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Microstructural study of titanium carbonitride produced by combustion synthesis

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Abstract

The self-propagating high-temperature synthesis (S.H.S.) process, which is promising for the fabrication of ceramic materials, was chosen to elaborate titanium carbonitride materials. The influence of parameters such as nitrogen gas pressure and carbon ratio on the microstructure was studied. A single phase product of Ti(C,N) is obtained for a carbon ratio under 15 at.% and a nitrogen pressure of 36 MPa. The increase of the carbon ratio corresponds to a decrease of the maximum temperature reached during the synthesis. Time resolved X-ray diffraction measurements (TRXRD) with the synchrotron radiation were used to determine the reaction mechanisms. We could observe that the synthesis of Ti(C,N) is preceded by the formation of titanium nitride. This reaction is initiated by the allotropic transition of α-Ti phase into β-Ti. In the final material the presence of sub-stoichiometric phases such as Ti_2N and α-Ti was observed.

Keywords: Time-resolved X-ray diffraction; Combustion; Titanium carbonitride; S.H.S.; Microstructure

1. Introduction

In a previous study [1], we synthesized titanium nitride by S.H.S. This material is a good candidate for cutting tools thanks to its good physical and chemical properties such as hardness, chemical stability and wear resistance [2,3]. We did not reach the stoichiometry on our materials due to a partial melting of the titanium during the reaction preventing nitrogen diffusion in the core of the sample. To improve the properties of the synthesized materials, an addition of carbon was decided on to synthesize titanium carbonitride Ti(C,N), which is also a hard and high melting point compound. Ti(C,N) has a face centred cubic (fcc) NaCl type structure, belonging to the *Fm*-3*m* space group, similar to TiN (titanium nitride) and TiC (titanium carbide) structures. According to Levi et al. [4], it is described as two sub-lattices of the fcc type, one of them containing titanium atoms and the other one carbon and nitrogen atoms randomly distributed.

Ti(C,N) is often employed in cermets, where its large domain of composition is used to favour a property over another one, by varying the C/N ratio [5,6]. Indeed, thus carbon can improve the hardness and nitrogen, the electrical conductivity of the material.

The synthesis of titanium carbonitride was studied on the Ti–C–N_2 system using the self-propagating high-temperature synthesis (S.H.S.) process. This process has often been used to synthesize nitrides and carbonitrides [7,8]. Here, the direct formation of titanium carbonitride by S.H.S. was studied using titanium and carbon powders, and nitrogen gas. The influence of the experimental parameters such as nitrogen gas pressure or carbon content on the microstructure of products was investigated. To control the process, it is also necessary to study the reaction mechanisms of the synthesis of Ti(C,N) by S.H.S. and the effect of the experimental parameters. Subsequently, thermal profiles were established during the reaction [AB]. For some materials, these data were correlated with structural evolutions determined by time-resolved X-ray diffraction [9–11].

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2. Experimental

2.1. Combustion synthesis

The combustion synthesis is made with a cold-pressed powder sample placed in a furnace under nitrogen gas (Fig. 1). The compact is a mixture of titanium and carbon powders. The reaction takes place in a high-steel chamber where the furnace is laid under high nitrogen pressure. Because of the thermal gradient of the furnace, the reaction between the titanium–carbon mixture and the nitrogen gas ignites in the highest temperature region. A minimal heating rate of 90 K/min was necessary to obtain sufficient heat accumulation on the sample to initiate the combustion reaction.

Three different compounds were synthesized during this study: TiN, Ti(C,N) and TiC. Concerning the carbonitride products, a mixture of titanium and carbon powders was prepared, with carbon ratios varying from 5 to 33 at.%. The titanium (99.98% pure) and graphite (99.99% pure) powders, with a maximum grain size of 40 μm, were supplied by Aldrich. The powder was uniaxially cold-pressed at a pressure of 300 MPa into a parallelepipedic pellet. The parallelepipedic pressed powder samples were 25 mm long, 4 mm wide and 3–4 mm high. A high compaction pressure had to be used to make good cohesion of the titanium and carbon powders mixture possible. The nitrogen pressure employed during the carbonitride synthesis varied from 6 to 50 MPa. Titanium nitride was synthesized from pressed titanium powder, under nitrogen pressure, whereas titanium carbide was synthesized from a stoichiometric mixture of titanium and carbon powders under argon pressure. The argon pressure for the synthesis of TiC, and the nitrogen pressure for the synthesis of TiN were 50 and 36 MPa, respectively. The temperature, measured by a PtRh6%–PtRh30% thermocouple was regulated by a Eurotherm temperature regulator. Thermal profiles describing the evolution of the temperature through the sample were obtained using three other thermocouples ($T_2 < T_3 < T_4$), T_4 representing the initiation zone of the reaction. Those four thermocouples were slid into two alumina sheathes. From these profiles, the reaction ignition temperature, T_{ig}, and the reaction combustion temperature, T_c (maximum measured temperature) were determined for each thermocouple.

