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Role of some technological parameters during carburizing titanium dioxide

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Abstract

The influence of technological parameters is followed during the carbothermal synthesis of titanium carbide from the dioxide. The carbon grain size, the homogeneity of the carbon/oxide mixtures and the ventilation of the powders' beds are the most important conditions for a rapid reaction. The oxide grain size, the mixing method and the compactness of the mixture has no influence, or very little. These results are explained by the carburizing mechanism where the Boudouard's reaction: $C+CO_2 \rightarrow 2CO$ plays a central role. This reaction is more rapid when fine carbon is used and when the carbon monoxide is eliminated as soon as formed. These conditions are those required for a complete synthesis of the carbide by: $TiO_2+3C \rightarrow TiC+2CO$ for mixtures having the stoichiometric composition. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: TiO_2; TiC; Carburizing; Carbon; Powders-solid state reaction

1. Introduction

In spite of progress in new technologies for the synthesis of carbides, the carbothermal reduction of oxides remains greatly the most used industrial process.

The chemical mechanism of these reactions is often unknown, however, but it is admitted that they are highly dependent on the conditions of reaction apart from the classical intensive parameters pressure and temperature [1–3]. But these extra parameters, such as the grain size (sometimes called 'technological parameters') have been studied rarely in an exhaustive manner. It seemed to us interesting to focus this paper on them, within the context of the system TiO_2/C, which is now one of the best known and which presents also an industrial importance because of the great number of uses of the carbide TiC [4–7].

With the other carburizing reactions, the formation of titanium carbide from the dioxide is very complex and comprises three successive reactions:

- the rapid initial reduction of the dioxide into sub-oxides: Ti_6O_{11}, Ti_5O_9, Ti_4O_7 and Ti_3O_5; [8]
- the formation of an intermediate oxycarbide Ti_2OC; [9]
- the final carburizing via a slow diffusional mechanism which produces TiC. [10]

The weight loss accompanying these reactions is rather weak for the first one (8.1 g for 100 g of initial mixture) and for the last one (12.1 g in the same conditions), the major effect being due to the formation of Ti_2OC (28.2 g of loss for 100 g initial) which is, for this and for a kinetical reason, the most interesting step.

So, the aim of this work is to follow the behaviour of mixtures TiO_2/C or Ti_3O_5/C in different conditions of reactivity.

2. Experimental

The powders used have very different characteristics. They are reported in Table 1, which gives, in particular, the provider, the specific area S measured by nitrogen absorption using the BET method (Micromeritics ASAP 2000) and the mean diameter ϕ calculated by the classical relation with the density ρ:

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$$\phi = \frac{6}{\rho \times S} \tag{1}$$

