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The Production of Titanium Nitride by the Carbothermal Nitridation of Titanium Dioxide Powder

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Abstract

Titanium dioxide powders have been nitrided using a nitrogen–5% hydrogen gas mixture in the presence of carbon at temperatures between 1200 and 1500°C. The rate of titanium nitride formation is sensitive to the titanium dioxide particle surface area, and the morphology of the product corresponds closely to that of the starting oxide. Titanium nitride grain growth becomes appreciable at temperatures approaching 1500°C.

TiO_2-Pulver wurden in einer N_2–5%H_2 Atmosphäre in der Gegenwart von Kohlenstoff im Temperaturbereich von 1200 bis 1500°C nitridiert. Die Geschwindigkeit der TiN-Bildung hängt von der spezifischen Oberfläche des TiO_2-Pulvers ab. Die Morphologie des Reaktionsproduktes entspricht nahezu der des Ausgangsmaterials. Ab etwa 1500°C nimmt das TiN-Kornwachstum deutlich zu.

On a nitruré des poudres de dioxyde de titane par un mélange de gaz azote–5% hydrogène en présence de carbone à des températures variant entre 1200 et 1500°C. La vitesse de formation du nitrure de titane est sensible à la surface spécifique des particules de dioxyde de titane et la morphologie du produit final correspond étroitement à celle de l'oxyde de départ. La croissance granulaire du nitrure de titane devient notable pour des températures de l'ordre de 1500°C.

1 Introduction

Titanium nitride (TiN) has the useful properties of hardness (micro-indentation ~20 GPa), a high melting point (2940°C) and a high room-temperature electrical conductivity (4 MS m^{-1}).[1] It has found use as a thin, wear-resistant coating material on metal and tungsten carbide cutting surfaces, and has been widely used as a particulate strengthening phase in metal alloys.[2,3] TiN particles are incorporated into ceramic matrices to give improved fracture toughness and strength.[4] Interest has also been focused on TiN because of the possibility of obtaining electrical conductivity, and therefore an electric discharge machining capability, in silicon nitride and sialon-based materials.[5,6] There are few reported current commercial applications for monolithic TiN components, although micrometre dimension TiN powders are readily sinterable at high temperature.[7]

TiN powder can be prepared in several ways, for example by:

- Nitridation of titanium metal or titanium hydride powders;
- vapour-phase reaction between titanium chloride vapour and ammonia;
- nitridation of titanium dioxide powder in the presence of carbon.

These reactions, with standard Gibbs functions at 1600 K, can be expressed as:

$$Ti_{(s)} + \tfrac{1}{2}N_{2(g)} = TiN_{(s)} \qquad \Delta G^\circ = -164\,\text{kJ mol}^{-1} \quad (1)$$

$$TiH_{(s)} + \tfrac{1}{2}N_{2(g)} = TiN_{(s)} + \tfrac{1}{2}H_{2(g)} \qquad \Delta G^\circ = -265\,\text{kJ mol}^{-1} \quad (2)$$

$$TiCl_{4(g)} + 4/3NH_{3(g)} = TiN_{(s)} + 1/6N_{2(g)} + 4HCl_{(g)} \qquad \Delta G^\circ = -211\,\text{kJ mol}^{-1} \quad (3)$$

$$TiO_{2(s)} + 2C_{(s)} + \tfrac{1}{2}N_{2(g)} = TiN_{(s)} + 2CO_{(g)} \qquad \Delta G^\circ = -35\,\text{kJ mol}^{-1} \quad (4)$$

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The carbothermal nitridation of titanium dioxide (TiO_2) has the advantage that it uses readily available and inexpensive raw materials, a comparatively simple reaction environment, and has the potential for large-scale production. A number of publications deal with aspects of this reaction. Reduction of TiO_2 in the presence of carbon becomes detectable at temperatures in the region of 850°C.[8,9] With the stoichiometric molar ratio of $C/TiO_2 = 2$, the rate of formation of titanium nitride becomes appreciable at temperatures in the range 1100 to 1300°C.[10,11] At temperatures above 1300°C the formation of titanium carbide (TiC) becomes thermodynamically favoured.[1] However, it has been reported that TiN can be obtained at temperatures as high as 1800°C on a reaction timescale of a few seconds.[12] The actual situation is slightly more complex because of the possibility of solid solution formation. Both TiC and TiN have the halite crystal structure, and in the Ti–C–N system a complete range of stoichiometry between TiC and TiN can be obtained, depending on the temperature, the proportion of carbon present in the system and the nitrogen pressure.[12–14] In practice under flowing gas conditions TiN is normally obtained from a powder mixture of C/TiO_2 ratio of 2; for C/TiO_2 ratios between 2·1 and 2·6 single-phase titanium carbonitride (TiC_xN_{1-x}) is formed. Excess carbon remains in the product for ratios $>2{\cdot}7$.[12]

XRD examination of the TiO_2–C reaction products with increasing time at temperatures in the range 850 to 1300°C shows that the reduction of TiO_2 occurs in steps involving the production of shear structures, and the new phases Ti_4O_7 and Ti_3O_5, which contain titanium in lower oxidation states.[8,9,11] The oxide of stoichiometry Ti_3O_5 thus appears to be an important reaction intermediate, being nitrided to TiN with the release of CO. However, it has also been concluded that reduction of titanium dioxide down to TiO (also with the halite structure) can occur before significant nitrogen substitution into the oxide lattice takes place.[15] The rate of TiN formation has been reported to be insensitive to nitrogen flow rate, and carbon specific surface area; under flowing gas conditions with the correct C/TiO_2 stoichiometry the final product would be expected to be single-phase TiN.