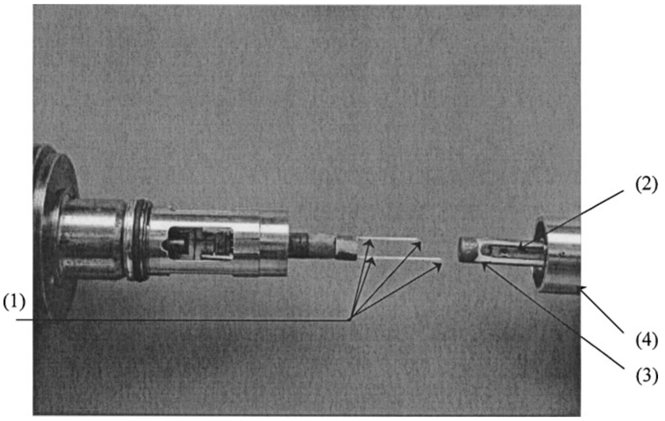


Fig. 1. Furnace dismantled: (1) thermocouples; (2) sample; (3) crucible; (4) furnace.

The S.H.S. products were characterized using X-ray diffraction analysis (Philips Expert with copper ($K\alpha_1$) anticathode) with ground materials, and the scanning electron microscopy (Leo S260 and Hitachi 4500I) was used on sample fracture surfaces.

2.2. TRXRD experiments

A device was used to monitor very fast structural and thermal changes using an X-ray diffractometer coupled with an imaging infrared camera (Fig. 2). This device has already been used to characterize solid–solid and solid–liquid combustion synthesis [11–13]. This experimental campaign was the first one in which a solid–gas reaction was characterized. The synchrotron radiation (LURE Ligne H10 Orsay, France) wavelength was selected at 0.15406 nm to better distinguish the XRD peaks of the various phases involved during the process. An aperture of 200 μm (vertical) by 1.5 mm (horizontal) was chosen to obtain a good signal to noise ratio. This led to an irradiated zone of around 1 mm width on the sample. The angular aperture of the fast X-ray detector was 93.5° and was centred on 57°. This range allowed us to observe reactants and products peaks such as Ti, TiN, Ti(C,N) or Ti_2N.

The configuration of the detection system was chosen for a short acquisition time to study the phase transitions. One thousand twenty-four scans of 512 channels were collected: each scan lasted 40 ms for a total acquisition time of 40.96 s. The initial and final states were obtained with long acquisition time scans, collected before and after the reaction by 4096 channels for 120 s. A standard titanium powder was used to calibrate each pattern in the angular range previously defined. The thermal evolution of the sample surface was observed with an infrared camera configured for a spectral window in the mid-infrared wavelength domain (3–5.4 μm) with a variable acquisition frequency. The Ti, TiN and Ti(C,N) emissivity values were assumed to be 0.3. The resolution of the infrared thermography is 40 ms between two consecutive images. The images realized can give a two-dimensional representation of the thermal evolution of the sample surface and allow us to follow the combustion front propagation.

The reaction took place in a reacting chamber on materials which present the same dimensions as previously described. The syntheses were made under a nitrogen flow which allowed us to maintain a nitrogen pressure of 0.115 MPa. This pressure, lower than that we used to work with, was used due to the low toughness of some parts of the TRXRD reacting chamber, and because of the high X-ray absorption of high pressure gases, which did not permit a different experimental setup. The sample is placed 1 mm apart from a carbon ribbon, which is heated by the passage of electrical current to initiate the combustion synthesis.

3. Results

3.1. Description of the combustion products

A study of the influence of the carbon ratio was carried out for carbon ratios varying from 5 to 33 at.%, and for nitrogen