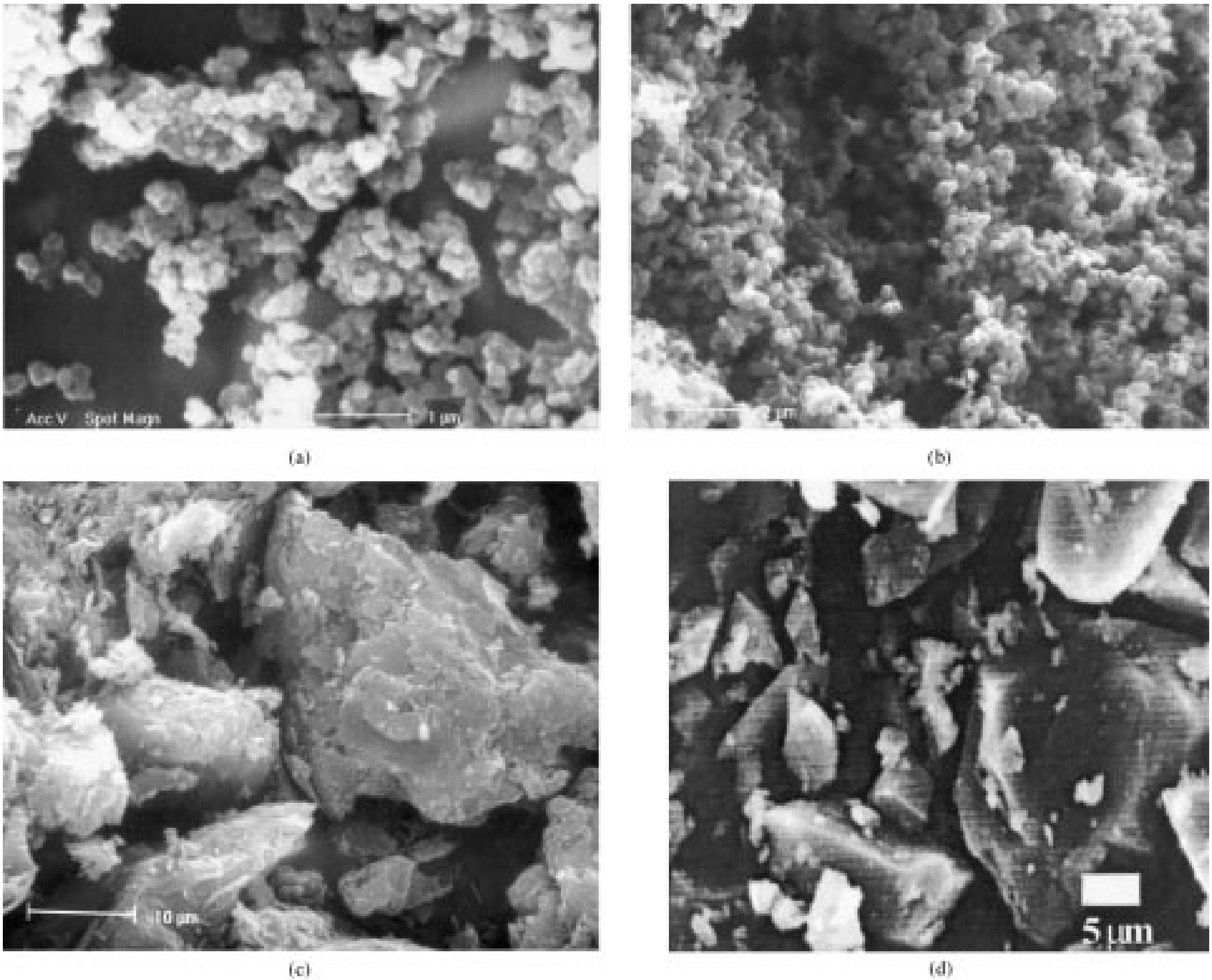
and the mean diameter measured by microscopy. Fig. 1 presents their morphologies, showing that the grains of fine TiO_2 [Fig. 1(a)] look like those of fine carbon [Fig. 1(b)] and that they are very different from the coarse ground graphite [Fig. 1(c)] or TiO_2 [Fig. 1(d)]. This last powder was obtained by sintering the fine TiO_2 at 1200 °C during 4 h. It was then ground in a mortar and finally sifted between 2 and 40 µm. The mixtures so obtained were made either manually in a mortar or with a mixer Turbula (Prolabo, France) by batches of 4 g. The quantities of TiO_2 (68.9 wt%) and C (31.1 wt%) were those of the reaction:

$$TiO_2 + 3C \rightarrow TiC + 2CO \tag{2}$$

The mixtures were poured into a vitreous crucible, covered or not, and then put in a graphite furnace (V.A.S.,

Table 1
Main characteristics of the starting powders

Powder (provider)	Variety	Specific area	Mean diameter (calculated) (µm)	Mean diameter (measured) (µm)	Purity (%)
C (Prolabo)	Lamp black	25.7	0.1	0.25	Ashes < 0.75
C (Carbone-Lorraine)	Graphite	9.2	0.3	19.1	Ashes < 0.1
TiO_2 (Prolabo)	Anatase	11.5	0.2	0.2	99
TiO_2 coarse	Rutile	< 0.1	14	–	99



(a) (b) (c) (d)

Fig. 1. SEM micrographs of (a) fine TiO_2; (b) fine carbon; (c) graphite and (d) coarse TiO_2.

France). The samples were first heated under vacuum (# 10^2 Pa) up to 350 °C, where the gas was introduced, and then to the required temperature with a heating rate of 1200 Kh^{-1}. The atmosphere was generally flowing argon (30 lh^{-1}) alone, but sometimes also carbon monoxide. The progress of the reaction was followed by weighting after cooling, which determined a conversion degree α by the ratio of the observed weight loss to its theoretical maximum for producing TiC. For testing the effect of compaction, small discs (diameter = 14 mm, thickness = 6.4 mm for $P = 100$ MPa) were achieved with an uniaxial press by using a pressure varying between 25 and 100 MPa.

For the tests with Ti_3O_5 (frequently used for eliminating the first and the last reaction), this suboxide was obtained by heating during 8 h at 1383 K under flowing argon (30 lh^{-1}) a mixture of fine TiO_2 (7.62 g) and lamp black (0.38 g) with respect of the stoechiometry of the reaction:

$$3TiO_2 + C \rightarrow Ti_3O_5 + CO \tag{3}$$

The weight loss obtained in these conditions was exactly the theoretical one (11.1%) and the phases observed were a mixture of the varieties' high temperature (JCPDS file no. 23-606) and low temperature (JCPDS no 11-217) of the suboxide Ti_3O_5. The powder so obtained had grains strongly bigger than those of TiO_2 (ϕ calculated # 1.6 μm) as it can be seen in Fig. 2, round and slightly sintered with a very weak specific area (0.9 m^2g^{-1}). This powder is then mixed with carbon for the reaction:

$$2Ti_3O_5 + 10C \rightarrow 3Ti_2OC + 7CO \tag{4}$$

with 78.9 wt% of Ti_3O_5 for 21.1 wt% of carbon.

