II, No. 1-3).

The variation of the reducing agent by using a mixture of CaCl₂ and silicon led to the same titanium suboxides as for the reaction without the chloride, when the experiments took place in a streaming gas atmosphere. However, for reactions in a stationary argon atmosphere, the circumstances for the reduction were improved by the addition of CaCl₂. The titanium suboxides Ti_nO_{2n-1} ($n = 7-9$) were already formed after a reaction time of 4 h. After 12 h, the rutile powder was reduced to a dark blue product and the titanium suboxides Ti₂O₃ and γ -Ti₃O₅ were identified in the X-ray diffractogram (Table II, No. 4-7).

The conditions for the reduction of anatase are more restricted than for rutile. Anatase could not be reduced by silicon alone; an observation which does not depend on the gas atmosphere. Only the transformation to rutile could be detected by X-ray diffraction (Table II, No. 8-10). A reduction of anatase was only possible in a stationary argon atmosphere by the addition of CaCl₂ to the reaction mixture. After a reaction time of 4 h, a bluish black material was formed and the suboxides Ti₂O₃, γ -Ti₃O₅ and Ti₄O₇ were detected. In the X-ray pattern of the sample which was heated at

TABLE II Reaction parameters and products of reduction of TiO₂ powders (temperature 1000 °C, weight ratio rutile or anatase: Si = 100 : 25 for No. 1-3 and 8-10, rutile or anatase: Si : CaCl₂ = 100 : 8 : 3 for No. 4-7 and 11-12)

No.	Starting mixture	Time (h)	Gas atmosphere stat. = stationary	Identified titanium oxides	Colour
1	Rutile + Si	4	N ₂ or Ar, 120 l/h	Rutile	Light blue
2	Rutile + Si	12	N ₂ or Ar, 120 l/h	Ti _n O _{2n-1} ($n = 7-9$)	Light blue
3	Rutile + Si	12	Ar, stat.	Ti _n O _{2n-1} ($n = 7-9$)	Light blue
4	Rutile + Si + CaCl ₂	4	N ₂ , 120 l/h	Rutile	Light blue
5	Rutile + Si + CaCl ₂	12	N ₂ , 120 l/h	Ti _n O _{2n-1} ($n = 7-9$)	Light blue
6	Rutile + Si + CaCl ₂	4	Ar, stat.	Ti _n O _{2n-1} ($n = 7-9$)	Light blue
7	Rutile + Si + CaCl ₂	12	Ar, stat.	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
8	Anatase + Si	4	N ₂ or Ar, 120 l/h	Rutile	White
9	Anatase + Si	12	N ₂ or Ar, 120 l/h	Rutile	White
10	Anatase + Si	12	Ar, stat.	Rutile	White
11	Anatase + Si + CaCl ₂	4	Ar, stat.	Ti ₂ O ₃ + γ -Ti ₃ O ₅ + Ti ₄ O ₇	Dark blue
12	Anatase + Si + CaCl ₂	12	Ar, stat.	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue

the same conditions for 12 h, only Ti_2O_3 and $\gamma\text{-Ti}_3\text{O}_5$ were found, while Ti_4O_7 obviously was an intermediate product during the reduction of anatase, and was reduced in the further process to Ti_2O_3 and $\gamma\text{-Ti}_3\text{O}_5$ (Table II, No. 11–12). Fig. 1 shows the X-ray diagram of the blue product prepared from anatase by reduction with a silicon/ CaCl_2 mixture for 12 h.

3.2. Reduction of TiO_2 on mica

The conditions for the reduction of TiO_2 on mica are given in Table III. No relevant difference between the modifications rutile and anatase on mica were observed using comparable conditions of reduction. However, the experiments for the reduction of rutile and anatase on mica by silicon using a streaming gas atmosphere have shown that rutile on mica is more stable against reduction than anatase. The reduction of rutile on mica was only observed by using the smallest particle size (Table III, No. 1), while the reduction of anatase was possible for all particle sizes of the mica substrate (Table III, No. 13–15). In a stationary argon

atmosphere, the reduction of both TiO_2 modifications on mica to dark blue powders was possible during 2 h (Table III, No. 2–4 and No. 16–18). Fig. 2 shows the X-ray pattern of the rutile/mica powder with the mean particle size of $7\ \mu\text{m}$ after the reaction with silicon (Table III, No. 2).