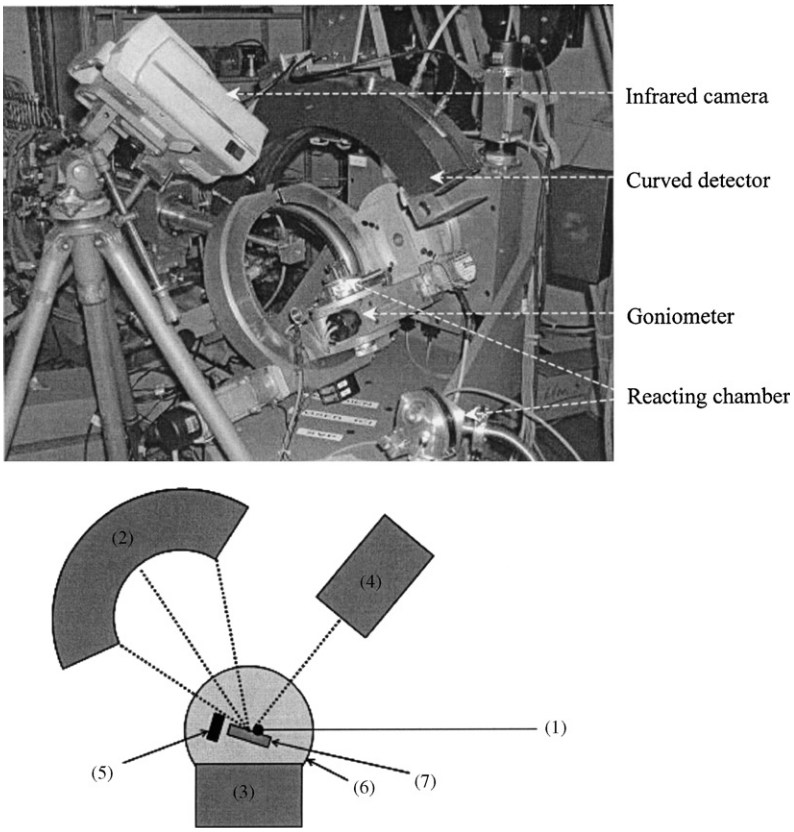


Fig. 2. TRXRD experimental setup (LURE H10, Orsay): (1) synchrotron radiation λ = 0.15406 nm; (2) fast X-ray detector; (3) sample holder; (4) infrared camera; (5) carbon ribbon; (6) reacting chamber under nitrogen atmosphere; (7) sample.

pressures of 19, 36 and 50 MPa. The synthesized materials presented the same aspect than those realized from titanium powder only. The latter presented a golden surface with shrinkage in the ignition zone (Fig. 3). On the carbonitride materials, the increase in the carbon ratio reduced the shrinkage. The latter disappeared above the carbon ratio of 5 at.%. The carbonitride materials kept the golden surface except for the carbon ratio of 33 at.%. For this ratio, the sample presented a purple colour on the surface. This colour variation could be due to a difference in chemical composition. Lengauer et al. [6] showed that the carbonitride colour changed from yellow for TiN to grey for TiC, going through purple when the ratio [C]/([C] + [N]) increased. This resulted in differences in electrical and thermal conductivities, and hardness. He could deduce that nitrogen sub-stiochiometric carbonitrides, i.e. those which did not present a composition near that of the stoichiometric titanium nitride, presented a linear reflectivity curve without pronounced minimum, which was related to their grey appearance. It was also reported that titanium carbonitride had a grey colour when the composition reached $Ti(C_{0.6}N_{0.4})$. Even if this study only allowed us to draw conclusions concerning the surface of synthesized materials, it remained interesting to observe the influence of the initial composition of the materials on the final composition of the material in surface. During this study, the maximum composition in relation to the carbon ratio was obtained with 33 at.% of carbon. Calculated by weight change, the composition reached for the carbon and nitrogen ratios was $TiC_{0.5}N_{0.5}$, and the final material presented a purple colour. Thus, the characteristic grey colour of the high carbon ratios in

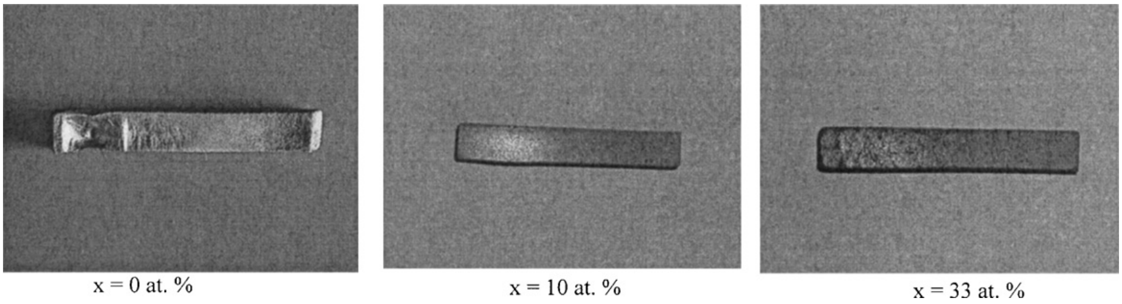
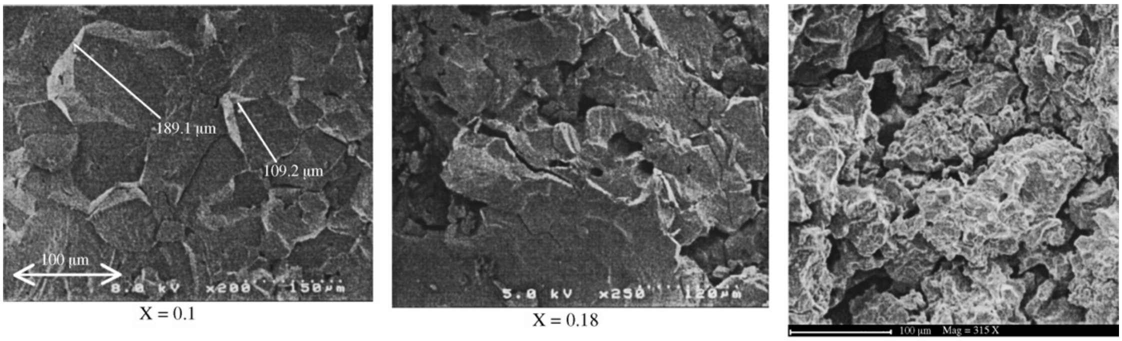


