Carbothermal Reduction and Nitriding of TiO$_2$

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Abstract

Reduction of finely dispersed TiO$_2$ by carbon in nitrogen flow begins at approximately 1000°C. In the initial stages up to approximately 1170°C reduction of TiO$_2$ into lower titanium oxides takes place. Ti$_4$O$_7$ was identified as one of the intermediates. Significant nitriding begins above 1200°C. The solid solution Ti(N, C, O) containing 17·2–19·6 mass% N, 1·5–6·4 mass% C and 0·9–4 mass% O with grain morphology related to the morphology of starting titanium oxides was obtained at 1300–1500°C for 1·5–6 h of isothermal heating. When sintering and grain growth of finely dispersed TiO$_2$ was intentionally suppressed (e.g. by the carbon layer formed on the TiO$_2$ grain surface), powder products with particle sizes comparable with that of the starting TiO$_2$ were obtained.

Die Reduktion von fein dispergiertem TiO$_2$ durch Kohlenstoff im Stickstoffstrom beginnt ab etwa 1000°C. Im Bereich bis c. 1170°C wird das TiO$_2$ zu niederen Oxiden reduziert, wobei Ti$_4$O$_7$ als eine der Zwischenstufen auftritt. Eine bedeutende Nitridierung beginnt oberhalb von 1200°C. Im Temperaturbereich zwischen 1300 und 1500°C mit Haltezeiten von 1·5–6 Stunden kann ein Ti(N, C, O) hergestellt werden, das 17·2–19·6 Gew.-% N, 1·5–6·4 Gew.-% C und 0·9–4·0 Gew.-% O enthält und die Kornmorphologie des TiO$_2$-Ausgangspulvers aufweist. Wenn das Sintern und das Kornwachstum der fein dispersen TiO$_2$-Teilchen unterdrückt wird (z.B. durch eine Kohlenstoffschicht, die auf den TiO$_2$-Kornoberflächen gebildet wird), können Pulverprodukte mit einer Teilchengröße hergestellt werden, die mit der des Ausgangspulvers vergleichbar ist.

La réduction du TiO$_2$ finement dispersé par du carbone sous flux d'azote commence à 1000°C environ. Dans un premier temps, jusqu'à environ 1170°C, le TiO$_2$ est réduit en des oxydes de titane de degré inférieur; Ti$_4$O$_7$ a été identifié comme l'un des intermédiaires. La nitruration commence à être significative au-dessus de 1200°C. Les solutions solides de Ti(N, C, O) contenant de 17·2 à 19·6% massiques d'azote, de 1·5 à 6·4% massiques de carbone et de 0·9 à 4% d'oxygène, avec une morphologie de grains liée à la morphologie des oxydes de titane de départ, ont été obtenues entre 1300 et 1500°C pour des durées d'isothermes variant de 1·5 à 6 h. Lorsque le frittage et la croissance de grains du TiO$_2$ finement dispersé ont été volontairement inhibés (par exemple par la couche de carbone formée à la surface des grains de TiO$_2$), des produits pulvérulents de granulométrie comparable à celle du TiO$_2$ initial ont été obtenus.

1 Introduction

Titanium nitride (TiN), titanium carbide (TiC) and their substitution solid solutions, Ti(N, C), are used in the making of high speed cutting tools (e.g. Al$_2$O$_3$–TiC) because of their hardness and resistance to abrasion. These substances are also applied as coatings on tools to improve their wear resistance.

It was shown[1–5] that reduction of TiO$_2$ by carbon in nitrogen at temperatures above 1100°C can produce titanium nitride or carbonitride powders. The titanium carbide is formed at temperatures below 2200°C in atmospheres of argon or hydrogen, or in vacuum.[4–6]

2 Thermodynamics

The carbothermal reduction and nitriding of TiO$_2$ are described by the overall reaction:
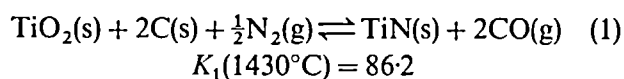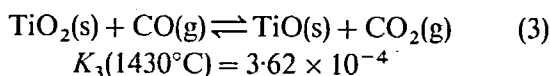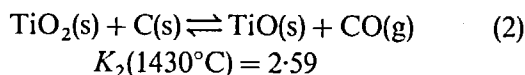
$$TiO_2(s) + 2C(s) + \tfrac{1}{2}N_2(g) \rightleftharpoons TiN(s) + 2CO(g) \quad (1)$$
$$K_1(1430°C) = 86·2$$

Table 1. Equilibrium constants K of reaction (8)

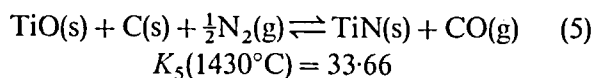| Source	Temperature T (°C)					
	1300	*1480*	*1500*	*1700*	*1800*	*1940*
Experimental data (Ref. 5)	—	—	—	—	—	1·7 from chemical analysis
Experimental data (Ref. 5)	—	—	—	—	—	1·9 from lattice constant
Experimental data (Ref. 8)	0·42	—	0·60	—	1·0	—
Experimental data (Ref. 9)	—	0·55	—	0·9–1	1·3	1·6–1·9 at 1930°C
Calculation according to eqn (10)	0·25	0·51	0·55	1·01	1·31	1·81

where K_1 is the equilibrium constant of reaction (1) at 101 kPa, calculated from the data in Ref. 7. Reaction (1) has to be considered as a sum of a more complex set of partial reactions. It is generally accepted that the initial stage of the reaction is the reduction of TiO_2 to lower titanium oxides—Ti_3O_5, Ti_2O_3 and finally TiO, which forms solid solutions with titanium nitride:
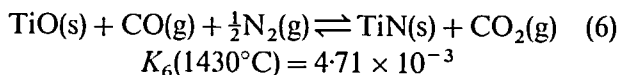
$$TiO_2(s) + C(s) \rightleftharpoons TiO(s) + CO(g) \qquad (2)$$
$$K_2(1430°C) = 2·59$$

$$TiO_2(s) + CO(g) \rightleftharpoons TiO(s) + CO_2(g) \qquad (3)$$
$$K_3(1430°C) = 3·62 \times 10^{-4}$$