After reaction, samples were observed with SEM (Philips XL 30), and analysed by XRD (Siemens D 5000) using the Cu-K_α radiation, with a step of 0.04°, a collection time varying between 4 and 16 s for angles 2θ in the range 30–125°. The lattice parameter of the phases Ti_2OC and TiC was calculated by the software package 'Eracel' from the deconvolution of X-ray diffraction patterns with the 10 most intense peaks.

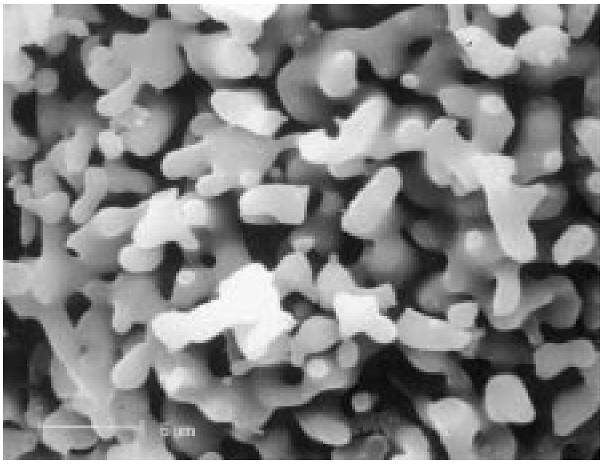


Fig. 2. SEM micrograph of Ti_3O_5 obtained after 8 h at 1383 K under flowing argon.

3. Results

3.1. Influence of the grain size

Three types of mixtures were used:

- fine TiO_2 and lamp black (a);
- fine TiO_2 and coarse graphite (b);
- coarse TiO_2 and lamp black (c).

The corresponding kinetic curves obtained at 1573 K are drawn in Fig. 3. Each point represents a separated test, for durations varying between 0.5 and 20 h. The isotherms were always very rapid at the beginning ($\alpha < 0.17$) during the formation of the suboxides, then regularly decelerated with the synthesis of the oxycarbide ($\alpha < 0.75$) and very slow after. The most rapid reaction was observed with the finest powders [mixture (a)] while the effect of the change of fine dioxide by coarse TiO_2 [mixture (c)] was appreciable but not very important. At the opposite, the replacement of lamp black by graphite considerably slowed down the rate of the reaction.

The nature of the phases produced were Ti_3O_5 ($\alpha < 0.17$), then Ti_2OC and finally substoichiometric TiC with fine powders, [mixture (a)], as previously observed.[9] With coarse TiO_2, the suboxide firstly obtained was the sesquioxide Ti_2O_3 instead of Ti_3O_5 ($\alpha < 0.25$), which

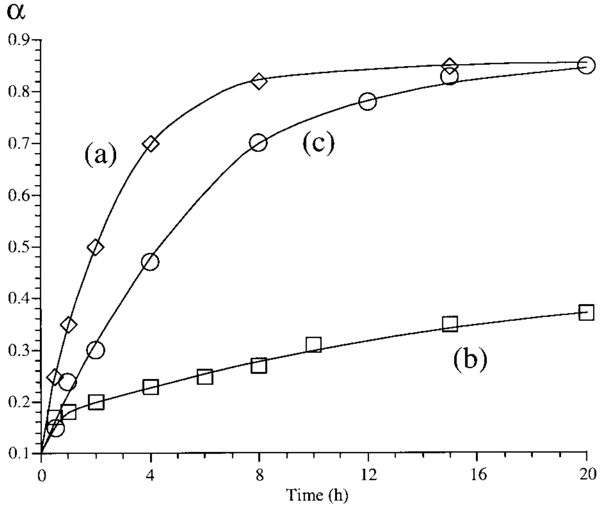


Fig. 3. Influence of grain size on the isotherms of reduction of TiO_2 at 1573 K: (a) mixtures fine TiO_2/lamp black; (b) fine TiO_2/graphite; (c) coarse TiO_2/lamp black.

later advanced towards the oxycarbide and itself towards the carbide. With graphite, there was a mixture of suboxides Ti_3O_5 and Ti_2O_3 which slowly give way to Ti_2OC. When coarse powders were used (carbon or oxide) Ti_3O_5 was never found alone and it was not possible to separate clearly the initial reduction of the oxide from the formation of the oxycarbide. For the following experiment, the oxide used is Ti_3O_5, prepared as explained above.