Fig. 3. Products of the S.H.S. reaction under nitrogen pressure with 0, 10 and 33 at.% carbon.



X = 0.1

X = 0.18

X = 0.5

Fig. 4. Bulk microstructure of the titanium carbonitride product for different carbon ratios in the ignition zone of the S.H.S. reaction (P_{N_2} = 36 MPa).

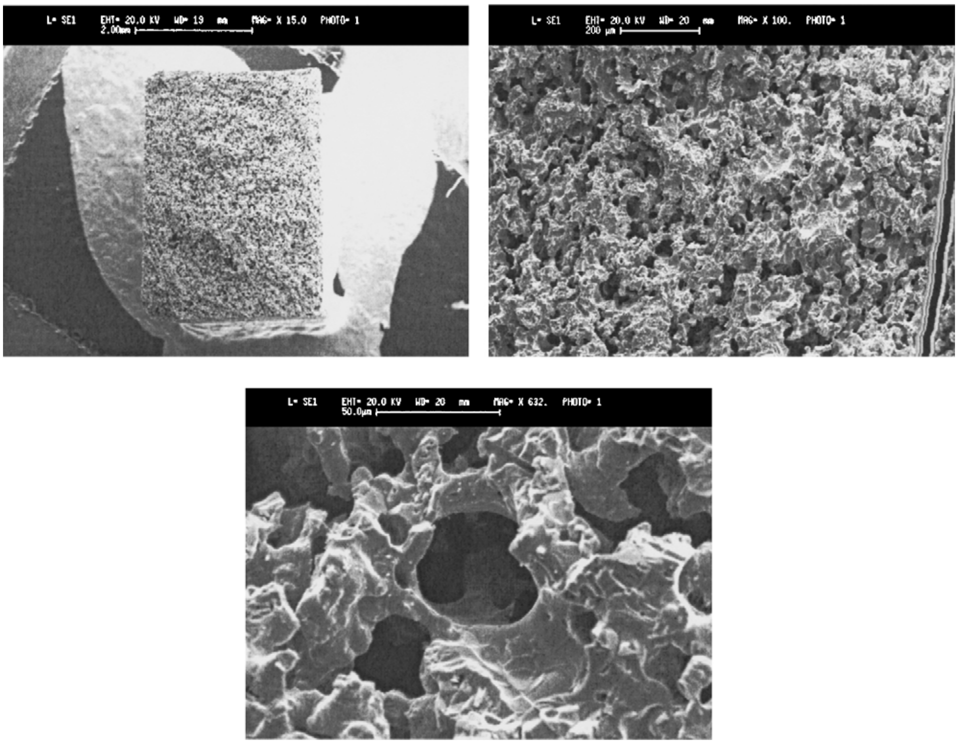


Fig. 5. Sample fracture surface of the titanium carbide product (P_{comp} = 250 MPa; P_{Ar} = 50 MPa).

the titanium carbonitrides wasn't obtained on the surface. However, it could be noticed that the synthesized titanium carbide material presented a grey colour on the surface.

The samples fracture surfaces were observed by SEM. Titanium nitride and low carbon ratios titanium carbonitrides (<15 at.%) presented the same structure: a porous layer on the surface and a dense bulk structure. We observed an increase in the thickness of the porous layer with the carbon ratio. Moreover, the dense bulk structure gradually became porous (Fig. 4): the layer extended to the whole sample when the carbon ratio reached 20 at.% (Table 1). The observation of the titanium carbide fracture surface allowed us to study the porous structure at the core of the whole sample. The aspect of this structure led us to think that a melting occurred during the reaction (Fig. 5). These results gave us an idea of the temperatures reached during these reactions.