Carbon dioxide is then reduced by carbon, present in the system:

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g) \qquad (4)$$
$$K_4(1430°C) = 7·14 \times 10^3$$
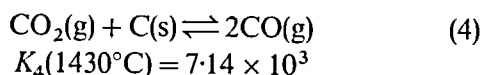
Reactions (3) and (4) have to be considered especially in the latter stages of the reduction, when intimate contact of the solid reactants is interrupted. Titanium nitride is obviously formed by a substitution of oxygen atoms by nitrogen atoms in the TiO structure, or in the structure of Ti(O, N) solid solutions, according to the reactions:

$$TiO(s) + C(s) + \tfrac{1}{2}N_2(g) \rightleftharpoons TiN(s) + CO(g) \qquad (5)$$
$$K_5(1430°C) = 33·66$$

or

$$TiO(s) + CO(g) + \tfrac{1}{2}N_2(g) \rightleftharpoons TiN(s) + CO_2(g) \qquad (6)$$
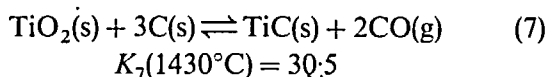$$K_6(1430°C) = 4·71 \times 10^{-3}$$

By heating specially prepared TiO, Ti_2O_3 and TiO_2 in nitrogen at 1300°C for 2 h, Umezu[1] concluded that TiO is a precursor of TiN.

Because of their thermodynamic stability, the formation of titanium carbonitrides, Ti(N, C), or titanium carbide, TiC, must also be considered:

$$TiO_2(s) + 3C(s) \rightleftharpoons TiC(s) + 2CO(g) \qquad (7)$$
$$K_7(1430°C) = 30·5$$

The content of carbon (or of titanium carbide) in the

titanium carbonitride solid solutions will be influenced by the equilibrium:

$$TiN(s) + C(s) \rightleftharpoons TiC(s) + \tfrac{1}{2}N_2(g) \qquad (8)$$
$$K_8(1430°C) = 0·35$$
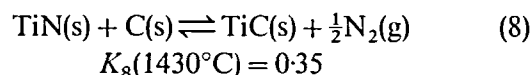
Equilibrium (8) was studied experimentally by Zelikman and Gorovits,[8] and by Portnoi and Levinskii.[9] Zelikman and Gorovits[8] studied nitriding of titanium carbide at nitrogen partial pressures of 26·6, 12 and 6 kPa, at temperatures of 1300, 1500 and 1800°C, and for times of isothermal heating up to 150 h. However, the experimental results obtained were interpreted incorrectly, since the equilibrium constant of eqn (8) was calculated according to an incorrect equation. The mistake was noticed by Portnoi and Levinskii,[9] who calculated the equilibrium constant by the equation

$$K_p = [p(N_2)]^{1/2} \left[\frac{c(TiC)}{c(TiN)} \right] \qquad (9)$$

Portnoi and Levinskii[9] studied equilibrium (8) using the $TiC + N_2$, $TiN + C$ and $Ti + N_2 + C$ systems in the temperature range 1480–2480°C at a nitrogen partial pressure of 101 kPa. However, the statistical evaluation of the results was incorrect, and for the temperature dependence of the equilibrium constant of reaction (8) a wrong equation was derived. In the present work the results of Refs 8 and 9 are processed. The equilibrium constants are given in Table 1. Based on the data in Ref. 9 for the temperature dependence of the equilibrium constant, the following equation was derived:

$$\log K_8 = -\frac{4667}{T} + 2·37 \qquad (10)$$

where temperature T is in kelvin. The equilibrium compositions of the Ti(N, C) solid solutions calculated from the data in Refs 8 and 9, and also using the thermodynamic data[7] at 101 kPa N_2, are presented in Fig. 1. Good agreement between the different dependences was achieved and significant differences are only observed at lower temperatures (1200–1400°C) where equilibrium can hardly be

achieved because of slow diffusion of nitrogen and of carbon atoms in the solid solutions. However, the values obtained by eqn (10) are extrapolated into the lower temperature range, and therefore the experimental values[8,9] need not be relied upon. However, because different diffusion rates of nitrogen and carbon in solid intermediates can be supposed, the real content of carbon in the products of carbothermal reduction and nitriding of TiO_2 can differ from the calculated equilibrium values. Recent data[5] on the Ti(N, C) solid solution equilibrium composition at $1940 \pm 40°C$ in nitrogen (101 kPa) are also included in Table 1 and in Fig. 1. Solid solution with the composition $TiC_{0.63}N_{0.37}$ (by chemical analysis) or $TiC_{0.66}N_{0.34}$ (derived from the lattice constant $a = 0.4297$ nm) was obtained by arc image heating of TiO_2 and C mixtures with C to TiO_2 mole ratio of 2.7 to 3.5 for 30 to 300 s. Despite the short times of isothermal heating, achievement of equilibrium can be assumed because of the high temperature and the extremely high heating rate. The reason will be discussed later.