Unlike the formation of silicon nitride by the carbothermal reduction of SiO_2,[16] the formation of TiN appears to be, as far as the titanium-containing species is concerned, a solid-state reaction, because TiO has very low volatility.[17] This being the case, close relations would be expected between the morphology of the starting TiO_2 powder and that of the product. A recent examination[14] of the carbothermal reduction and nitridation of two TiO_2 powders, one of median size 0·2 μm and the other of size 10–12 μm, showed a difference in rate of evolution of CO, and that the particle sizes of reactant and product were similar in each case. The findings broadly support these results, and also show that sintering of fine particle size TiO_2 powder[18] during heating to nitriding temperature can have a significant effect on nitridation rate. There appears to be little practical advantage in using TiO_2 powders of very high surface area unless steps are taken to suppress TiO_2 sintering.

The work described in this paper was carried out in order to examine in greater detail the relationships between reaction parameters, starting materials' properties, and the rate of formation and nature of the titanium nitride powder produced. This study was planned as the basis for a subsequent investigation into the carbothermal nitridation of titanium dioxide and silicon dioxide mixtures with the object of preparing directly mixed silicon nitride and titanium nitride powders. Because it was intended to use nitrogen–hydrogen mixtures to facilitate the silicon dioxide nitridation reaction, a nitrogen–5% hydrogen gas mixture was also used as the nitriding gas in the present study. The C/TiO_2 starting ratio was held at 2·00.

2 Experimental

Four grades of TiO_2 powder (Tioxide (UK) Ltd, Stockton-on-Tees, UK), giving a range of specific surface areas (a_s) were used. The carbon was either 'lamp black' (BDH, Poole, UK) of $a_s = 21\ m^2\ g^{-1}$, or obtained by pyrolysis of sucrose. Nitrogen–5% hydrogen (BOC Ltd, Guildford, UK) was the standard nitridation atmosphere. Powder surface areas were determined using the standard single-point gas adsorption technique and BET equation (Sorptometer model 2120, Perkin Elmer Ltd, UK). Scanning electron microscopy (SEM) was carried out on gold-coated samples using an Hitachi S700 instrument, and transmission electron microscopy (TEM) using carbon coatings with a Joel 200 CX STEM. Powders were first dispersed in acetone before placing on the aluminium stub or plastic-coated copper grid. Physical property data for the starting powders are given in Table 1.

Powders were normally first dispersed separately in deionised water before mixing. TiO_2 powders were dispersed by ultrasonic vibration using a 45 W probe (MSE Scientific Instruments, Crawley, UK)

Table 1. Titanium dioxide starting powders

Material	*Major phase*	(a_s; $m^2 g^{-1}$)	*Calculated* (d; *nm*)
T1	Rutile	3	500
T2	Rutile	53	30
T3	Anatase	81	20
T4	Anatase	106	10

d = equivalent particle diameter, assuming $d = 6/\rho a_s$.
Densities (ρ): rutile, 4·74 $Mg\,m^{-3}$; anatase, 3·84 $Mg\,m^{-3}$.

for 30 s at pH 8·5 obtained by the addition of aqueous ammonium hydroxide. Lamp-black carbon was dispersed by ball-milling with yttria-stabilised zirconia elements in a polypropene jar for 2 h using Glascol LS16 (Allied Colloids Ltd, Bradford, UK), a 30% aqueous solution of a carboxylated acrylic copolymer dispersant. The two powder dispersions were then thoroughly mixed by ball-milling for a further 2 h, followed by 20 min in a high shear rate stirrer, before being spray-dried at 190°C with constant magnetic stirring.

Pyrolysed sucrose was used as an alternative source of carbon. Sucrose solutions (33 mass % in water) were mixed with the TiO_2 powder dispersed in water, and the mixture was evaporated to dryness with constant stirring. The sucrose was converted to carbon by pyrolysis under argon at 280°C for 10 h. TiO_2–carbon mixtures were prepared so as to give a C/TiO_2 molar ratio of 2·00, taking into account the small amount of carbon resulting from pyrolysis of the dispersant.

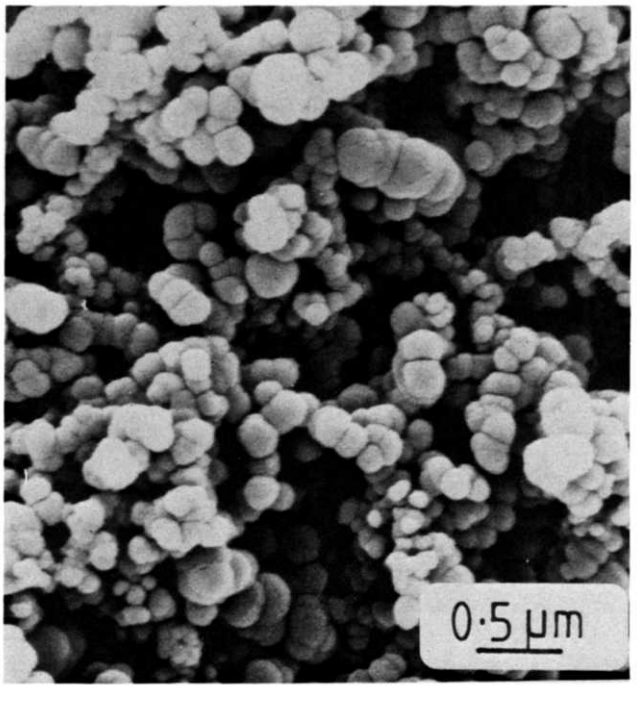

Fig. 1. Scanning electron micrograph of carbon black starting material.

Mixed powders were pressed into small cylindrical pellets of diameter 8 mm and containing ~0·5 g of powder, using a uni-axial pressure of 140 MPa. Pellets were placed in a small graphite crucible (50 mm × 10 mm × 10 mm) and covered with a thin layer of carbon black. The furnace was purged with nitriding gas at a flow rate of 0·5 $cm\,s^{-1}$, before heating to the required temperature at 4°C min^{-1}. Nitridation was carried out under flowing nitrogen–5% hydrogen at temperatures in the range 1100 to 1500°C, for times of up to 30 ks. A range of gas flow rates was used.