3.2. Influence of the mixing method

Fig. 4 compares the isotherms at 1523 K observed when the mixing of Ti_3O_5 and lamp black [Eq. (4)] was made manually in a mortar or with the mixer Turbula during different times. It appeared that the method used had no great kinetical influence but the mechanical mixing was slightly less good than the manual one, since 16 h in the Turbula were required for obtaining the same result as with the mortar. The conversion degree α increased with the length of mixing, for instance for a same duration of 4 h of thermal treatment whose results are reported in Table 2.

This effect was not due to a change of the compactness of the mixtures with the mixing time since this value is quite constant at about 19–21%. Table 2 also provides the measurements of the specific area of these mixtures, which shows that there is no significant modification of the grain size whatever the method and duration could be. The morphological aspect of the powder was also the same as with the mortar and the Turbula. Fig. 5(a) illustrates the morphology of initial mixtures, with grains gathered in kinds of heaps or agglomerates of 20 to 50 µm whose general shape did not change during the thermal treatment. However, the size of their grains grew strongly with the advance of the reaction and finally they took the shape of shells more or less hollow [Fig. 5 (b)].

During all these tests, the only phases detected by XRD were the starting Ti_3O_5 and the oxycarbide Ti_2OC with a lattice parameter of 0.4296 nm.[11,12]

So, we have to conclude that the weak kinetical effect of the mixing was probably due only to a best distribution of the carbon around the suboxide grains when increasing the mixing time, which is very difficult to illustrate since the carbon grains are very small.

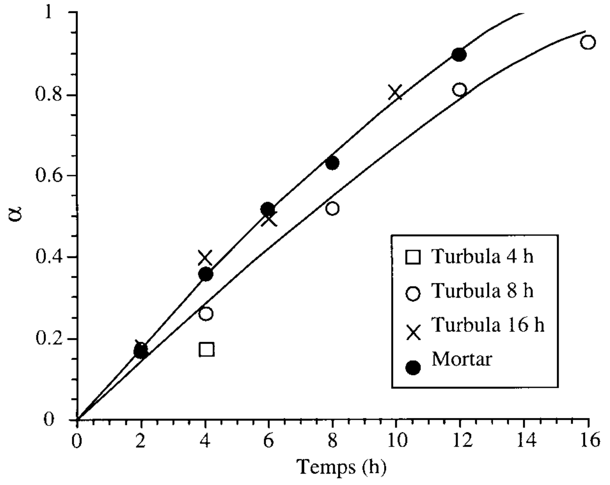
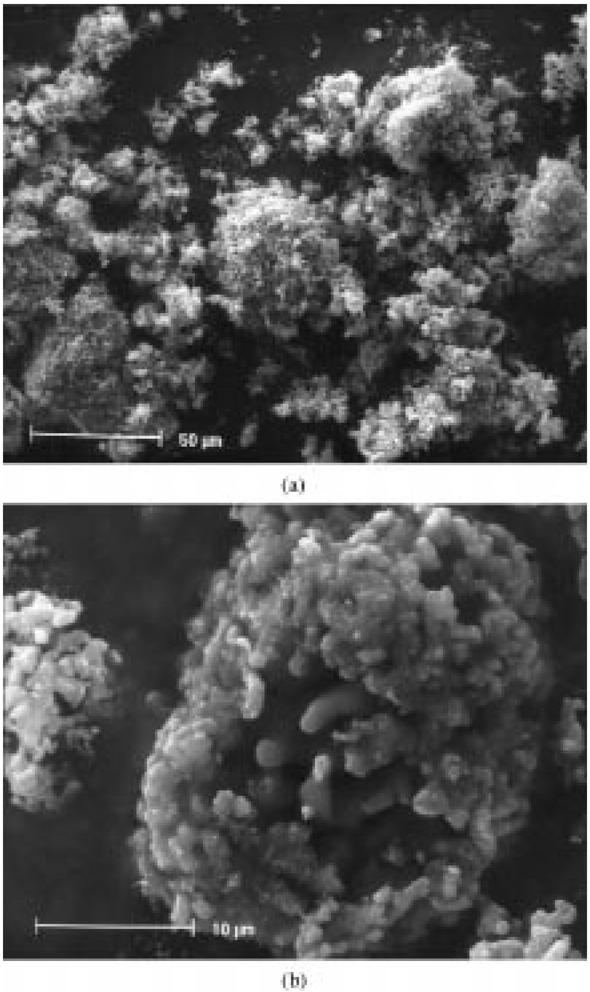


Fig. 4. Influence of mixing mode on the reaction rate of mixtures Ti_3O_5/C at 1523 K.

Table 2
Advance of the reaction related to the characteristics of the starting mixtures and their mixing mode after 4 h at 1523 K

Mixing mode	Mortar	Turbular (4 h)	Turbula (8 h)	Turbula (16 h)
Compacity (%)	19	21	20	20
Specific are (m_2/g)	5.9	5.7	5.6	5.7
α (t = 4h)	0.36	0.17	0.26	0.41



(a)

(b)

Fig. 5. Morphology of the heaps Ti_3O_5/lamp black formed by a 16 h mixing in Turbula after (a) 2 h and (b) 10 h at 1523 K.