In the present work reduction of TiO_2 by carbon in nitrogen atmosphere at 101 kPa and at temperatures up to 1490°C was studied. The influence of temperature, nitrogen flow, dispersion of TiO_2, and composition and the method of mixing of solid reactants on the kinetics of the reaction, chemical and phase composition and morphology of the products was investigated.

3 Experimental

3.1 Preparation of reaction mixtures

For preparation of reaction mixtures the following starting materials were used:

TiO_2(A)—rutile, TiO_2 content >99 mass%, mean particle size c. 0.2 μm, $S_{BET} = 6.9$ m² g⁻¹ (see Figs 10 and 11).

TiO_2(B)—rutile, TiO_2 content >99 mass%, mean particle size 10–12 μm (see Figs 10 and 11).

Acetylene carbon black—ash content 0.1 mass%, $S_{BET} = 80$ m² g⁻¹.

Five different starting mixtures were prepared:

I. $n[TiO_2(A)]:n(C) = 1:5$ (mole ratio),
II. $n[TiO_2(A)]:n(C) = 1:2$,
III. $n[TiO_2(B)]:n(C) = 1:2$,
IV. $n[TiO_2(A)]:n(C) = 1:2$,
V. $n[TiO_2(A)]:n(C) = 1:2$.

Mixtures I and II were dry-milled in a laboratory planetary mill using a steel jar and balls for 30 min.

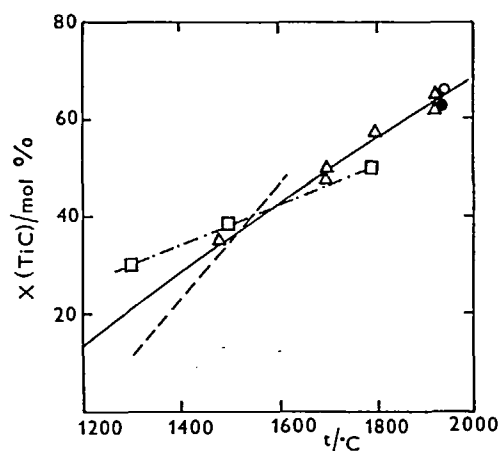Fig. 1. The equilibrium TiC content in Ti(N, C) solid solutions: — — —, calculated from the thermodynamic data;[7] — · -□- · —, calculated from the data in Ref. 8; △, obtained in Ref. 9; ——, calculated according to eqn (10); ○, obtained in Ref. 5 from lattice constant; ●, obtained in Ref. 5 by chemical analysis.

The ground mixtures were boiled in diluted hydrochloric acid, filtered, washed by deionised water and dried at 160°C. Mixture III was prepared by mixing the starting powders for 12 h in a homogeniser without influencing the initial grain size of the TiO_2. Mixtures IV and V were prepared in the following way: TiO_2(A) was ultrasonically dispersed in a saccharose aqueous solution. After evaporation of water the solid mixture of TiO_2 and saccharose was slowly heated in the nitrogen atmosphere up to 600°C. Thus, the grains of TiO_2 were coated by carbon and a more homogeneous distribution of carbon in the mixture was achieved. After pyrolysis the contents of carbon (relative to the amounts of TiO_2) were about 5 mass% (mixture IV) and 15 mass% (mixture V), respectively. The carbon content was then adjusted to the required value by adding acetylene carbon black. Finally, the mixtures were homogenised in an agate planetary mill for 20 min.

The mass of the batch in a reactor was 10 or 13.2 g, which corresponded to 5.7 or 10 g of TiO_2, respectively. Nitrogen flow (at 25°C) was 10 or 20 dm³ h⁻¹, respectively.

3.2 Reactor

A packed bed graphite reactor, described in Ref. 10, was used in our experiments (Fig. 2). The inlet and outlet tubes (1) were bolted on tapped holes on the internal perforated bottom plate (6) and on the crucible lid (4), respectively. In this arrangement all nitrogen led into the reactor passed through the reaction mixture (5) placed between the perforated plate and the lid.

Nitrogen was dried and deoxidised by passing through a chromium(II) oxide–silica gel absorption
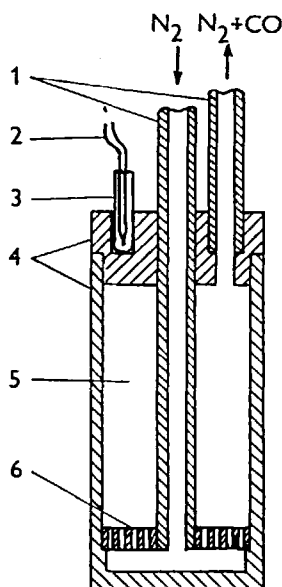
Fig. 2. Graphite reactor: 1—inlet and outlet tubes; 2—thermocouple; 3—protective alumina tube with one end closed; 4—crucible with lid; 5—reaction mixture; 6—perforated bottom.

column. Temperature was measured by a PtRh6/PtRh30 thermocouple (2) protected by an alumina tube (3). The temperature gradient along the height of the reactor was about 20°C with the higher temperature at the bottom. The reactor was placed vertically in a protection alumina tube and heated in an adapted laboratory chamber furnace. The heating rate was $10°C\,min^{-1}$.