The sintering behaviour of the TiO_2 dioxide powders in the presence of carbon was examined independently using an argon atmosphere. Similarly prepared pellets were heated in a graphite boat at 1300°C for times up to 4 ks under flowing argon.

Nitrided products were analysed for nitrogen and carbon chemically, and by X-ray diffraction (XRD) for phase content. The nitrogen content and residual carbon were determined after complete combustion by gas chromatography. Extent of nitridation is expressed in terms of f_N, defined as:

$$f_N = \frac{x_N}{(1 - x_C)} \cdot \frac{1}{0{\cdot}226} \tag{5}$$

where 0·226 is the nitrogen mass fraction to three significant figures in pure stoichiometric TiN, and x_C and x_N are the carbon and nitrogen mass fractions, respectively, of the nitrided material.

3 Results

Scanning electron micrographs of the carbon and TiO_2 starting powders are shown in Figs 1 and 2. Initially nitridations were carried out at 1300°C and with varying gas flow rates to establish the optimum nitriding conditions. Data for the extent of nitridation of T4 (106 $m^2 g^{-1}$) TiO_2 powder after 4 ks at 1300°C, as a function of gas flow rate, are shown in Fig. 3. It can be seen that the nitridation rate is independent of flow rate for rates > 2·5 $cm^3 s^{-1}$. The effect of temperature on nitridation rate under a gas flow rate of 3·7 $cm^3 s^{-1}$ is shown in Fig. 4, with the extent of nitridation appearing to reach a plateau at $f_N = 0{\cdot}93$ after 4 ks at 1400°C. f_N values for the same powder as a function of time at four temperatures are shown in Fig. 5. For nitridations carried out at 1420°C and giving the maximum extent of nitridation, x_c was of the order of 0·005, which, if all the carbon is assumed to be present in the nitride lattice, corresponds to a composition $TiN_{0{\cdot}97}C_{0{\cdot}03}$. Figure 6 is the Arrhenius plot of the nitridation data shown

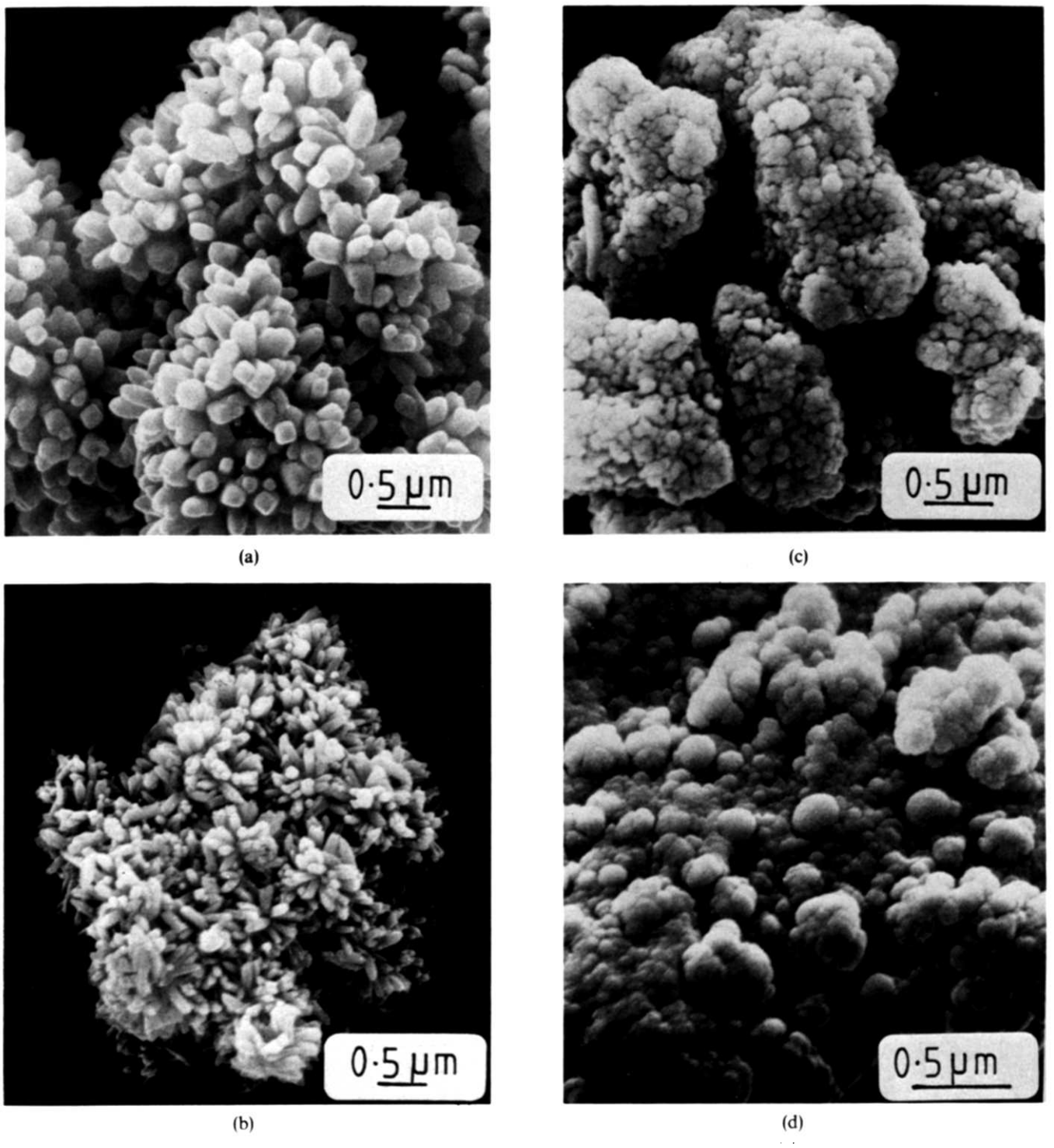

Fig. 2. Scanning electron micrographs of titanium dioxide starting material. (a) T1; (b) T2; (c) T3; (d) T4.