3.3. *Effect of a CO atmosphere*

The influence of a pure CO atmosphere was tested at 1613 K for mixtures Ti_3O_5/lamp black obtained with mortar. The flowing rate was fixed at 20 l h^{-1}. The kinetical curves are presented in Fig. 6. The carbon monoxide atmosphere slowed down the reaction rate which was reduced more than 4 times. Although this drastic slackening, the product of the reaction, was always the oxycarbide Ti_2OC characterised by the constance of its lattice parameter and the morphology of the powder, it was not different from that previously observed.

3.4. *Effect of confinement*

Until then, the whole experimental was performed in a crucible (diameter = 30 mm, height = 35 mm) covered by a disk of vitreous carbon. The role of the cover was to prevent the finest powder grains from being blown off when the furnace was emptied or during the introduction of the gas, and also to avoid the deposition of fine carbon dust which could be pulled out of the graphite insulating felt during the pressure changes. It was only put on the crucible, so that it could not stop gas exchanges.

Nevertheless, it seemed useful to test another morphology of reactor, and the powder was only laid down in an open crucible for improving the ventilation of the powder bed. For these tests the furnace was emptied very slowly and gas was introduced very carefully. Powders of Ti_3O_5 and lamp black were mixed with mortar with respect to the stoichiometry of Eq. (4). Fig. 7(a) shows that the kinetical effect obtained was very important since the reaction rate was trebled more or less when the mixture was not confined. To ensure that it was not due to an artifact (powder loss) the same test was made on strongly pressed mixtures ($P = 100$ MPa), the samples so obtained being markedly less susceptible of blowing off. Here again, we observed [Fig. 7(b)] the same acceleration of the reaction rate when there was no cover on the sample.

XRD revealed that, before forming the oxycarbide Ti_2OC, the first step of the reaction was here the conversion of Ti_3O_5 into the sesquioxide Ti_2O_3 ($\alpha > 0.15$), which was never observed when lamp black was used. Thus the conditions of ventilation are a major parameter for the reaction.

3.5. *Effect of the compaction*

After having pressed the starting mixtures Ti_3O_5/lamp black in the stoichiometric ratio of Eq. (4) obtained

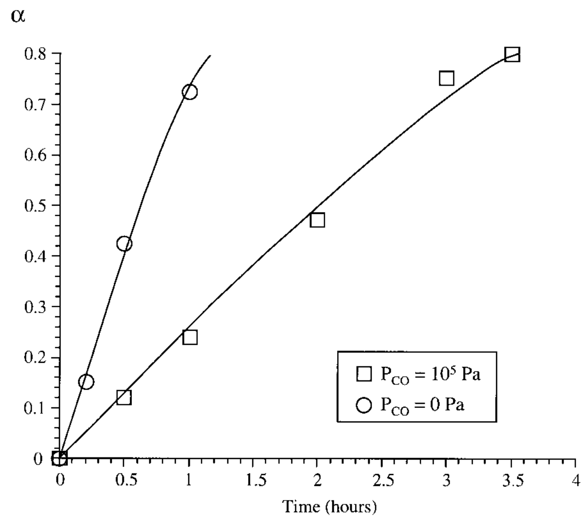
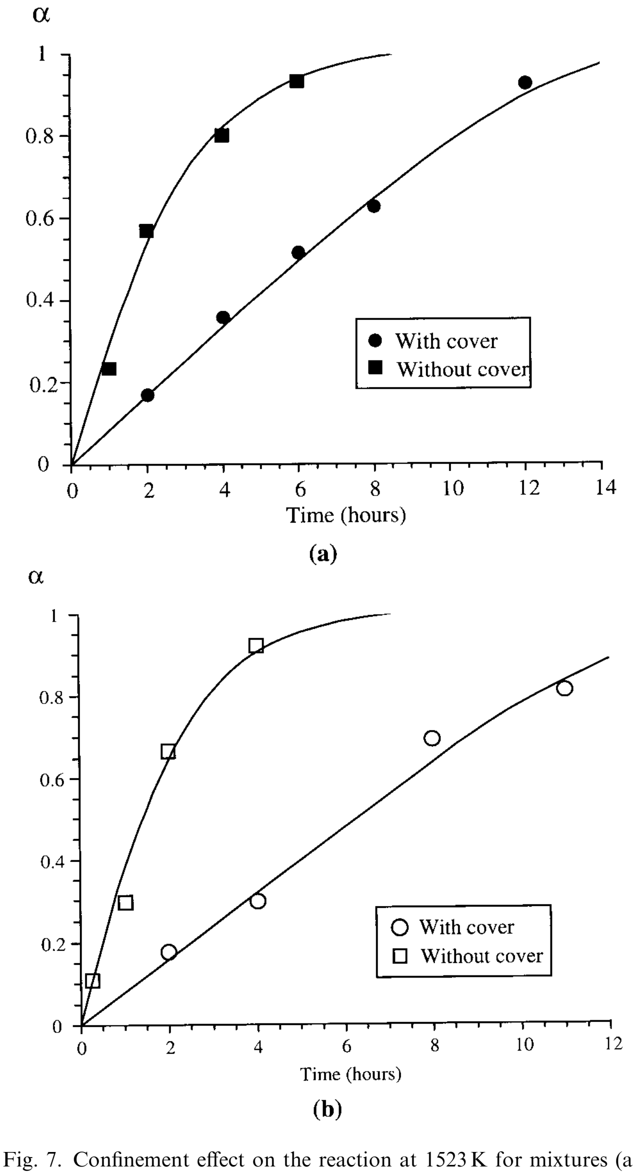