The detected products of the reduction of TiO_2 modifications on mica were the titanium suboxides Ti_2O_3 and $\gamma\text{-Ti}_3\text{O}_5$. It is remarkable, that the products of reactions which took place under stationary argon atmosphere have a more intensive blue colour than samples which have been prepared in streaming nitrogen or argon atmospheres.

By addition of CaCl_2 to the reducing agent, the reaction temperature could be reduced from 1000 to 800°C (experiments were done in a stationary argon atmosphere and in a streaming nitrogen atmosphere). Although the products had a light blue colour, no titanium suboxides could be detected in the X-ray patterns. Reflections of rutile and of mica were exclusively present, even for samples which had been prepared from anatase on mica. Obviously, the amount of titanium

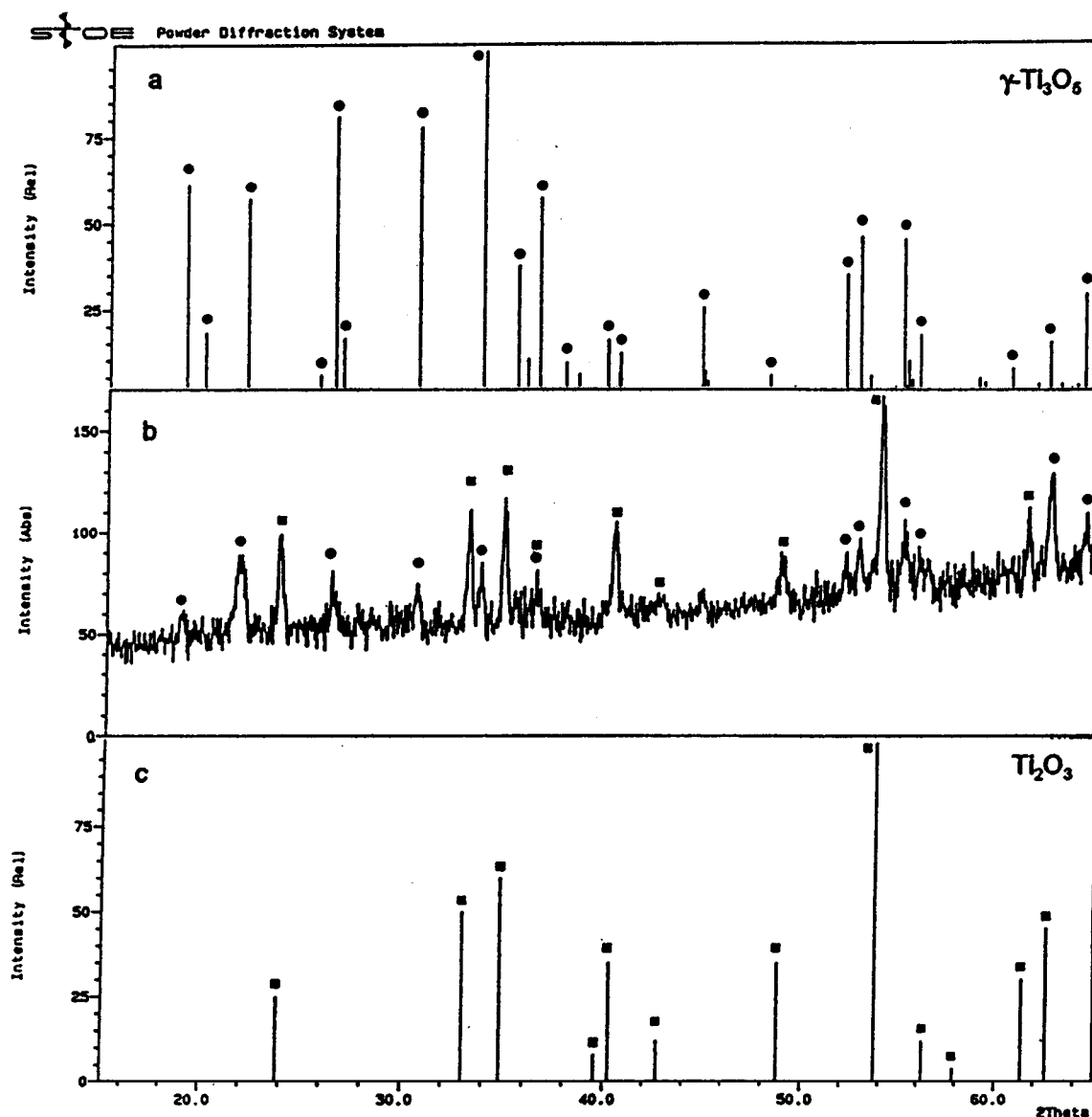


Figure 1 X-ray diagram of the dark blue product prepared from anatase by reduction with a silicon/ CaCl_2 mixture for 12 h (Table II, No. 12). (a) Calculated diagram for $\gamma\text{-Ti}_3\text{O}_5$; (b) measured diagram; (c) calculated diagram for Ti_2O_3 ($\text{CuK}\alpha_1$ -radiation).

TABLE III Reaction parameters and products of reduction of TiO₂ on mica (the X-ray patterns of mica were identified for all samples, reaction time in all cases 2 h, weight ratio rutile or anatase : Si = 100 : 25 for No. 1–4 and 13–18, rutile or anatase : Si : CaCl₂ = 100 : 8 : 3 for No. 5–12 and 19–27)

No.	Starting mixture	Mean particle size (μm)	Gas atmosphere stat. = stationary	Temperature ($^{\circ}\text{C}$)	Identified titanium oxides	Colour
1	Rutile on mica + Si	7	N ₂ or Ar, 120 l/h	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Blue
2	Rutile on mica + Si	7	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
3	Rutile on mica + Si	15	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
4	Rutile on mica + Si	30	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
5	Rutile on mica + Si + CaCl ₂	7	N ₂ , 120 l/h	800	Rutile	Blue