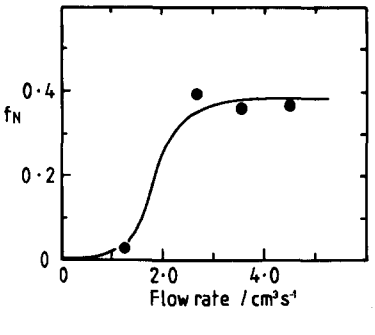

Fig. 3. Extent of nitridation (f_N) as a function of gas flow rate for T4 powder after 4 ks at 1300°C.

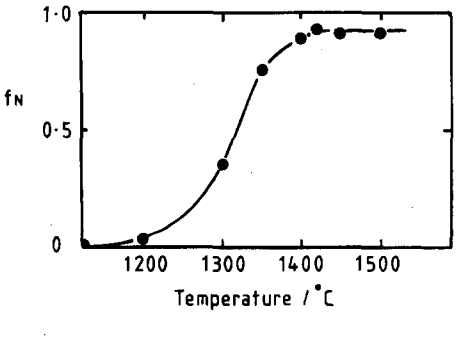

Fig. 4. Extent of nitridation (f_N) as a function of temperature for T4 powder after 4 ks with gas flow rate 3·7 $cm^3 s^{-1}$.

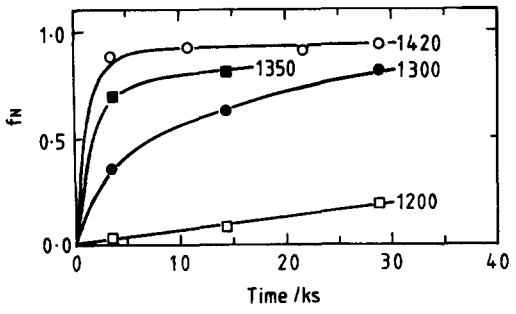

Fig. 5. Extent of nitridation (f_N) as a function of time for T4 powder with gas flow rate $3{\cdot}7\,cm^3\,s^{-1}$.

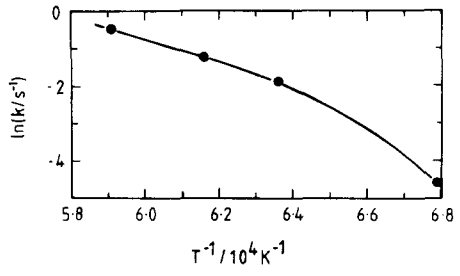

Fig. 6. Arrhenius treatment of initial reaction rates shown in Fig. 5.

in Fig. 5, using initial reaction rates. An estimated activation energy, based on the higher temperature section of the plot, is 260 kJ mol^{-1}. Nitridation kinetic data for 1300°C are presented in Fig. 7 using a modified Jander equation,[18] which assumes the reaction of spherical particles of initial radius r_0:

$$[1+(z-1)\alpha]^{2/3}+(z-1)(1-\alpha)^{2/3} = z+(1-z)\frac{KD}{r_0^2}t \quad (6)$$

where α is the volume fraction of particle reacted, z is the volume of product formed per unit volume of reactant (in the case of TiO_2 (rutile) → TiN, $z = 0{\cdot}67$), D is a diffusion coefficient related to the mobility of the rate controlling species.

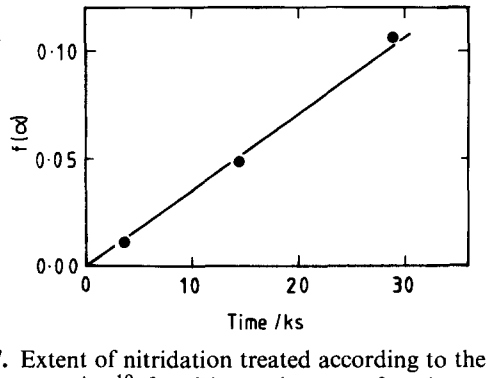

Fig. 7. Extent of nitridation treated according to the modified Jander equation[19] for T4 powder as a function of time at 1300°C with gas flow rate $3{\cdot}7\,cm^3\,s^{-1}$.

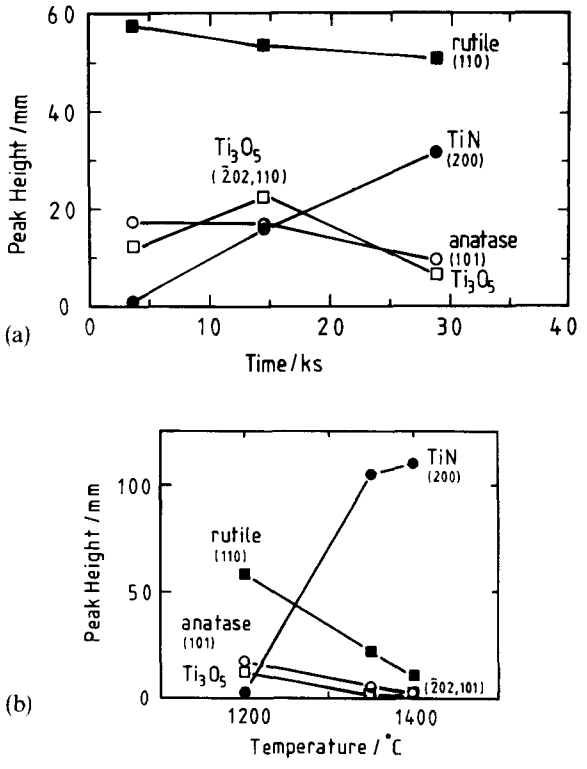

Fig. 8. XRD peak height data for the products of nitridation of T4 powder (a) as a function of time at 1200°C and (b) as a function of temperature after 4 ks reaction with gas flow rate $3{\cdot}7\,cm^3\,s^{-1}$.