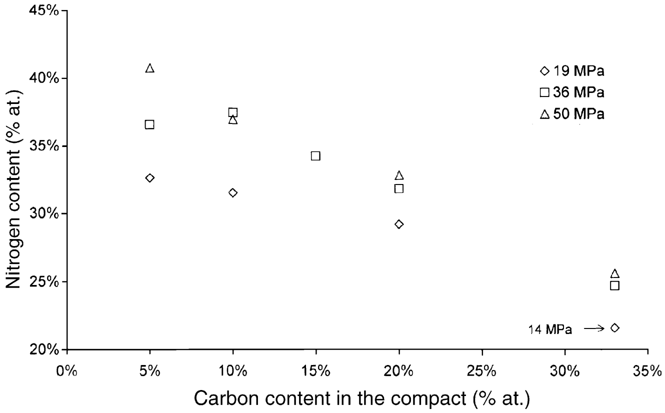


Fig. 6. Variation of the nitrogen ratio with the carbon ratio for different pressures in carbonitride materials.

Table 1
Variation of the thickness of the porous layer of titanium carbonitride materials with the carbon ratio

Carbon ratio (at.%)	Zone	
	Ignition	End of propagation
10	100–300 μm	80–100 μm
15	400–700 μm	70–100 μm
20	>700 μm	50–70 μm
33	The whole cross-section	The whole cross-section

The nitrogen uptake of the synthesized materials was determined by weight difference between the pressed sample and the corresponding synthesized sample. The nitrogen uptake was calculated for materials elaborated at nitrogen pressures of 19, 36 and 50 MPa and for carbon ratios between 5 and 33 at.% (Fig. 6). We could observe that the nitrogen uptake decreased when the carbon ratio increased. All syntheses followed this rule except for the materials synthesized with a carbon ratio between 5 and 10 at.% and a nitrogen pressure of 19 MPa. This phenomenon was already evidenced at low nitrogen pressures [14]. This could be due to samples which were less homogeneous.

3.2. Thermal profiles

The profiles were established from the three thermocouples placed near the sample. T_4, T_3 and T_2 were placed at the ignition, the middle and the end of propagation zones, respectively. The same samples as mentioned above were characterized. We could observe that the propagation of the combustion front to the whole sample was very fast. The latter could not be measured but seemed to be about a few cm/s (Fig. 7). The combustion synthesis resulted in a sharp increase in the temperature which signalled the beginning of the reaction. The temperature increased in every zone of the sample during the displacement of the heating wave. We could observe a decrease in the combustion temperature