Fig. 6. Comparison of the reaction rate at 1613 K under flowing argon and flowing CO for mixtures Ti_3O_5/C.



(a)

(b)

Fig. 7. Confinement effect on the reaction at 1523 K for mixtures (a) Ti_3O_5/C not compacted or (b) pressed under 100 MPa.

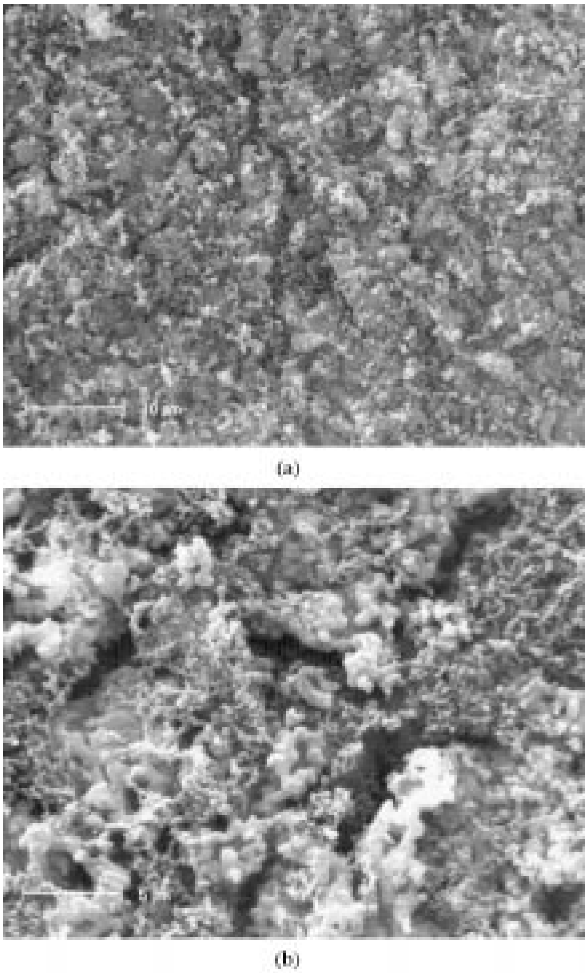


Fig. 8. SEM micrographs of mixtures Ti_3O_5/C (a) compacted under 100 MPa and then (b) heated during 2 h at 1523 K.

with mortar, the initial heaps had naturally disappeared [Fig. 8(a)], and, after a thermal treatment at 1523 K, the grain size grew such as previously observed [Fig. 8(b)] but without any particular arrangement. The kinetical effect of this compaction obtained in a crucible not covered seemed to be a little positive as illustrated in Fig. 9, but no serious conclusion could be drawn as far in as the results were situated within the uncertainty of the point by point method used (estimated at ±0.05 on the conversion degree α) for applied pressures varying between 0 and 100 MPa.

4. Discussion

Five kinds of parameters have been studied: grain size; mixing method; pressure of CO; confinement; and compaction, with their effects on the reactional behaviours of mixtures oxide/carbon. One can classify them in three categories, those which have apparently no kinetical effect: mixing mode and compaction; those which have a weak effect: oxide grain size, time of mixing; and those which have a great importance: pressure of carbon monoxide, confinement, and size of the carbon grains. It is interesting to justify this, i.e. to open the discussion on the reaction mechanism.

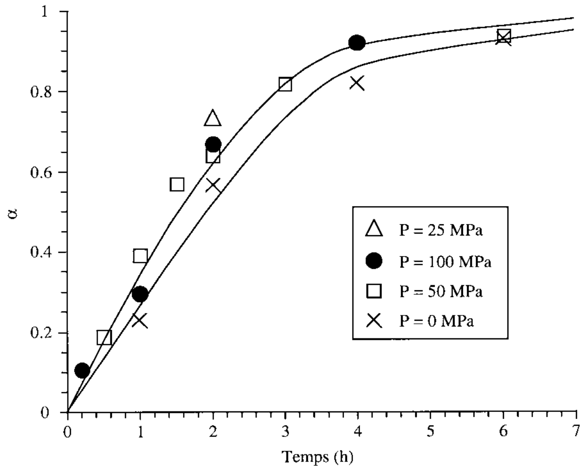


Fig. 9. Kinetical effect of compaction on mixtures Ti_3O_5/lamp black heated at 1523 K.