The y axis is defined as the function:

$$f(\alpha)=\left(\frac{[1+\alpha(z-1)]^{2/3}}{1-z}-(1-\alpha)^{2/3}-\frac{z}{1-z}\right) \quad (7)$$

Typical XRD data for the reaction are given in Fig. 8(a) and (b), which show the peak height changes for the major phases with increasing time of nitridation at 1200°C, and after 4 ks at temperatures between 1200 and 1400°C. The influence of titanium dioxide specific surface area on powder reactivity is illustrated in Fig. 9 showing, on a semi-logarithmic scale, f_N as a function of surface area after reaction for times between 4 and 28 ks. The type of carbon used appears to have only a slight influence. In experiments designed to test the possible importance of this effect by using conditions not giving complete

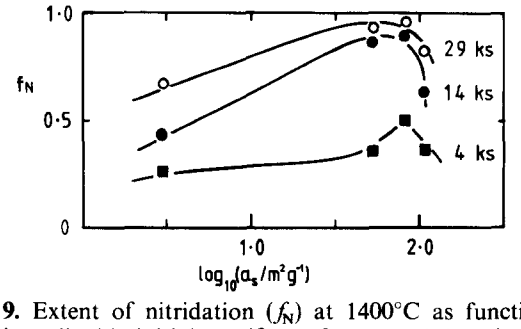

Fig. 9. Extent of nitridation (f_N) at 1400°C as functions of titanium dioxide initial specific surface area (a_s) and reaction time.

Table 2. Effect of sintering at 1300°C for 4 ks on TiO_2 specific surface area

Material	*Initial* a_s ($m^2 g^{-1}$)	*Final* a_s ($m^2 g^{-1}$)
T1	3·3	3·8
T2	53	4·7
T3	81	4·3
T4	106	4·2

nitridation (1400°C for 4 ks) carbon black gave f_N = 0·88 and sucrose gave 0·82, while at 1300°C in the same time carbon black gave f_N = 0·36 and sucrose gave 0·47.

Because of the ready sinterability of fine titanium dioxide powders at temperatures above 1000°C[19] a qualitative examination of the sintering behaviour of mixed TiO_2/carbon powders was carried out at 1300°C. Table 2 shows the measured specific surface area changes after heating under flowing argon for 4 ks at 1300°C and subsequent burn-off of the carbon.

The effect of sintering on the morphology of the highest surface area powder (T4) is shown in Fig. 10, where a slight shrinkage of the soft agglomerates, but without marked overall particle fusion, is seen.

SEM and TEM micrographs of normally nitrided powders are shown in Fig. 11, for nitridation at 1400°C, and for nitridations at 1420°C and 1500°C in Figs 12 and 13.

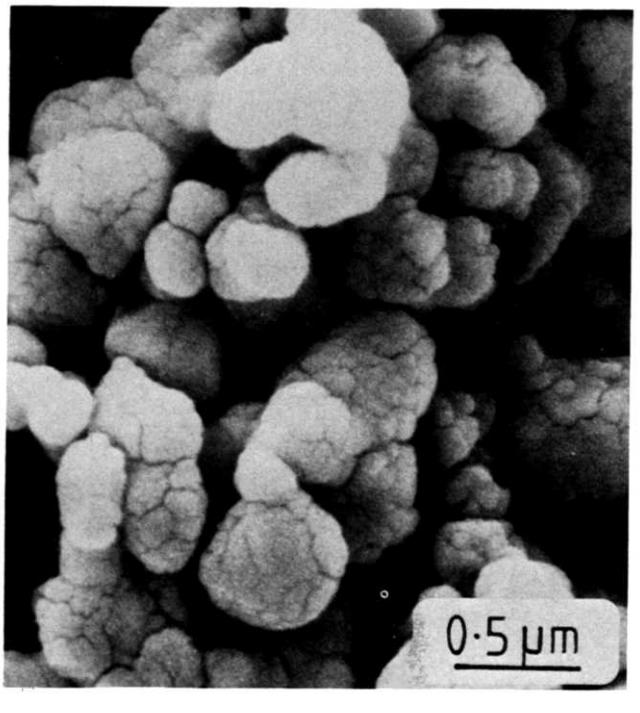

Fig. 10. Scanning electron micrograph of titanium dioxide (T4) powder after heating for 4 ks under argon.

