Oxidation behavior of nano-scaled and micron-scaled TiC powders under air

M. Gherrab a,b, V. Garnier a,⁎, S. Gavarini b, N. Millard-Pinard b, S. Cardinal a

a MATEIS, INSA de Lyon, bld. Blaise Pascal, 20 Avenue A. Einstein, 69621 Villeurbanne Cedex, France
b Université de Lyon, CNRS/IN2P3, UMRS5622, IPNL, Université Lyon 1, F-69622 Lyon, Villeurbanne, France

A R T I C L E   I N F O

Article history:
Received 29 May 2013
Accepted 28 July 2013

Keywords:
TiC
Oxidation
Nanopowder
XRD

A B S T R A C T

The oxidation behavior of several batches of TiC nanopowders and micropowders under air has been studied. Using TGA, the oxidation of nanopowders is completed faster and at a lower temperature compared to micropowders. This is related to the higher specific surface area of the nanopowders. Using an amount of powder of about 41.6 mg through DTA, three different exothermic peaks were observed for both kinds of powders. Correlated to the in-situ temperature XRD diffractograms, these peaks were attributed to the following oxidation reactions: i) TiC → TiC0.5x → TiO. The same successive oxide phases for nanopowders and micropowders were observed, meaning that the oxidation mechanism is similar in both cases but with a shift of temperature. In this article, the role of the oxygen trapped in the powder and the effect of powder quantity on the oxidation kinetics and on the occurrence of one or three oxidation peaks are discussed.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Titanium carbide (TiC) ceramic has very good mechanical properties, such as hardness and wear resistance [1]. As a result, it has been extensively used as the second phase in ceramic composites for metal-cutting tools [2] or as thin films for wear-resistance applications [3–5]. It is also a refractory material, with a high melting point (3067 °C), good thermal conductivity even under irradiation [6] and a good stability over a wide range of stoichiometry which is an asset for irradiation resistance [7]. Due to these properties, TiC appears to be an interesting material for high temperature and radiative applications, as in the nuclear domain [8,9].

The use of nanopowders has significantly increased over the last few decades. Indeed, the elaboration of materials from those nanopowders has led to an improvement in their general properties [10,11]. However, manipulating nanopowders could present some issues. For instance, the reactivity of nano-scaled grains to oxygen could substantially modify their composition, and thereafter change their properties regarding synthesis processes, such as sintering [12].

Some studies have been reported regarding the oxidation of TiC micropowders in air using differential thermal analysis (DTA) and thermal gravimetric analysis (TGA). Shimada et al. [13,14] have shown that the exothermic oxidation of TiC micropowders started around 300 °C and finished at around 900 °C. Concerning nanopowders, Rudneva et al. [15] found that the onset temperature for the exothermic oxidation of TiC was 275 °C. Kurlov et al. [16] also recently shown that a decrease in the particle size of WC powders (from 20 to 6000 nm) leads to a decrease in the exothermic peak temperature of oxidation and growth of the oxidation rate.

Only a few papers have been published detailing the oxidation mechanism of TiC powders in air. Shimada et al. [17] proposed a four-stage kinetic model for the oxidation of TiC micropowders. This model is characterized by alternate slow and fast stages, each of these being associated with the formation of an oxide phase. For nanopowders only and using several sample amounts and scanning rates, Sempere et al. [18], proposed one direct oxidation mechanism from TiC to TiO2 which appears in two stages. According to them, the first stage consists in an extremely fast and exothermic step consuming the oxygen trapped inside the nanoparticle bed. The slower second stage could be controlled by the diffusion of oxygen through the sample.

The aim of our study is to determine the impact of the grain size on the oxidation behavior of TiC powders in air. We will focus on understanding the differences between nanopowders and micropowders in terms of mechanism and oxidation kinetics. In this article, the thermal oxidation stages of TiC nano- and micropowders and the follow up of the oxides formed during the heating process will be analyzed using DTA–TGA and in-situ XRD. Several commercial nano- and micropowders were tested to evaluate the influence of the initial composition and agglomeration state of the powder on subsequent oxidation.