6	Rutile on mica + Si + CaCl ₂	15	N ₂ , 120 l/h	800	Rutile	Blue
7	Rutile on mica + Si + CaCl ₂	30	N ₂ , 120 l/h	800	Rutile	Blue
8	Rutile on mica + Si + CaCl ₂	7	Ar, stat.	800	Rutile	Blue
9	Rutile on mica + Si + CaCl ₂	15	Ar, stat.	800	Rutile	Blue
10	Rutile on mica + Si + CaCl ₂	7	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
11	Rutile on mica + Si + CaCl ₂	15	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
12	Rutile on mica + Si + CaCl ₂	30	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
13	Anatase on mica + Si	7	N ₂ or Ar, 120 l/h	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Blue
14	Anatase on mica + Si	15	N ₂ or Ar, 120 l/h	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Blue
15	Anatase on mica + Si	30	Ar, 120 l/h	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Blue
16	Anatase on mica + Si	7	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
17	Anatase on mica + Si	15	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
18	Anatase on mica + Si	30	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
19	Anatase on mica + Si + CaCl ₂	7	Ar, stat.	800	Rutile	Blue
20	Anatase on mica + Si + CaCl ₂	15	Ar, stat.	800	Rutile	Blue
21	Anatase on mica + Si + CaCl ₂	30	Ar, stat.	800	Rutile	Blue
22	Anatase on mica + Si + CaCl ₂	7	N ₂ , 120 l/h	800	Rutile	Blue
23	Anatase on mica + Si + CaCl ₂	15	N ₂ , 120 l/h	800	Rutile	Blue
24	Anatase on mica + Si + CaCl ₂	30	N ₂ , 120 l/h	800	Rutile	Blue
25	Anatase on mica + Si + CaCl ₂	7	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
26	Anatase on mica + Si + CaCl ₂	15	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue
27	Anatase on mica + Si + CaCl ₂	30	Ar, stat.	1000	Ti ₂ O ₃ + γ -Ti ₃ O ₅	Dark blue

suboxides was too small to be detected by the X-ray powder method (Table III, No. 5–9 and No. 19–24). Increasing the reaction temperature to 1000 $^{\circ}\text{C}$ for these samples led to dark blue products. The X-ray powder patterns are consistent with a mixture of Ti₂O₃ and γ -Ti₃O₅ (Table III, No. 10–12 and No. 25–27).