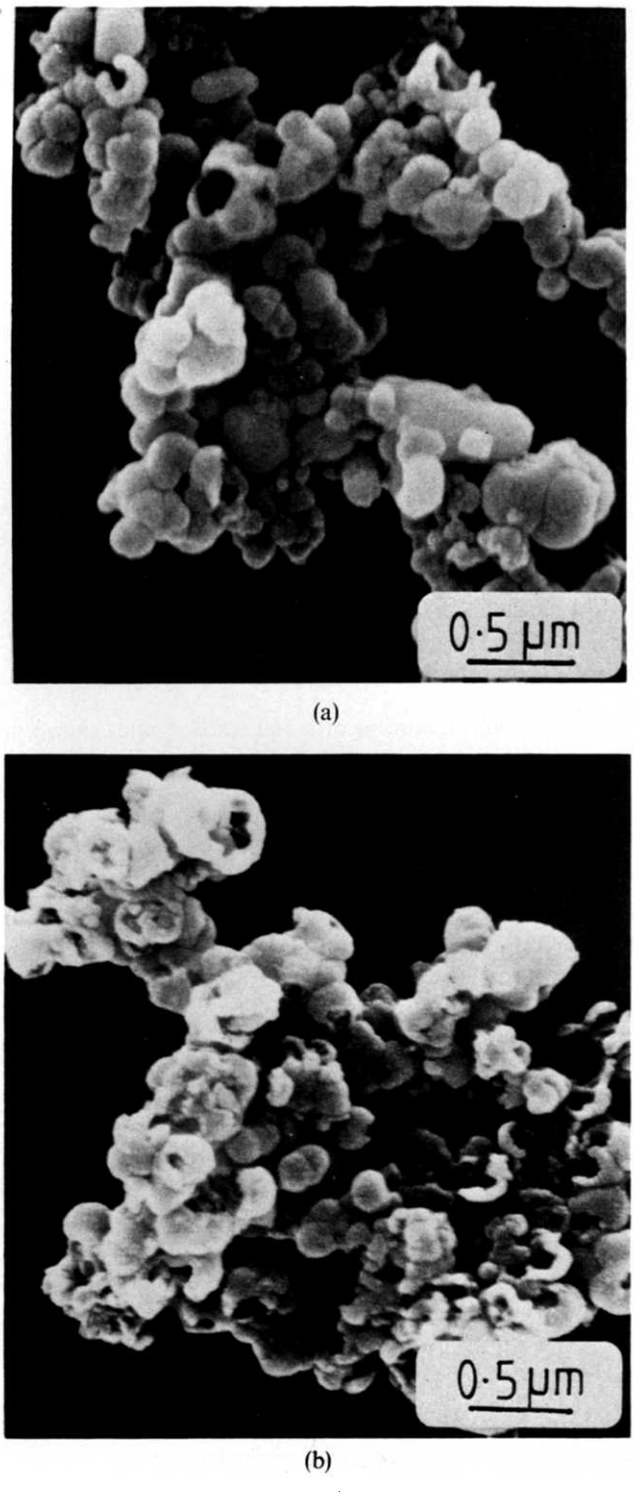

Fig. 11. Scanning electron micrographs of the product of nitridation of (a) T1 powder after 14 ks at 1400°C and (b) T4 powder after 14 ks at 1400°C.

4 Discussion

Analysis of standard thermodynamic data for TiO_2, TiN and TiC shows that the nitridation of TiO_2 to TiN under standard conditions is possible at temperatures above ~1170°C (Fig. 14). Nitridation of TiO_2 becomes favourable above 1220°C.

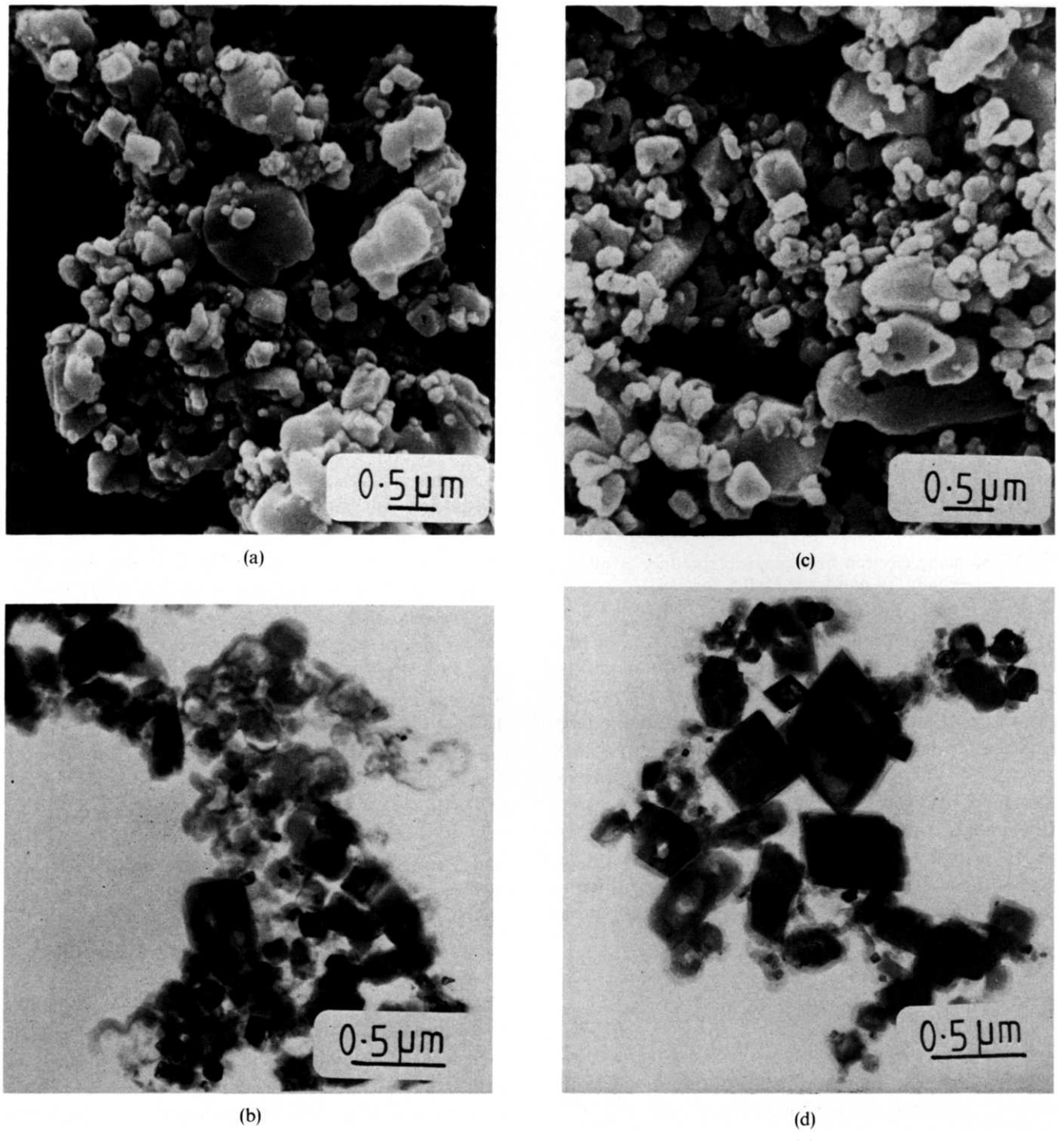

Fig. 12. Electron micrographs of the product of nitridation of T4 powder (a) at 1420°C for 14 ks, scanning mode; (b) at 1420°C for 14 ks, transmission mode; (c) at 1420°C for 32 ks, scanning mode; (d) at 1420°C for 32 ks, transmission mode.