2. Experimental

Different commercial batches of TiC powders were studied. These batches can be divided into two categories. The first gathers the
commercial TiC nanopowders with the following characteristics given by the manufacturers:

- Nano-1: 99% purity, particle size smaller than 40 nm and specific surface area (SSA) higher than 50 m$^2$/g (Iolitec Inc., Germany).
- Nano-2: One batch of 99% purity, particle size of 40 nm and SSA of 40 m$^2$/g (NanoStructured & Amorphous Materials Inc., USA).
- Nano-3: The same as Nano-2 but from a different batch (NanoStructured & Amorphous Materials Inc., USA).
- Nano-4: 99% purity, particle size ranging from 80 nm to 130 nm and SSA of 35 m$^2$/g (NanoStructured & Amorphous Materials Inc., USA).

The second category is composed of the commercial TiC micro-powders with the following characteristics:

- Micro-1: 97% purity and particle size ranging from 1 to 1.5 μm (H.C. Starck®, USA).
- Micro-2: 97% purity and particle size ranging from 2 to 3 μm (H.C. Starck®, USA). More details about those micropowders are given in Table 1.

The as-received powders were then characterized using different devices and techniques, such as:

- Scanning electron microscopy (SEM), Zeiss®, and transmission electron microscopy (TEM), Jeol®, to estimate the real particle size of the powders, their morphology and agglomeration state.
- Combustion analysis of the different powders to determine the carbon content extracted during the combustion in the programmable high frequency furnace of the Horiba® EMIA320 device.
- The Horiba EMGA820® elemental analyzer to measure the oxygen and nitrogen content.
- X-ray diffraction (XRD) measurements using the D8-Bruker® device to determine the phase composition of the as-received powders with a scan angle ranging from 20° to 120°.
- The diffractograms were analyzed with the TOPAS® program using the Scherrer equation (T = Kλ/βcosθ where T is the crystallite size in Å, K = 0.9 is the Scherrer constant, λ = 1.5418 Å is the X-ray wavelength, β is the line-broadening at full width half the maximum intensity and θ is the Bragg angle) to determine the average crystallite size for each nanopowder batch. The Scherrer method cannot be applied to a large crystallite size i.e. of several hundred nanometers (>500 nm). In fact, the average crystallite size, evaluated by TOPAS®, is related to the broadening of the peaks. As a result, the larger the peak, the smaller the average crystallite size.
- The BET ASAP-2010 device from Micromeritics®, is used to measure the specific surface area (SSA) of the as-received powders after drying at 110 °C during 24 h. These SSA values were used to evaluate the crystallite size considering the hypothesis of spherical grains.

After characterization, the powders were directly introduced into a combined DTA–TGA SETARAM® 92-18 with a mass of TiC equal to 41.6 $\pm$ 0.1 mg for all the experiments. This is the mass required to completely fill the crucible. These experiments were performed with a heating rate of 5 °C/min from ambient temperature to 1700 °C to follow up the thermal oxidation of TiC powders in air. Indeed, using an oxidation rate between 5 and 10 °C/min allows the observation of the whole oxidation phenomenon [17]. The heat flow and experimental weight gain due to the oxidation of TiC were measured by DTA and TGA, respectively. The measured experimental weight gain allows the oxidation rate to be defined as the ratio between this experimental value and the calculated total theoretical weight gain.

The in-situ XRD measurements were performed using a heating rate of 5 °C/min in order to compare with the DTA–TGA measurements. The TiC powders (about 0.5 g) were put on an alumina support. Diffractograms at ambient temperature and then from 150 °C to 1200 °C at every 10 °C interval, were collected. Intensities were obtained in the 2θ range between 23.5° and 29.5° for the first run and between 32.5° and 38.5° for the second run, each time using a step of 0.05° and a measuring time of 0.5 s for each point. These two diffraction angle ranges were chosen because they contain the peaks of the oxide phases that could be formed during the oxidation process from TiC to TiO$_2$.