4. Discussion

The reduction of pure TiO₂ or TiO₂ on mica by silicon or by mixtures of silicon and CaCl₂ with various conditions of the reaction shows that the presence of the chloride has the most important influence. The reaction temperature for the synthesis of blue suboxide powders can be reduced from 1000 to 800 $^{\circ}\text{C}$ and the amount of silicon can be decreased to one third of the original amount. The reason for this should be the formation of a CaCl₂ melt, which is able to improve the diffusion processes between silicon and titanium dioxide [10]. Experiments at temperatures below 800 $^{\circ}\text{C}$ were not successful. Concerning the specific modification of titanium dioxide, a different reactivity can be expected. Metastable anatase should be more reactive compared with rutile. This behaviour was detected by the reaction of TiO₂ modifications on mica with pure silicon. However, the difference between the reactivity of rutile on mica and anatase on mica was very small, and no longer detectable when CaCl₂ was added to the reducing agent.

Obviously, there is a significant effect of the chloride and different reactivities of rutile and anatase on mica do no longer lead to differences concerning the reaction products.

The results for the reduction of pure titanium dioxide powders (anatase or rutile) with silicon do not correspond with the idea of a higher reactivity of anatase. Instead, the reduction of anatase powders was not possible, whereas rutile was reduced to Magnéli phases (Ti_nO_{2n-1}, $n = 7-9$) at comparable conditions. On the other hand, the addition of CaCl₂ to the reaction mixtures leads to titanium suboxides in all cases. Anatase is reduced to Ti₂O₃, γ -Ti₃O₅ and Ti₄O₇ already after 4 h. The final product of the rutile reduction after 4 h preferably consists of Ti_nO_{2n-1} ($n = 7-9$). After 12 h reaction, only Ti₂O₃ and γ -Ti₃O₅ are identified in both cases.

The differences of the reduction behaviour of the rutile and the anatase powders in the experiments without CaCl₂ cannot be explained by thermodynamics or by morphologic properties (particle size distributions and specific surface areas are comparable). On the other hand, a significant influence of impurities of the TiO₂ modifications on the reactivity of the titanium dioxides can be expected. The rutile powder has a significant amount of Al, Si and organics especially on the surface of the particles which could enhance the reactivity of TiO₂ with the reducing agent silicon.