3.3 Analytical methods

The rate of the reduction was continuously recorded by measuring the CO concentration in the outlet gases with the help of a CO analyser (Infralyt 4, VEB, Junkalor Dessau, DDR).

The morphology of the starting materials and the products was inspected by optical and electron microscopy. The products were analysed by X-ray powder diffraction analysis for phase composition, by activation neutron analysis for oxygen content, and by LECO for total carbon content. Nitrogen content in samples was determined from the amount of NH_3 evolved during fusion at 700°C with an excess of CaO-NaOH (1:1 mass ratio) powdered mixture.

4 Results and Discussion

Data on the experiments are summarised in Table 2. The maximum concentrations of CO in the outlet gases (the value found in the first minutes after achieving the temperature of isothermal heating) are included in the last column.

Table 2. Experimental conditions and maximum concentration of CO in outlet gases on carbothermal reduction and nitriding of TiO_2

Sample	Mixture	Amount of TiO_2 in reaction mixture (g)	N_2 flow per 1 g TiO_2 ($cm^3 min^{-1}$)	Temp./time of isothermal heating Temp. (°C)	Time (h)	Maximum concentration of CO (vol%)
1	I	5·7	29·2	1 220	2	13
2	I	5·7	29·2	1 390	2	32
3	II	10·0	16·7	1 395	3	33
4	II	10·0	16·7	1 490	2	32
5	III	10·0	16·7	1 395	2	17·7
6	III	10·0	16·7	1 490	2	36·5
7	II	10·0	16·7	1 490	3	32
8	II	10·0	16·7	1 490	6	32
9	II	10·0	33·3	1 400	3	26
10	II	10·0	16·7	1 170	0·5	14·5
11	II	10·0	16·7	1 300	3	23
12	IV	10·0	16·7	1 410	3	58
13	V	10·0	16·7	1 400	1·5	59

Chemical and phase compositions of the products are given in Tables 3 and 4, respectively. In Table 4 the lattice parameters calculated from the positions of diffraction peaks (2,2,2) and (3,1,1) on X-ray patterns of prepared Ti(N,C,O) powders are also included. The parameters of pure titanium carbide and titanium nitride (Ventron, TiC or TiN content

Table 3. Chemical composition of the products (in mass%)

Sample	N	C total	O
1	5·3	—	12·7
2	10·4	—	—
3	19·2	2·8	2·5
4	19·2	2·8	1·8
5	17·3	6·4	3·2
6	17·2	4·5	3·6
7	18·8	2·8	1·6
8	19·6	2·7	0·9
9	19·4	3·2	2·4
10	0·1	—	28·6
11	18·4	5·4	3·9
12	19·1	1·5	3·7
13	18·4	3·0	4·0

Table 4. Phase composition and lattice constants of the products

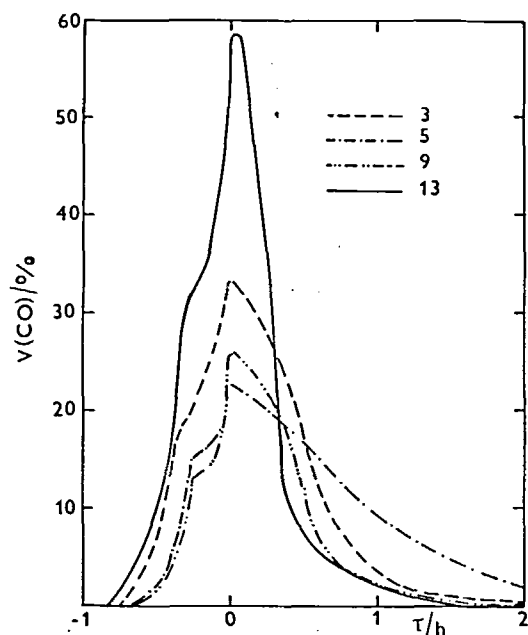| Sample	Phase composition	a_0 (nm)
1	Ti_xO_y, Ti(N,C,O), C	0·424 3
2	Ti(N,C,O), C	0·424 8
3	Ti(N,C,O)	0·424 8
4	Ti(N,C,O)	0·425 1
5	Ti(N,C,O), Ti_xO_y, C	0·425 4
6	Ti(N,C,O), Ti_xO_y, C	0·425 8
7	Ti(N,C,O)	0·424 6
8	Ti(N,C,O)	0·425 1
9	Ti(N,C,O)	0·424 3
10	Ti_4O_7, Ti_xO_y, C	—
11	Ti(N,C,O), C	0·424 4
12	Ti(N,C,O)	0·424 6
13	Ti(N,C,O)	0·424 4
Ventron	TiN	0·424 1
Ventron	TiC	0·432 8

Fig. 3. Dependence of CO concentration in outlet gases (vol%) on time of carbothermal reduction and nitriding of TiO_2 (heating rate $10°C min^{-1}$, $\tau = 0$—time to achieve isothermal heating).

>99 mass%) obtained in the present work are also shown for comparison.