3. Results and discussion

3.1.1. Crystallite/grain size and morphology

We show in Fig. 1 a TEM image of a TiC nanopowder (Nano-2) and an SEM image of a TiC micropowder (Micro-2). From Fig. 1a, we can see that the Nano-2 nanopowder has crystallites ranging from 20 to 50 nm. The nanopowder seems to agglomerate with the agglomerate size reaching several hundreds of nanometers. Equivalent features

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Composition of Micro-1 and Micro-2 micropowders.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{total}$ (wt.%)</td>
<td>O (wt.%)</td>
</tr>
<tr>
<td>Micro-1</td>
<td>19.2</td>
</tr>
<tr>
<td>Micro-2</td>
<td>19.2</td>
</tr>
</tbody>
</table>

Fig. 1. a): TEM image of the as-received Nano-2 nanopowder and b) SEM image of the Micro-2 micropowder.
were observed on all the other batches of TiC nanopowders. At this stage, we could not estimate the strength of the bonds between the crystallites.

In the case of the Micro-2 sample, in Fig. 1b, the TiC grains with a size ranging from less than 1 μm to about 10 μm were observed. The smallest particles are probably fragments resulting from larger particle milling. The particles have a plate-like morphology and do not seem to be agglomerated. The Micro-1 powder shows a similar plate-like morphology, even though the grain size was visually lower, as given by the manufacturer.

In the case of the nanopowders, the SSA was given by the manufacturer (unspecified technique); see Table 2 (first column). For all the TiC powders, the SSA was verified using BET measurements. The results are given in the second column of Table 2. In fact, the SSAs obtained are lower than the values indicated by the manufacturer for each nanopowder. The difference is probably due to the agglomeration state of the powders which can hide some crystallite surfaces, thus decreasing the apparent SSA value.

For each batch, crystallite size (CS) was determined by XRD using the TOPAS® software (column 4), and it was also deduced from BET measurements (Table 2 column 5). Globally, higher values of CS were found for nanopowders, with both techniques, compared to the manufacturer’s data (Table 2 column 3). However, there is good agreement between XRD and BET CS which could therefore confirm the tendency of observing the higher CS values compared with those given by the manufacturer, except for the Nano-4 batch. For this batch, the discrepancies between the CS values obtained by XRD and BET are representative of the agglomeration state of the powder [19]. This means that this batch is much more agglomerated than the other nano-batches. Nevertheless, it is interesting to note that the CS range given by the manufacturer for the Nano-4 batch corresponds to the range between the values obtained here by XRD and BET. However, for the micropowders, the CS values are slightly higher than those indicated by the manufacturer (Table 2 column 3), although our results confirm their ratio of ~2 between CS values for Micro-1 and Micro-2 powders.

### 3.1.3. Structural characterization

XRD measurements were performed on the initial powders to identify the phases present. In the case of the nanopowders, for example Nano-2 in Fig. 2, the main phase which we identified is TiC (JCPDF number = 00-003-1213) as well as small peaks corresponding to the presence of titanium dioxide due to the anatase or rutile phase (JCPDF number = 01-078-2486) and rutile phase (JCPDF number = 00-021-1276). For the micropowders, such as Micro-2 seen in Fig. 2, the main signal also corresponds to TiC but signals of titanium dioxide due to the anatase or rutile phase were not detected. For each powder, the average TiC lattice parameter was calculated using accurate TiC peak position and the values reported in Table 3 (column 4). The TiCxNyOz lattice parameter has been plotted as a function of the atomic carbon composition in Fig. 3 for the present study, together with other experimental values (JCPDF database for TiC, N, O, and from Zou et al. for TiCxOy, and from Jian et al. for TiCxNyOz). We observed that the lattice parameter tends to increase with the carbon content whatever the considered set of data. The values for the present study are well placed in the average of the values obtained in literature for TiC, TiCxNyOz, and TiCxOz; and thus indicate the presence of both nitrogen and oxygen as impurities in the nanopowders studied here. As observed in Fig. 3, the presence of those two elements in the lattice results in a lowering of the lattice parameter compared to the pure TiC and to the under-stoichiometric TiC.
3.2. Oxidation in air