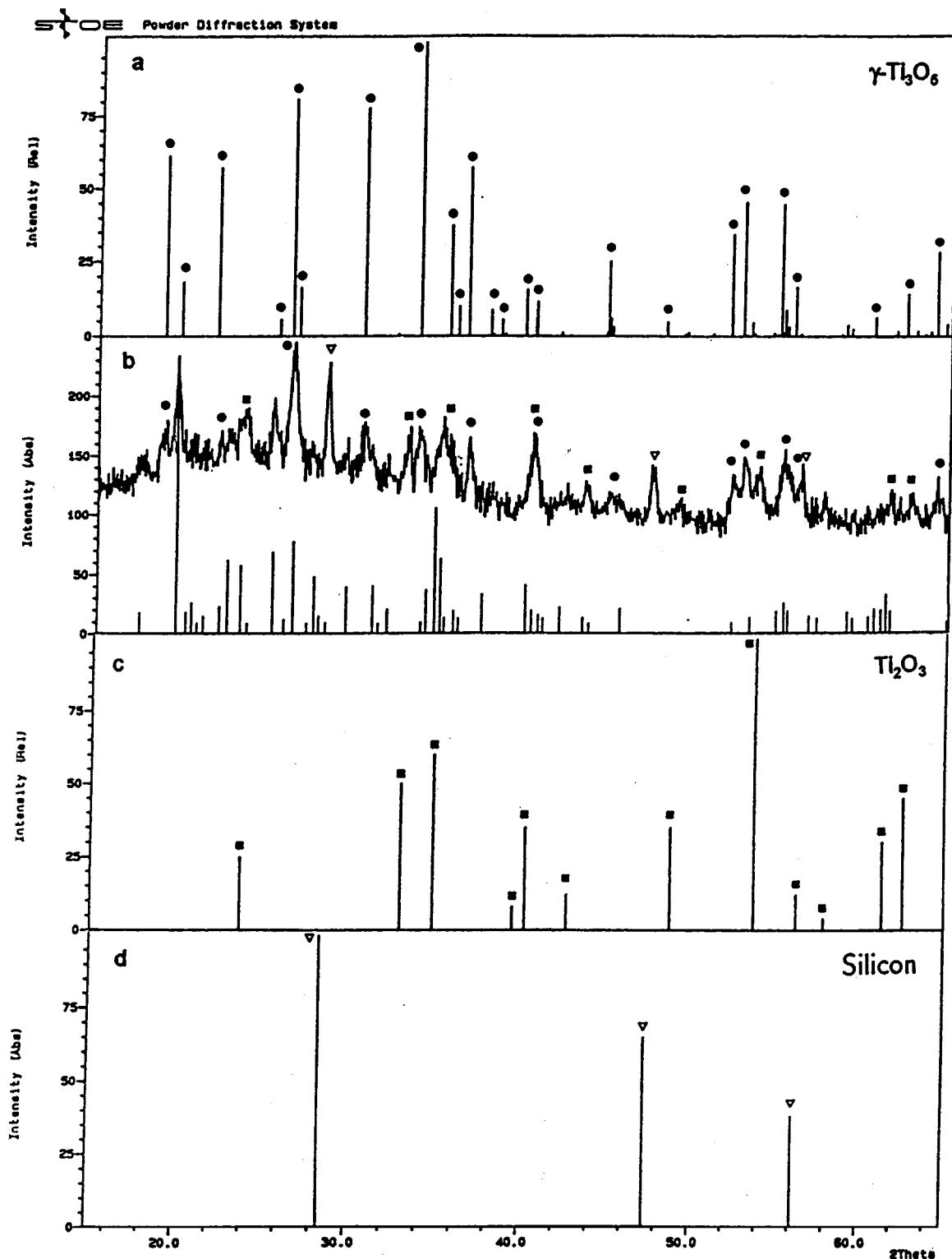


Figure 2 X-ray diagram of the rutile/mica powder with the mean particle size of $7 \mu\text{m}$ after the reaction with silicon for 2 h (Table III, No. 2). (a) Calculated diagram for $\gamma\text{-Ti}_3\text{O}_5$; (b) measured diagram with the calculated diagram for mica; (c) calculated diagram for Ti_2O_3 ; (d) calculated diagram for silicon ($\text{CuK}\alpha_1$ -radiation).

Problems with the preparation of single-phase titanium suboxide powders are caused by the specific thermodynamic stabilities of the $\text{Ti}_n\text{O}_{2n-1}$ phases [11, 12]. Calculations and experiments of Bowden *et al.* [12] show that the composition Ti_4O_7 has an appreciable window of thermodynamic stability over a broad temperature range. There is also an indication of the stability of Ti_7O_{13} , Ti_8O_{15} , and Ti_9O_{17} in the temperature range between 700 and 1000 °C [11, 12]. The reason

for this can be seen in the crystal structures: Furthermore, phases $\text{Ti}_n\text{O}_{2n-1}$ with integral values of $n = 4-9$ have structures derived from the TiO_2 (rutile) type by regular crystallographic shear on (121) planes [13]. The phases Ti_3O_5 and Ti_4O_7 show no detectable homogeneity range. The formation of a definite suboxide is therefore expected to be dominated by nucleation effects.

The stability of Ti_2O_3 can be explained by its corundum structure [2]. The reduction of TiO_2 to the lowest

detected suboxide Ti_2O_3 occurs in all observed cases via the intermediates Ti_9O_{17} , Ti_8O_{15} and Ti_7O_{13} in a first step. Further reduction leads to the suboxides Ti_4O_7 , Ti_3O_5 and finally to Ti_2O_3 . A reduction to TiO was not observed, an effect which can be explained by the relatively low thermodynamic stability of this phase [4].

The colour properties of the reaction products depends on the amount and type of titanium suboxides formed. Slightly reduced TiO_2 is light blue whereas more strongly reduced samples show dark blue or bluish-black colours [1, 2]. This is also consistent with the observations of this work [9]. The presence of Magnéli phases Ti_nO_{2n-1} ($n = 7-9$) leads to light blue materials. On the other hand, the products containing Ti_4O_7 , $\gamma-Ti_3O_5$ and Ti_2O_3 show the expected dark blue colour. The resulting titanium suboxide/mica powders show an excellent lustre, especially as candidate materials for paint, plastics or printing ink systems [10, 14].

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