Reduction of TiO_2 during some experiments is represented in Fig. 3 by the dependences of CO concentration in the outlet gas (vol%) on time, where $\tau = 0$ is the time at which the temperature of isothermal heating is achieved. Before reaching a maximum a shoulder can be observed in the curves at temperatures 1200–1300°C. Experiment 10 (Table 2) is related to the above-mentioned phenomenon. After 30 min of isothermal heating at 1170°C no titanium nitride was found in the products, Ti_4O_7 being the dominant phase. In the initial stage of the reaction only reduction of TiO_2 takes place and nitriding occurs in the later stages. Formation of other lower titanium oxides can be assumed according to the reaction mechanism mentioned in Section 2. Further peaks were found in the powder diffraction patterns of sample 10, as well as of the other partially reduced sample 1, which could not be assigned to any phase given in Ref. 11. Formation of nonstoichiometric titanium oxides with a defect structure should therefore also be supposed. For example, the total amounts of vacancies in the structure of practically stoichiometric TiO is about 15% and this value rises to about 20% for nonstoichiometric $TiO_{1-0.248}$ oxide.[12]

The kinetics of TiO_2 reduction are represented in Figs 4 to 8 as a dependence of the actual rate of CO evolution (in $cm^3 min^{-1}$ per 1 g of TiO_2 in the starting mixture) on time. The correction for a

change in total outlet gas flow was included in evaluation of the dependences. The rate of CO evolution decreases rapidly in the latter stages of the reaction (compare also Fig. 3) and reaches practically zero before the reduction is finished. This may be due to formation of thermodynamically stable Ti(N, C, O) solid solutions, as was also stated in Ref. 13.
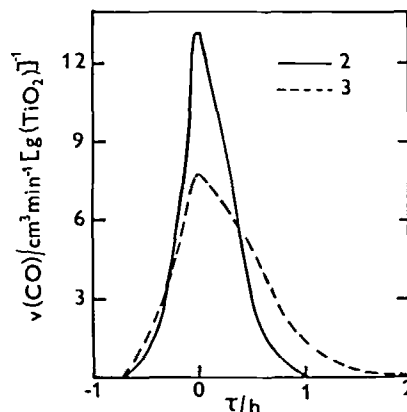

Fig. 4. Rate of CO evolution during carbothermal reduction and nitriding of TiO_2. Sample $2—n(TiO_2){:}n(C) = 1{:}5$. Sample $3—n(TiO_2){:}n(C) = 1{:}2$.
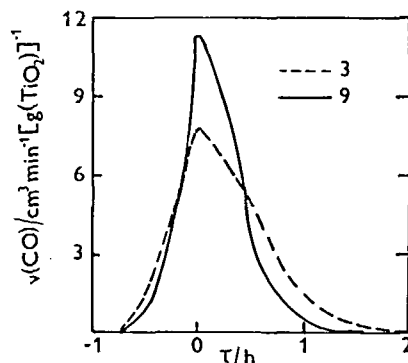

Fig. 5. Rate of CO evolution during carbothermal reduction and nitriding of TiO_2. Sample 3—nitrogen flow $10 dm^3 h^{-1}$. Sample 9—nitrogen flow $20 dm^3 h^{-1}$.

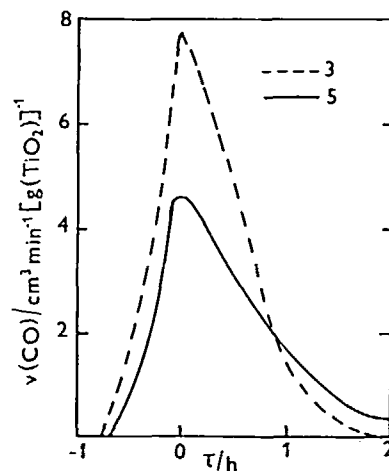Fig. 6. Rate of CO evolution during carbothermal reduction and nitriding of TiO_2. Sample 3—fine $TiO_2(A)$. Sample 5—coarse $TiO_2(B)$.
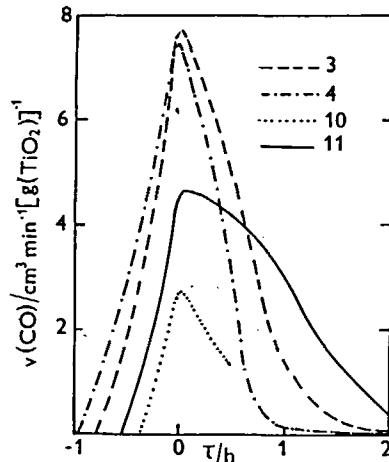
Fig. 7. Rate of CO evolution during carbothermal reduction and nitriding of TiO_2. Sample 3—1395°C. Sample 4—1490°C. Sample 10—1170°C. Sample 11-1300°C.
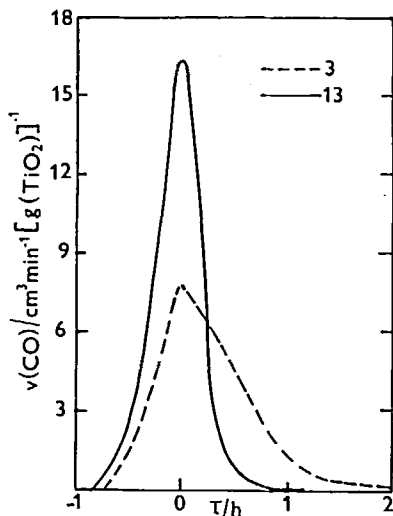

Fig. 8. Rate of CO evolution during carbothermal reduction and nitriding of TiO_2. Sample 3—reaction mixture II. Sample 13—reaction mixture V.