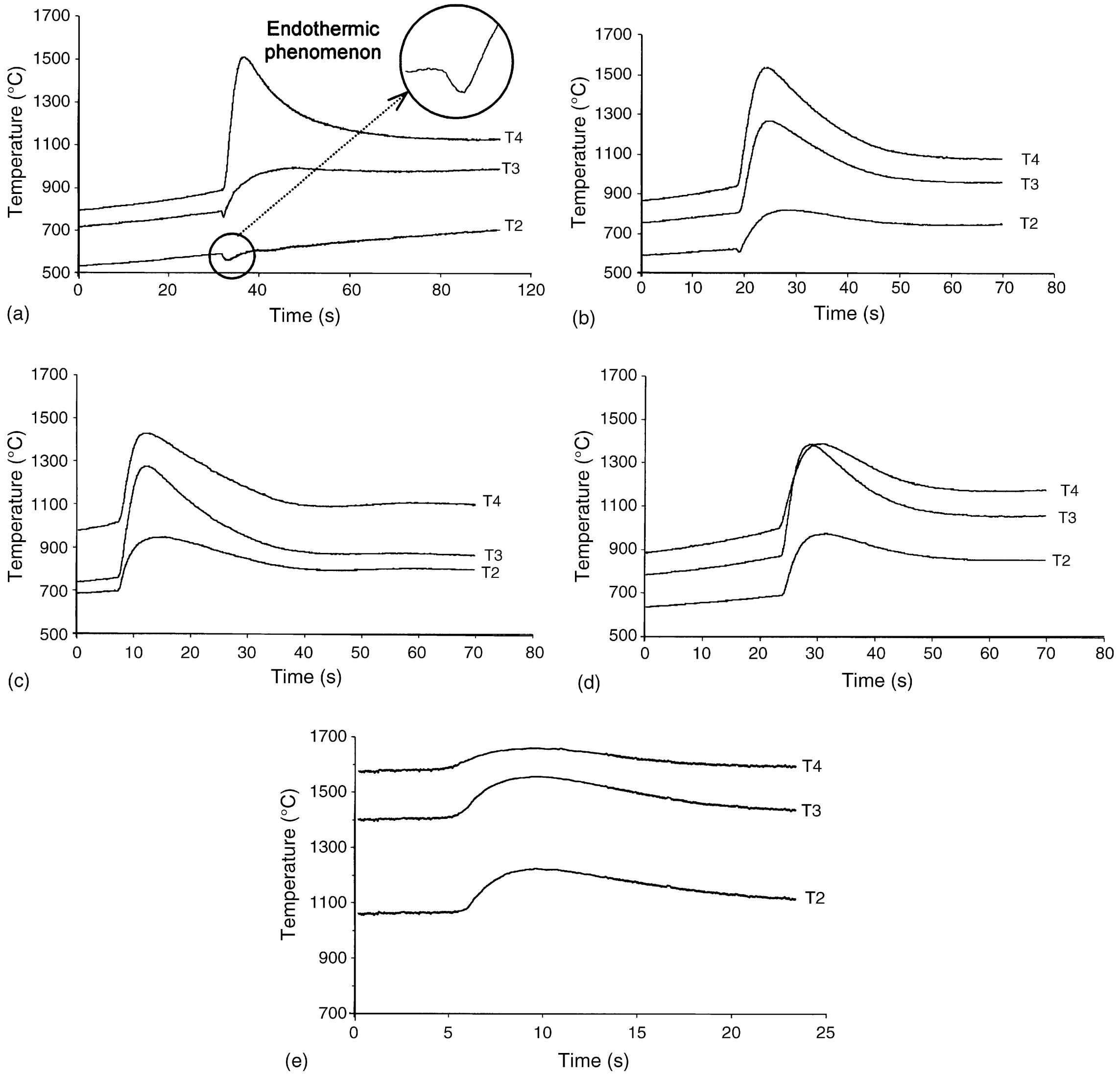


Fig. 7. Thermal profiles of (a) titanium nitride synthesis (P_{N_2} = 36 MPa), material elaborated under a nitrogen pressure of 36 MPa with (b) 10 at.% of carbon, (c) 20 at.% of carbon, (d) 33 at.% of carbon and (e) titanium carbide synthesis (P_{Ar} = 50 MPa).

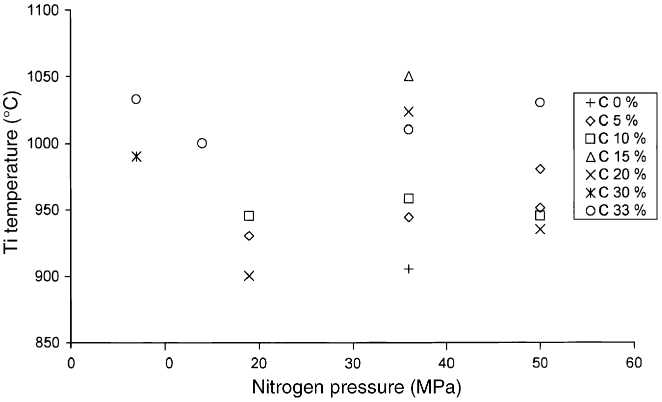


Fig. 8. Variation of the ignition temperature with the nitrogen pressure for several carbon ratios.

reached all along the material during the propagation of the reaction.

The addition of carbon played an important role on the thermal characteristics of the combustion reaction between titanium and nitrogen gas. A change seemed to appear from a 15 at.% carbon ratio. The ignition temperature was about 950 °C for carbon ratios lower than 15 at.% and increased to about 1050 °C for the highest carbon ratios (Fig. 8). This increase was due to the increase in the transition temperature of the α-Ti (hcp) to β-Ti (fcc) along with the carbon ratio. This transition occurred at 885 °C without any carbon (titanium nitride synthesis). High temperatures were reached during the reaction, especially with the synthesis of titanium nitride and the low carbon additions in which the combustion temperature reached between 1500 and 1550 °C in the ignition zone (Fig. 9). Above the carbon ratio of 10 at.%, the increase in the carbon ratio resulted in a decrease in the combustion temperature. T_c was 1550 °C for a carbon ratio of 10 at.%, and reached 1400 °C for a carbon ratio of 33 at.% (Fig. 9), for a nitrogen pressure of 36 MPa (Table 2).