4.1. *Absence of effect of mixing mode or compaction*

The main consequence of the way of mixing and the compaction is to modify the number of contacts between grains of different natures. This no real influence on the reaction rate and it is significant in terms of reaction mechanism: it means that the limiting step is not a solid–solid reaction between carbon and oxide grains which would be governed by the diffusion through the necks between the grains. This point invalidates some previous assertions[13] and is confirmed by the shape of the kinetic curves which can be linearized by the classical function:[14]

$$F(\alpha) = 1 - (1 - \alpha)^{1/3} = \frac{k(T, P)}{r_0} t \qquad (5)$$

where $k(T, P)$ is a function of temperature and pressure (constant in isothermal and isobaric conditions) and r_0 the initial radius of the grains, where the limiting step of the reaction is located. $F(\alpha)$ is drawn in Fig. 10 on the example of the mixtures Ti_3O_5/lamp black compacted under 50 MPa. This function, sometimes called 'contracting sphere model', involves that the limiting step is located either at the internal surface of the oxide grains during their conversion into oxycarbide or at the surface of carbon grains which decreases also as reaction advances, but it has no relation with the number of contacts between the grains.

4.2. Role of the time of mixing and of the oxide grain size

When the mechanical mixer Turbula was used it was necessary to extend the mixing. Indeed, the lamp black is a sticky powder which gathers easily in relatively dense heaps, whose behaviour is then analogous to that observed with coarse graphite grains, inducing a slowing down of the reaction rate. A long mechanical mixing finally breaks these heaps. With the manual mixing, carbon is slowly added, avoiding the agglomeration of the fine grains.

To explain the role of oxide grain size it is necessary to remember that the first reaction is the decomposition of the titanium dioxide or suboxides[1,8,13] by:

$$x\mathrm{TiO_2} + (2x-y)\mathrm{C} \rightarrow \mathrm{Ti}_xO_y + (2x-y)\mathrm{CO} \qquad (6)$$

which has its own specific rate v (expressed for instance in liter of CO by cm^2 and by s). Let us admit, in a first simplifying approach, that the global rate of carbon monoxide emission V is proportional to the surface of the oxide grains S by:

$$V = v \times S \qquad (7)$$

the unity of V being in l s^{-1}. If the flow of argon, expressed in the same unit is V_0 the partial pressure of carbon monoxide becomes:

$$P_{\mathrm{CO}} = \frac{V}{V_0} = \frac{v}{V_0} \times S = k \times S \qquad (8)$$

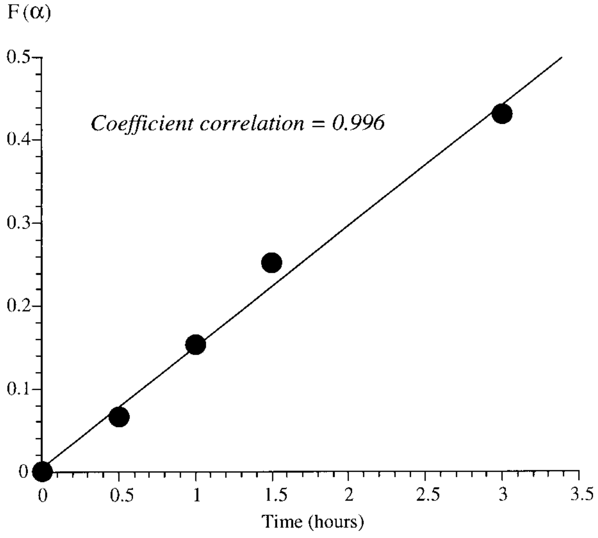


Fig. 10. Plots of $F(\alpha)$ versus time for the mixtures $\mathrm{Ti_3O_5}$/lamp black compacted under 50 MPa and heated at 1523 K.

where k is constant for a temperature and an argon flow fixed. In reference to Table 1, the surface of the oxide grains is divided by more than 10^2 when using coarse $\mathrm{TiO_2}$ instead of a fine one, and this induces a similar reduction of the partial pressure of carbon monoxide. Now, the nature of the thermodynamically stable titanium oxide phase depends on the pressure of carbon monoxide. This is well illustrated by the volatility diagram whose construction mode is given elsewhere.[15] For this system it is reported in Fig. 11. So, if $P_{\mathrm{CO}} = 10^4$ Pa (for instance when fine $\mathrm{TiO_2}$ is used) the stable phase is $\mathrm{Ti_3O_5}$, but in the same conditions with coarse $\mathrm{TiO_2}$ P_{CO} becomes near to 10^2 Pa and then $\mathrm{Ti_2O_3}$ is more stable.