The total theoretical weight gain for fully stoichiometric TiC is determined considering the following reaction:

\[ \text{TiC} + 2\text{O}_2 \rightarrow \text{TiO}_2 + \text{CO}_2 \]

The evolution of the oxidation rate (ratio of experimental and total theoretical weight gain) as a function of the TGA temperature was plotted, for each TiC batch in Fig. 4. On the one hand, in the case of nanopowders, the maximum oxidation rate is lower than 100% which can be explained by the fact that the commercial TiC nanopowders are non-stoichiometric. These powders contain relatively large amounts of nitrogen and oxygen, as shown in Table 3. On the other hand, the micropowders present a final oxidation rate slightly higher than 100%. This excess weight gain compared with the theory was already observed by other authors but without an explanation [15]. A possible reason could be the presence of unknown impurities and/or carbon deficiencies in the material.

For both nano- and micropowders, oxidation starts at around 300 °C and stabilizes at around 800 °C and 900 °C, respectively. These results are in agreement with the literature [14,15,17]. The micropowders seem to present the same kind of behavior as the nanopowders but the initial slope of the oxidation curves in Fig. 4 is clearly higher for the nanopowders than for the micropowders. The higher SSA of the former may be responsible for the higher reactivity of nanograins resulting in a faster oxidation process (steeper slope).

The evolution of heat flow as a function of temperature was measured using DTA for all the powders. For the purpose of clarity and because the four nanopowders behave similarly and the two micropowders also behave similarly, only one nanopowder (Nano-2) and one micropowder (Micro-2) have been plotted in Fig. 5.

As can be seen from Fig. 5, three different exothermic peaks appear for both powders. They occur at lower temperatures for nanopowders (peak 1 = 390 °C, peak 2 = 430 °C, and peak 3 = 620 °C) compared to micropowders (peak 1 = 460 °C, peak 2 = 475 °C, and peak 3 = 720 °C). This is in accordance with the previous TGA curves, indicating a faster oxidation process in the case of nanograins. From these results, it is not yet clear if these three peaks correspond to the formation of several oxide phases or if they are only due to one direct oxidation step from TiC to TiO2 as suggested by Sempere et al. [18]. Therefore, in order to identify the phases present in the powder during heating, in situ XRD measurements were performed. The same heating rate (5 °C/min) was used for the DTA–TGA and XRD measurements. The diffractograms in Fig. 6 show the evolution of the peak intensity depending on the temperature for the two ranges of 2θ scan angle 23.5°–29.5° (Fig. 6a and c) and 20°–120° (Fig. 6b and d).
32.5°–38.5° (Fig. 6b and d). Thus, the thermal oxidation mechanism of TiC nanopowders in air can be described as follows:

- The first DTA peak at 390 °C corresponds to the disappearance of the TiC phase (JCPDF number = 00-003-1213) as shown on the diffractograms. Indeed, TiC is present from ambient temperature up to around 380 °C.
- The next step is the formation of the suboxide, Ti$_3$O$_5$ (JCPDF number = 01-072-2101) which occurs from 330 °C to around 600 °C in both diffractograms. The maximum intensity of the Ti$_3$O$_5$ peak is obtained at a temperature corresponding to the second DTA peak i.e. at 430 °C.
- The last step is the appearance of TiO$_2$ of the anatase phase (JCPDF number = 01-078-2486) at around 600 °C (corresponding to the third DTA peak at 620 °C) and its progressive transformation to the rutile phase (JCPDF number = 00-021-1276). The complete oxidation is reached at around 800 °C.