The influence of the composition of the starting mixture on the reaction rate is presented in Fig. 4. An excess of carbon positively influences the rate of the process, which may be due to the higher interfacial solid–solid and solid–gas surface area where reactions (1) to (7) occur. However, excess carbon cannot be removed from the product by oxidation in air since oxidation of the product takes place simultaneously. Oxidation of product 8 in air is presented in the TG curve in Fig. 9. The TG curve for pure titanium nitride (Ventron) is also shown for comparison. Due to the finer dispersity (about 1 μm) the oxidation of sample 8 begins at a lower temperature (400 to 450°C) than with relatively coarse (about 10 μm) commercial titanium nitride powder.

The kinetics of the reaction are positively influenced also by higher nitrogen flow (Fig. 5), use of finer TiO_2 powder (Fig. 6) or by higher temperature (Fig. 7). At higher nitrogen flow the gaseous products of the reaction are more effectively
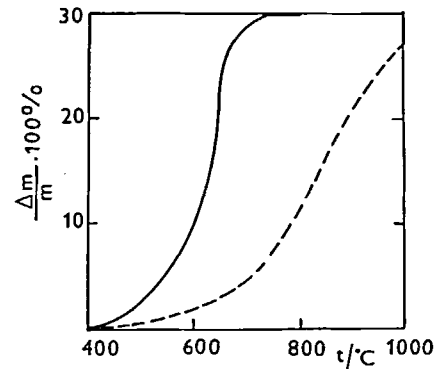

Fig. 9. Oxidation of TiN powder in air (TG, heating rate 10°C min^{-1}): – – –, TiN Ventron; ——, sample 8.

removed from the reaction zone and more favourable conditions for titanium nitride formation arise. Therefore, it can be supposed that reactions (3) and (6) with low equilibrium constants, for which effective removal of CO_2 is essential (in connection with reaction (4)), also take place in reduction and nitriding of TiO_2.

The positive influence of the higher dispersion of TiO_2 powder is connected with the higher interfacial area available for the reaction and also with the shorter diffusion paths for oxygen removal from, and nitrogen entry into, the intermediates.

An increase of the reaction rate with increasing temperature is obviously due to faster diffusion processes during the reaction. However, it is to be noted that with increasing temperature the equilibrium concentration of carbon in Ti(N, C) solid solutions also increases (Fig. 1). This trend can also be observed by comparing the lattice parameters of the synthesised products, which are slightly increased at higher temperatures (Table 4) and correspond to the values given in Refs 13–15. The influence of oxygen (or TiO) is less significant in the given compositional range, since the lattice constant of Ti(N, C, O) solid solutions is only slightly decreased by an oxygen increase at low concentrations of TiO.[14]

The influence of the starting mixture preparation method on the reaction kinetics is documented in Fig. 8. More intimate contact of the reactants significantly accelerates the reaction, especially in its initial stages.

The morphology of the TiO_2 starting powders and the morphology of the products prepared from reaction mixtures II and III is represented in Figs 10 and 11. Some relation between the morphology of the starting powders and the products can be observed. During heating of mixture II fine grains of TiO_2(A) sinter together and grow, and nitriding goes on within the agglomerates formed by primary grains of 0·3 to 3 μm (Figs 10(a,b) and 11(a,b)).
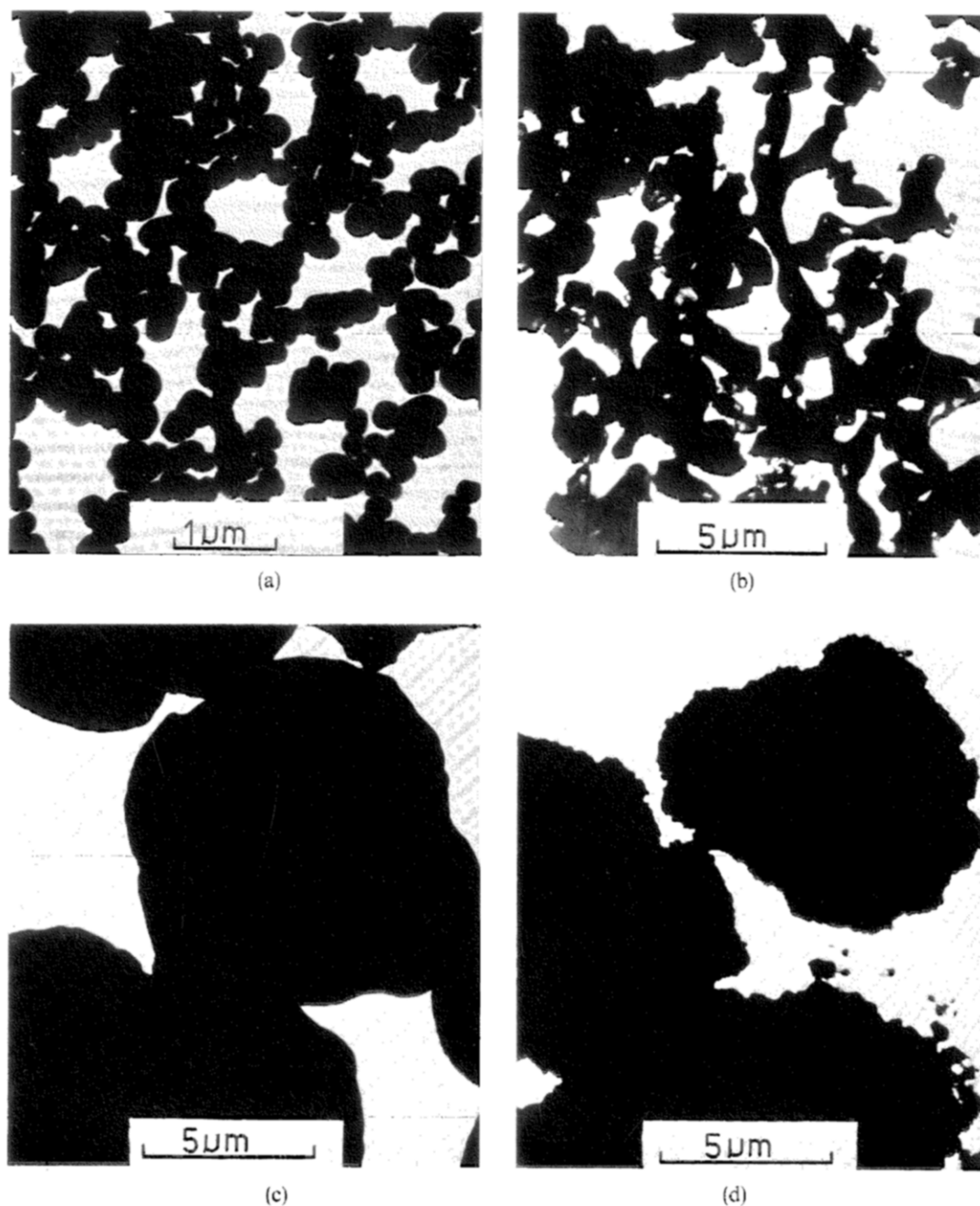
Fig. 10. TEM micrographs of starting TiO_2 powders and of some typical products: (a) TiO_2(A); (b) product 3; (c) TiO_2(B); (d) product 6.