This effect justifies the change of nature of the intermediate suboxide with the size of oxide grains, but it does not explain the slight slowing down of the reaction rate observed in Fig. 3. Its possible origin is that the mixture of grains of very different sizes such as coarse $\mathrm{TiO_2}$ (ϕ # 20 μm) with very fine carbon (ϕ # 0.2 μm) is difficult and there are certainly a lot of carbon heaps, such as described above, which cannot be avoided and which have a negative effect on the reaction rate.

4.3. Influence of carbon size, P_{CO} and confinement

The reaction is highly dependent on carbon grain size. This result is not original: such an effect is found in a great number of carbothermal reactions (reduction of oxides, nitridations and carburization). It has already been pointed out[16] that TiC synthesis is limited by the reaction on the surface of the carbon grains. By considering Eq. (5) it means that r_0 is the carbon grains radius and hence that the limiting step is located on the external surface of the carbon grains which oxidizes during the reaction. From this, and on the basis of previous works,[9,17] an analytical presentation of the carburizing of $\mathrm{Ti_3O_5}$ consists of cutting off the slow reaction on carbon by:

$$10\mathrm{C} + 10\mathrm{CO_2} \rightarrow 20\mathrm{CO} \qquad (9)$$

the rest of the reaction being the equilibrium:

$$2\mathrm{Ti_3O_5} + 13\mathrm{CO} = 3\mathrm{Ti_2OC} + 10\mathrm{CO_2} \qquad (10)$$

for the overall result:

$$2\mathrm{Ti_3O_5} + 10\mathrm{C} \rightarrow 3\mathrm{Ti_2OC} + 7\mathrm{CO} \qquad (4)$$

This proposal of mechanism cannot also justify the negative P_{CO} effect: neither Eq. (9) nor (10) is elementary, but it is worth noting that the reaction rate of Eq. (4) is, in fact, governed by the Boudouard's (9) reaction on which an increase of P_{CO} has a negative kinetical

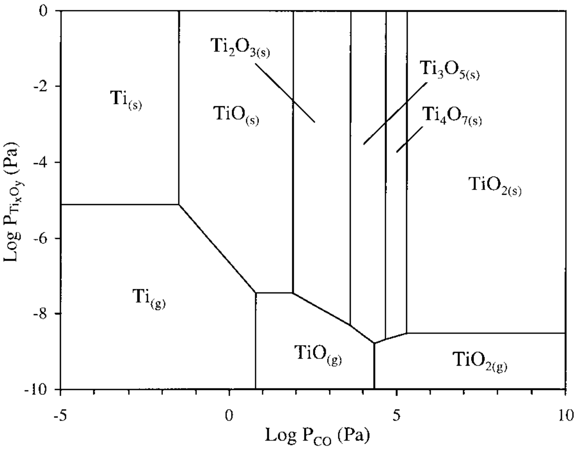


Fig. 11. Volatility diagram for the system Ti/O at 1400 K as a function of partial pressure of carbon monoxide.

effect.[18] If P_{CO} increases in the reactor, the overall reaction rate decreases correlatively, as observed in Fig. 6.

The negative effect of confinement (Fig. 7) is a direct consequence of the influence of P_{CO}: carbon monoxide produced by Eq. (4) is carried away by flowing argon more easily when the reactor is open. When it is closed by a cover, it is highly probable that the carbon monoxide pressure in the powder bed is markedly higher than without cover, and the reaction rate decreases correlatively. This interpretation of the influence of P_{CO} is consistent with all our experimental results. The previous works in this topic were contradictory and difficult to to be exploited.[13,19]

5. Conclusion

The carburizing rate of titanium dioxide can be accelerated by using the finest carbon possible, and with an important gas flow for reducing the partial pressure of carbon monoxide in a open reactor. Special attention must be paid to the mixing but only for guaranteeing that the carbon distribution is homogeneous without heaps formation. Other parameters have no influence, or only a very small one: the oxide grain size or the compaction. All these parameters never influence the final characteristics of the oxycarbide or of the carbide obtained. The grains are always round with a size near 2 μm which is not really modified by changing the conditions of the reaction at a fixed temperature. These remarks allow better understanding of why the industrial productions sometimes increase the carbon content for accelerating the reaction: in this way they make the reaction surface (the carbon surface) higher. But this has the consequence that it remains free carbon after reaction, which cannot be easily eliminated without degrading the carbide. It is possible to obtain directly TiC of good purity with reasonable reaction times, by a careful initial choice of powders (fine, with similar grain sizes), a good mixing and above all an important ventilation of the powder bed.

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