The same protocol was also used for the Micro-2 sample, and the two corresponding XRD scans are given in Fig. 6c and d. The same succession in phase(s) formation as for the Nano-2 powder was observed, meaning that the oxidation mechanism is similar in both cases. However, in the case of the Micro-2 micropowder, the kinetics is much slower. Indeed, TiC disappears at around 380 °C for Nano-2 whereas it disappears at around 460 °C for Micro-2.

Moreover, the maximum intensity of Ti$_3$O$_5$ is obtained at about 475 °C compared to 430 °C for Nano-2. Finally, the anatase phase is formed above 720 °C (620 °C for Nano-2) and complete oxidation is achieved at around 900 °C compared to about 800 °C for the nanopowder.

3.3. Discussion

An interesting point outlined by Sempere et al. [18] is that the number of “apparent” stages in DSC (Differential Scanning Calorimetry) experiments depends on the quantity of nanopowder introduced in the crucible. A small sample amount (about 1 mg) results in one apparent oxidation step through DSC. For larger amounts, multiple peaks are observed at higher temperatures. One possible explanation for this behavior was given by Ribeiro [23] who assumed that the first stage of oxidation is due to the fast reaction between TiC and oxygen trapped inside the nanoparticle bed, the trapped oxygen being then totally consumed. The other peaks at slower rates would be due to the same oxidation reaction but controlled by the diffusion of oxygen.

Fig. 4. Evolution of the oxidation rate as a function of the TGA temperature.

Fig. 5. Evolution of the heat flow as a function of the DTA temperature.
and carbon dioxide through the sample, after the total consumption of initially trapped oxygen. Considering Sempere’s DSC results [18], a one-step fast oxidation mechanism is assumed in the case of small amounts of nanoparticles through the global reaction $\text{TiC} + 2\text{O}_2 = \text{TiO}_2 + \text{CO}_2$.

However, by in-situ XRD (Fig. 6), we show that each DTA peak could be associated with the formation of a particular oxide up to TiO$_2$. We believe that the dependence of kinetic aspects on the powder amount is effectively related to the oxygen quantity trapped inside the powder. However, calculation of the molar oxygen quantity at 298 K ($7 \times 10^{-7}$ mol O$_2$) present in the trapped air inside the $41.6 \text{ mg}$ crucible indicates a negligible quantity of oxygen in the nanoparticle bed compared to the amount of TiC ($6.9 \times 10^{-4}$ mol TiC representing 10 μL) introduced in a 100 μL crucible. This means that the different oxidation steps are controlled by the oxygen diffusion through the powder and by the resulting oxygen partial pressure (PO$_2$) decrease during oxidation. In the case of small amounts of powder (about 1 mg), the oxygen partial pressure can be considered as constant until complete oxidation because the most part of the powder is in contact with O$_2$. Thus, a shortening of the interval between successive oxidation reactions can be expected resulting from the relatively high oxygen partial pressure. However, in the case of larger amounts of powders, the oxygen partial pressure decreases notably which results in a longer interval between the formation of each oxide until the rutile phase of TiO$_2$. As a consequence, the activation energy calculated by Shimada [17] for the different oxidation steps should also be linked with the decreased oxygen partial pressure and not using a stoichiometric oxidation reactions. Sempere [18] has shown that one direct oxidation step may occur when the oxygen partial pressure was sufficient and could allow the calculation of the activation energy. However, as shown through XRD, several oxidation steps correspond to several and different oxidation reactions which makes the calculation of the activation energy for a direct transformation from TiC to TiO$_2$ unlikely.