A singular phenomenon was observed on thermal profiles obtained for the titanium nitride and the low carbon ratios carbonitrides (<15 at.%). In the end of propagation zone, we could observe a fast decrease in the temperature for a short duration just before the ignition of the reaction. The same phenomenon was observed in the centre of the material during the synthesis of the titanium nitride. This endothermic phenomenon could have several origins: it could be attributed to the endothermic allotropic transition of the α-Ti phase to β-Ti phase, this hypothesis being realized in the case of the synthesis of titanium nitride. It could also be due to the sudden heating of the nitrogen gas at the ignition of the reaction during the passage of the heating wave. This endothermic event was observed only in the colder zone of the sample ($T_2 < T_3 < T_4$), a zone where the temperature difference between the sample and the thermal wave temperature was the lowest. In this zone low temperature variations could be observed. The thermal profile achieved during the synthesis of titanium carbide (Fig. 7) showed an ignition temperature significantly higher than that observed for the synthesis of TiN or Ti(C,N). For thermocouple T_4, the reaction was initiated at 1600 °C, which was close to the melting temperature of titanium ($T_{m_{Ti}} = 1660\,°C$). The combustion temperature was 1660 °C, which evidenced little difference between the ignition temperature and the maximum temperature.

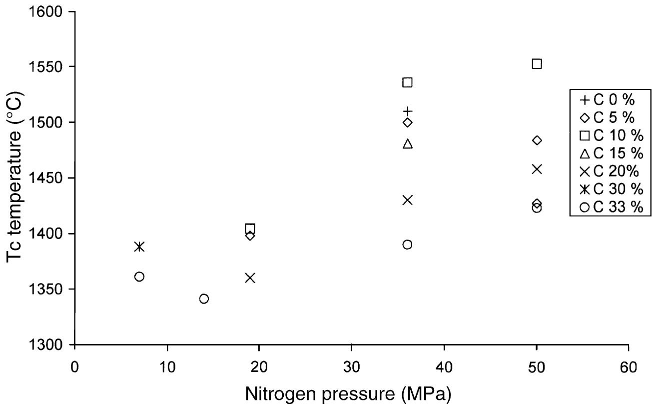


Fig. 9. Variation of the combustion temperature with the nitrogen pressure for several carbon ratios.

Table 2
Ignition and combustion temperatures measured for titanium nitride, carbonitride and carbide synthesized at different pressures (19, 36 and 50 MPa for TiCN, 50 MPa for TiC, 34 MPa for TiN)

Synthesized materials	TiN	Ti(C,N)					TiC
		5	10	15	20	33	
T_{ig}	900	945	960	1050	1025	1010	1600
T_c	1510	1500	1550	1480	1430	1400	1660

3.3. XRD analysis of combustion products

3.3.1. X-ray diffraction on high pressure products

The synthesis of titanium carbonitride by combustion was confirmed by the presence of the Ti(C,N) solid solution diffraction peaks on X-ray diffraction patterns. Those revealed an increase in the titanium carbonitride solid solution lattice parameters with the carbon ratio, which were then getting closer to the titanium carbide ones (Fig. 10). When the carbon ratio reached 15 at.%, one could observe an additional peak corresponding to the presence of unreacted carbon. This result showed that the composition determined by weight change was in fact deficient in carbon, and thus enriched with nitrogen. The evolution of the lattice parameters with the carbon ratio is linear (Fig. 11) according to the relation:

$$a = 0.00015x + 0.42249\,\text{nm} \qquad (1)$$

where a (Å) is the lattice parameter and x is the carbon molar percentage. This linear evolution evidences the formation of a titanium carbonitride solid solution.

3.4. Time resolved X-ray diffraction and infrared camera recordings

The time resolved X-ray diffraction analysis made during the titanium nitride synthesis was carried out from titanium

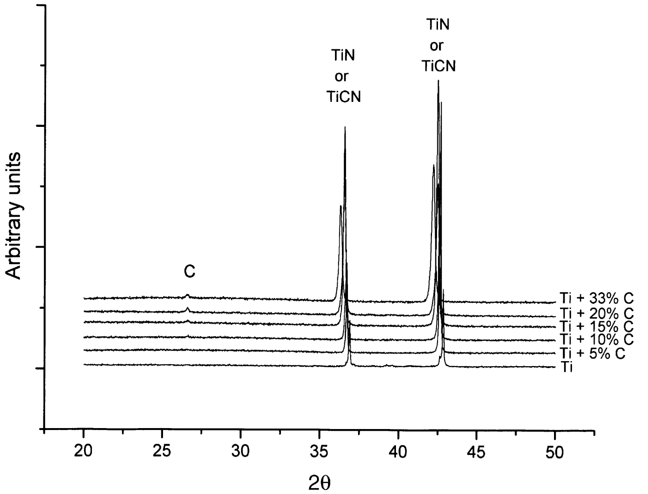


Fig. 10. X-ray diffraction patterns realized at different carbon ratios (P_{N_2} = 36 MPa); the both peaks on the right represent titanium nitride peaks in the case of a compact of titanium and titanium carbonitride peaks in case of addition of carbon.