Theoretically conversion of TiO_2 to Ti_3O_5 is possible above 1130°C. Under flowing gas conditions where the carbon monoxide pressure is maintained lower than the theoretical equilibrium value (for example 2 bar at 1300°C), nitridation should be readily possible at lower temperatures. The observed initiation of significant nitridation under 0·95 bar N_2 at a temperature in the region of 1200°C is thus broadly in accord with thermodynamic predictions. The influence of hydrogen in the presence of nitrogen will be to aid the conversion of TiO_2 to TiN. Under standard conditions ΔG° for the reaction between TiO_2 and H_2 yielding TiN and water is positive (Fig. 14), but in the presence of carbon, and assuming a maximum value for the partial pressure of CO (p_{CO}) of 1 bar, the partial pressure of water vapour (p_{H_2O}) will be maintained at a sufficiently low value ($\sim 10^{-5}$ bar at 1500°C) to permit the equilibrium to move to the right. The question of competition between carbon and

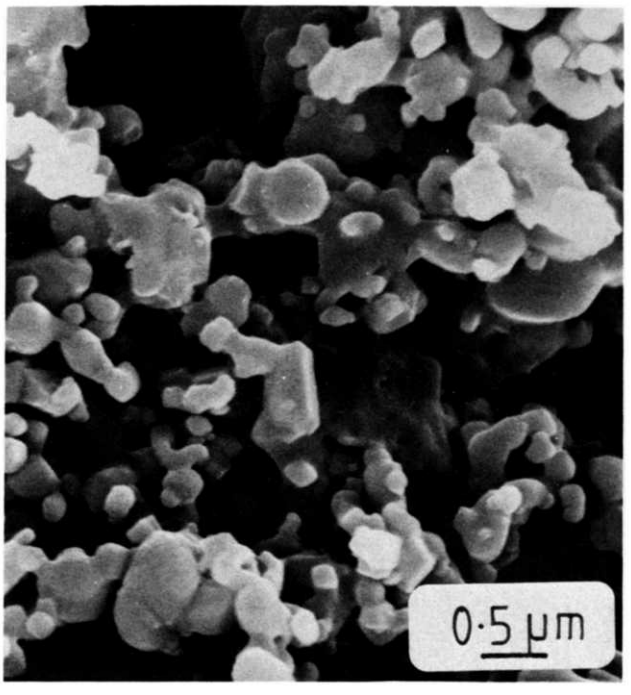

Fig. 13. Scanning electron micrograph of product of nitridation of T4 powder at 1500°C for 4 ks.

hydrogen as the major reducing species is resolved by examination of the residual carbon content (x_c) as a function of extent of nitridation (f_N). Figure 15 shows points for powders T1 and T2, and the line corresponding to the theoretical relationship based on eqn (4). This implies that carbon is the ultimate carrier of oxygen away from the reaction zone, although the possibility that within the nitriding pellets, and on the microscale, hydrogen is an oxygen carrier cannot be discounted. The loss under flowing gas conditions of some carbon by reaction with hydrogen:

$$C_{(s)} + 2H_{2(g)} = CH_{4(g)}$$
$$\Delta G^\circ_{1500\,K} = 74{\cdot}9\,\text{kJ mol}^{-1} \qquad (8)$$

is theoretically possible, but at this temperature and with 0·05 bar H_2 the equilibrium pressure of CH_4 is 6×10^{-6} bar, and thus probably negligible.

At higher temperatures, in the region of 1600°C, titanium carbide becomes stable, and titanium nitride should react with excess carbon to form titanium carbide. There is thus a temperature window of 1200–1600°C, within which TiN should be the major equilibrium product, provided the C/TiO_2 ratio is close to 2. (This point is of importance for the anticipated situation where SiO_2 and additional carbon would be present for the preparation of mixed titanium nitride and silicon nitride powders.) In practice titanium carbide was not detected by XRD as a separate phase and the small amounts of carbon found in the nitride were

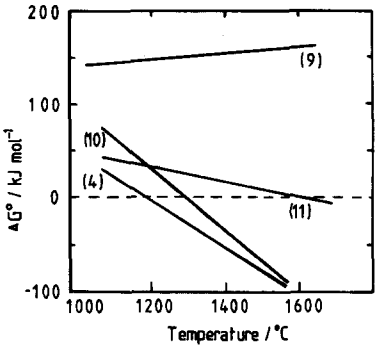

Fig. 14. Summarised thermodynamic data: ΔG° as a function of temperature for the reactions:

$$TiO_{2(s)} + 2C_{(s)} + \tfrac{1}{2}N_{2(g)} = TiN_{(s)} + 2CO_{(g)} \qquad (4)$$
$$TiO_{2(s)} + 2H_{2(g)} + \tfrac{1}{2}N_{2(g)} = \tfrac{1}{2}TiN_{(s)} + 2H_2O_{(g)} \qquad (9)$$
$$TiO_{2(s)} + 3C_{(s)} = TiC_{(s)} + 2CO_{(g)} \qquad (10)$$
$$TiN_{(s)} + C_{(s)} = TiC_{(s)} + \tfrac{1}{2}N_{2(g)} \qquad (11)$$

attributed to residual free carbon, although the possibility theoretically exists that lattice incorporation of carbon forms the solid solution $TiN_{(1-x)}C_x$. Very small shifts of lattice constant would not have been detected by the XRD equipment used.