Reduction of coarser dense polycrystalline grains of TiO_2(B) leads to formation of porous pseudo-morphs (Fig. 11(c,d)) of the same dimensions as the initial TiO_2 grains (Fig. 10(c,d)). During reduction the oxygen content in titanium oxides decreases, the density of the intermediates increases and pores arise in the grains. Assuming that TiO_2 is reduced down to TiO, porosity of the pseudomorphs can achieve about 30 vol%. Formation of the porous pseudo-morphs from coarse TiO_2(B) grains, on the one hand, and sintering and grain growth of fine TiO_2(A), on the other hand, then results in slight differences in carbothermal reduction and nitriding

kinetics of both examined TiO_2 powders. Formation of microporous pseudomorphs during the high heating rate and relatively short times available for grain growth and sintering of the intermediates might also be one of the reasons why carbothermal reduction and nitriding of TiO_2 in Ref. 5 was finished in such extremely short times, as mentioned in Section 2.

Principally, the observed morphological relations follow from physical properties of titanium oxides, which have very small partial vapour pressures at these temperatures (about 10^{-2} Pa[16]) and, therefore, transport of titanium through the gas phase is
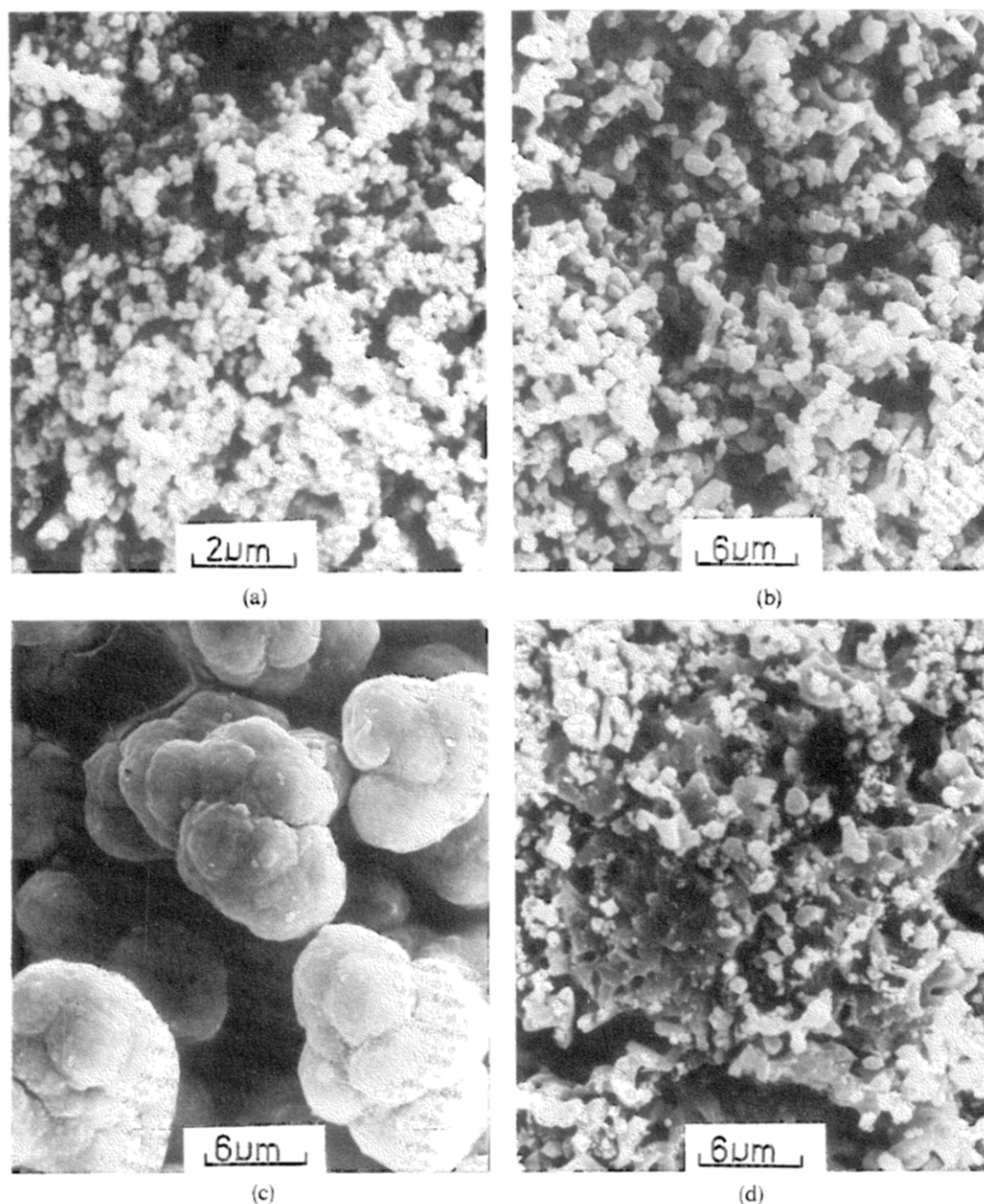
Fig. 11. SEM micrographs of starting TiO_2 powders and of some typical products: (a) $TiO_2(A)$; (b) product 3; (c) $TiO_2(B)$; (d) product 6.