From our results, we see that several oxidation steps occur. The first corresponds to the disappearance of the TiC phase which is counterbalanced by the progressive formation of oxycarbides $\text{TiC}_x\text{O}_{1-x}$ through to TiO. This transformation is associated with the progressive shift of the TiC diffraction peak toward high angles as the incorporation of oxygen results in a lowering of the lattice parameter (see Fig. 3). As an example, the slight shift of the TiC peaks for the nanopowder Nano-2 toward higher 2θ angles (smaller lattice parameter) is observed from the ambient temperature (peak position of 36.0° corresponding to a lattice parameter of 4.315 Å) to 380 °C (peak position of 36.1° corresponding to a lattice parameter of 4.298 Å). The same kind of shift has been observed for the micropowder from the ambient temperature (peak position of 35.9° corresponding to a lattice parameter of 4.321 Å) to 460 °C (peak position of 36.1° corresponding to a lattice parameter of 4.297 Å). Moreover, it has been shown that the formation of a compound or a solid solution structure between TiO and TiC is possible [24,25] and that the epitaxial growth of an oxide layer of well-ordered TiO on the TiC surface is favored [26,27] and strongly dependent on the crystallographic orientation [27].

We show that the second step is the formation of the suboxide Ti$_3$O$_5$. Surprisingly, there is no trace of Ti$_2$O$_3$ phase formation during the heating process. This compound could logically be expected as a transient suboxide phase between TiO and Ti$_3$O$_5$. Its absence from the diffractograms could be due to kinetic aspects as this phase may be too transient to be observed in our experimental conditions. In fact, with different experimental conditions used in a previous study of sintered samples obtained from micropowders, the samples were heated at a constant temperature under a controlled and very low oxygen partial pressure. The Ti$_3$O$_5$ phase was clearly observed by GIXRD (Grazing...
Incidence XRD) using a grazing angle nearly parallel to the surface [9]. However, in the present study, the corresponding XRZ peaks (normally at 23.8°, 33° and 43.8°) are not observed. This could be due to the much higher oxidizing conditions and the imposed dynamic thermal process.

The third step corresponds to the appearance of TiO₂ in the anatase phase and its progressive transformation to the rutile phase. The complete oxidation is reached when the rutile phase remains.

From these results, we can say that the lower kinetics observed for micropowders compared to nanopowders is a consequence of the diffusion distance of oxygen from the surface of each grain to its center. The SSA of the nanopowders, 50 times higher than for the micropowders, contributes to their faster oxidation. However, the oxidation mechanisms of both nano- and micropowders are identical. The temperature ranges over which each phase is stable during the oxidation of both nano and micropowders are summarized in Table 4.

4. Conclusion

To conclude, several batches of TiC nanopowders (from 40 to 130 nm) and micropowder (from 1.5 to 3 μm) were used to compare to the oxidation mechanisms under air.

Our TGA results show that complete oxidation is reached faster and at a lower temperature for TiC nanopowders than for micropowders. However, the DTA results show three exothermic peaks for both nano- and micro-powders. Each of these peaks corresponds to the formation of a specific oxide as observed in corresponding in-situ XRD diffractograms. The same oxidation mechanism has been observed for micro- and nano-powders but with faster kinetics in the latter case.

The first step of the mechanism corresponds to the disappearance of the TiC phase which is counterbalanced by the progressive formation of oxycarbide TiC₁₋ₓOₓ and the very likely formation of TiO. The formation of the suboxide TiO₂ has also been proven. If TiO₂ is formed, it may be too transient to be observed with our experimental conditions (RT to 1000 °C at 5 °C/min). Finally, the anatase then the rutile phase is formed at high temperature.

In the case of the oxidation of very small amounts of TiC nanopowder (1 mg), we suggest that the fast oxidation and a single exothermic oxidation peak, also observed in the literature, correspond to an extreme shortening of the interval between each oxide formation. These time intervals can be increased by increasing the amount of powder or by using micron-sized powders. In the case of micropowders, however, the longer diffusion distance of oxygen from the surface of each grain to the grain core also lowers the kinetics compared to nanoparticles.

Our results show that special care is required to estimate the activation energy as it could be biased because of the decrease of oxygen partial pressure inside the powder. This decrease delays the oxidation at higher temperature, slows the kinetics, and then artificially increases the activation energy.

Acknowledgments

This study was supported financially by the ARC ENERGIES program of the Région Rhône-Alpes. The authors would like to thank all the people who contributed to this work, and especially, Y. Leconte from the LFP laboratory of the CEA for the elemental chemical analysis.

References