The independence of reaction rate from gas flow rate for flow rates in excess of $2{\cdot}7\,cm^3\,s^{-1}$ is consistent both with previous observations and with the calculated equilibrium carbon monoxide partial pressure of 2 bar. This high pressure would ensure that the product carbon monoxide readily escaped from the reaction zone, allowing the reaction to proceed to the right and TiN to be formed. At the same time it can be envisaged that nitrogen depletion in the reaction zone might result, and clearly some nitrogen flow is required to maintain an adequate nitrogen partial pressure within the compacted powder.

Examination of the sintering behaviour of the TiO_2 powders at 1300°C shows that some loss of surface area, and thus reactivity, is inevitable. The powder particle dimension corresponding to the new area of $\sim 4\,m^2\,g^{-1}$ is $0{\cdot}4\,\mu m$, consistent with the visual evidence of Fig. 10. The results shown in Fig.

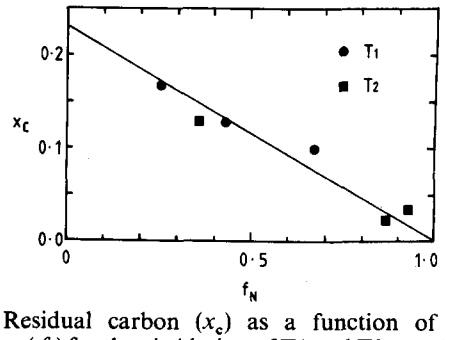

Fig. 15. Residual carbon (x_c) as a function of extent of nitridation (f_N) for the nitridation of T1 and T2 powders using a range of temperatures and times.

10 are also consistent with a powder that is simultaneously undergoing sintering, with loss of surface area, and nitridation. The higher surface area TiO_2 powders appear to have the highest intrinsic reactivities, but this factor is outweighed in the case of T4 powder by the rapid loss of surface area. In practice, therefore, under these nitridation conditions there appears to be an optimum value for the specific surface area of the titanium dioxide in the region of $50\,m^2\,g^{-1}$.

The use of a sugar as an alternative source of carbon gives nitridation rates which are close to those obtained with carbon black, with the small difference being more marked at lower temperatures. The overall conclusion from the use of sucrose is that the form of the carbon does have some slight influence on nitridation behaviour, but that it is not as marked as would have been expected from a simple influence of carbon specific surface area. It is possible that there is a barrier action by the dense pyrolytic carbon, which prevents nitrogen access to the titanium dioxide, or escape of carbon monoxide and which is more important at lower temperatures. This function has also been suggested as a possible way of inhibiting TiO_2 sintering.[14] The titanium nitride morphology is unchanged from that obtained with carbon black.

The TEM micrographs (Fig. 12) show that the morphology of the TiN is closely related to that of the starting TiO_2 powder. This is consistent with a reaction mechanism involving a progressive reduction of TiO_2 to Ti_3O_5 ($TiO_{1.67}$) and then to an oxide of stoichiometry approaching $TiO_{1.0}$, and more readily able to accept nitrogen into the lattice with simultaneous release of oxygen. This sequence of events is supported by XRD evidence showing the rapid initial appearance of Ti_3O_5 as a reaction intermediate, and its progressive decline with time as the amount of rutile (and anatase) present also decreases. Ti_3O_5 has the complex pseudo-brookite structure formed from TiO_6 octahedra sharing edges and corners. The next lowest oxide phase, Ti_2O_3, has the corundum structure with hexagonal close-packed oxygen. TiO with the halite structure can show a stoichiometry range to $TiO_{1.23}$, with up to 20% of site vacancies. It is thus likely, as has been suggested,[15] that its formation and an approach to 1:1 stoichiometry occurs during reduction and loss of oxygen. The morphology of the resulting titanium nitride particles is then necessarily close to that of the titanium dioxide.

In the presence of the carbon sink, the oxygen (and water vapour) partial pressures will be maintained at sufficiently low values to permit the titanium dioxide reduction process to continue. Because the reaction rate is strongly influenced by the titanium dioxide surface area, the rate-determining step seems likely to be either a surface reaction between the titanium oxide particle and gaseous CO, forming the intermediate CO_2 which is converted back to CO in a fast reaction at a carbon suface, or the exchange of O for N at the TiN surface (the effect of hydrogen would be similar, with the formation of intermediate H_2O). The overall nitridation mechanism thus seems likely to be the inwards diffusion of nitrogen into particles of reduced TiO_2, possibly already of approximately 1:1 stoichiometry, with the released oxygen being converted to CO at a carbon surface, or through reaction with H_2. The appropriate kinetic model would be that of the 'shrinking sphere', as suggested by Fig. 7 and mathematically described by a form of the Jander equation. There is evidence that the nature of the carbon also has some slight influence on the overall nitridation rate, and it is likely that on a microscale this operates by influencing access of gases at the titanium oxide/nitride surface. The experimental activation enthalpy of $260\,kJ\,mol^{-1}$ is very close to the value found by White *et al.*,[9] but in view of the complexity of the reaction sequence it is not easy to assign the value to one specific physical process.

The series of SEM micrographs (Fig. 11) and the TEM micrographs (Fig. 12) show that at 1420°C there is some tendency for TiN particle coarsening to occur. This effect is more marked at 1500°C, with appearance after 4 ks of a considerable extent of grain growth and particle bridging, and the development of partially sintered agglomerates.

5 Conclusions

Titanium dioxide powder is readily nitrided to TiN in the presence of carbon and hydrogen at temperatures in the range 1300–1450°C. The reaction rate is sensitive to the titanium dioxide specific surface area, which may be modified during the nitridation process by simultaneous sintering of the oxide powder. The optimum value for the titanium dioxide specific surface area is in the region of $50\,m^2\,g^{-1}$. The morphology of the titanium nitride is closely related to that of the starting oxide powder, though at temperatures above 1400°C Ostwald ripening and sintering of the TiN particles becomes significant. There appears to be some advantage in adding the carbon in the form of a soluble precursor material such as sucrose to aid its dispersion with the titanium dioxide.

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