negligible. Thus, preparation of titanium nitride powders with improved morphology directly related to that of the precursor is possible, provided that sintering of the starting titanium oxides and of reduced intermediates is largely suppressed. This was attempted in experiments 12 and 13 through formation of a carbon layer of pyrolysis of saccharose on the grain surfaces of the starting TiO_2. The amount of pyrolytic carbon was sufficient to reduce TiO_2 to Ti_3O_5 (sample 12) or down to TiO (sample 13). In such a reduction stage (especially with sample 13) simultaneous nitriding can be supposed, which can slow down sintering and grain growth in the later stages of the reaction. The

morphology of the products of experiments 12 and 13 is shown in Fig. 12. Product 12 is partially aggregated and is characterised by a wide particle size distribution. Product 13 is less agglomerated and is formed by grains with a narrow size distribution (0·1 to 0·5 μm).

5 Conclusions

Reduction of finely dispersed TiO_2 by carbon in a nitrogen flow begins at approximately 1000°C. In the initial stages, up to approximately 1170°C, reduction of TiO_2 into lower titanium oxides takes
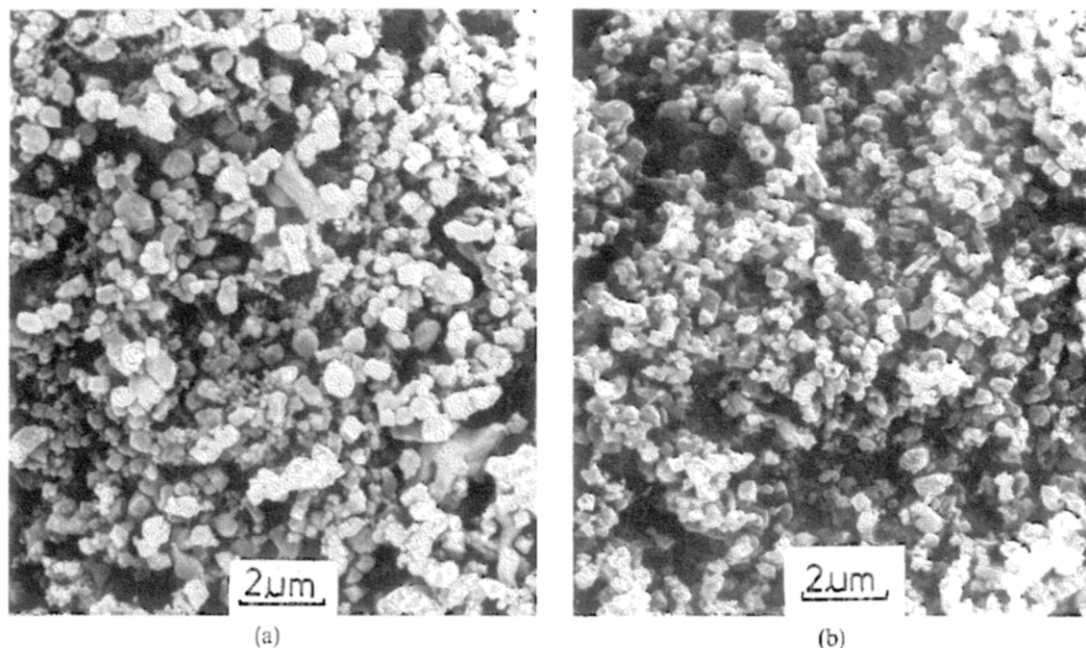
Fig. 12. SEM micrographs of the products of (a) experiment 12 and (b) experiment 13.

place and significant nitriding above 1200°C was observed.

Formation of products proceeds by substitution of oxygen by nitrogen (and also by carbon) atoms within the pseudomorphs of the intermediates. This reaction mechanism allows the preparation of Ti(N, C, O) powders with improved grain morphology closely related to the morphology of the precursor.

During heating of the reaction mixture, sintering and grain growth of the starting TiO_2 and of the reduced intermediates can be suppressed by a carbon layer formed by pyrolysis of saccharose on the surface of the TiO_2 grains.

Similar methods can probably be used for the preparation of fine powders of other carbides or nitrides, provided that transport of a metallic component through the gas phase does not occur (very low partial vapour pressures of precursors or of intermediates at the temperature of synthesis).

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