powder beforehand pressed to 150 MPa. The XRD patterns made before the reaction with the help of both acquisition systems evidenced the presence of a single phase of titanium in the pressed material. During the heating, the α-Ti XRD peaks shifted and decreased until the structural change of α-Ti to β-Ti occurred at 900 °C. This allotropic transition was difficult to evidence due to the nearness of the XRD peaks of the α-Ti phase ((0 0 2) plane) and β-Ti phase ((1 1 0) plane). These peaks, which are separated by 0.08° at room temperature, provided the β-Ti phase can be quenched, merge at temperatures higher than 800 °C, as the two titanium phases have different expansion coefficients.

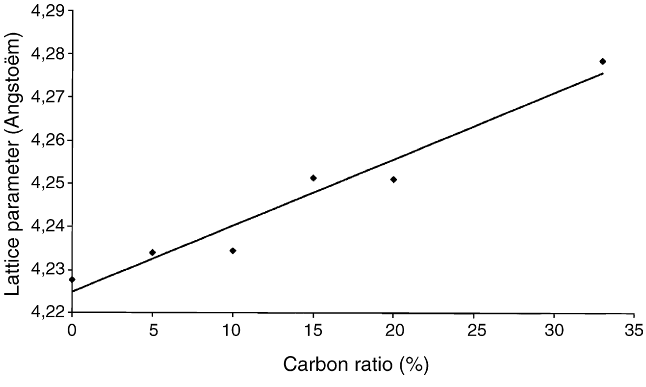


Fig. 11. Lattice parameters for different carbon ratios (P_{N_2} = 36 MPa).

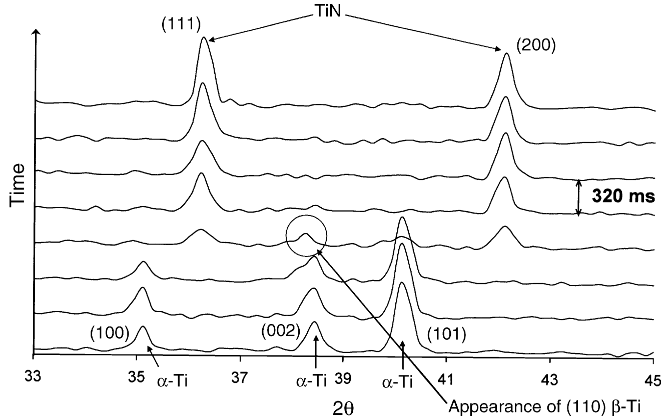


Fig. 12. S.H.S. diffraction patterns according to the time representing the average of eight acquisitions of 40 ms for titanium pressed sample.

However, during the TRXRD analyses, the structural change α-Ti to β-Ti could be partly evidenced by a progressive deformation of the XRD peak attributed to the (0 0 2) plane of α-Ti. Besides, the change in the intensity of the (1 0 1) plane of α-Ti is very weak whereas this is the most intense peak of the α-Ti phase. It is the same for the intensity of the (1 0 0) plane of α-Ti phase which is near zero. But, at the same time, the intensity of the (0 0 2) plane of the α-Ti phase decreases much less than for both the other peaks. This can be accounted for by the appearance of the (1 1 0) plane of the β-Ti phase combined to the disappearance of the (0 0 2) plane of the α-Ti phase.

The initiation of the reaction exactly corresponds to the allotropic transition (Fig. 12). The appearance of the β-Ti phase is followed by the appearance of peaks corresponding to titanium nitride. The appearance of the TiN phase, which happens 320 ms after the β-Ti phase, corresponds to the disappearance of the titanium phase. In this material made of pure pressed titanium powder, the reaction velocity of titanium nitride synthesis is very high (6.5 mm/s), and the β-Ti and TiN phases coexist during 320–640 ms, which indicates a sudden microstructural change. These observations confirm the hypothesis that the allotropic transition from the α-Ti phase to β-Ti phase is the first step in the synthesis of titanium nitride by S.H.S.

The combustion synthesis of a pressed titanium powder sample with 10 at.% carbon was realized. The specific effect of the addition of carbon is the low reaction velocity of the material (2.4 mm/s). The β-Ti phase lasts longer (960 ms) than is observed in the case of materials elaborated without carbon (Fig. 13). The reaction lasts more than 40 s, with the appearance of a new XRD peak about 4 s after the beginning of the reaction. However, the XRD intensity increases significantly only 40 s

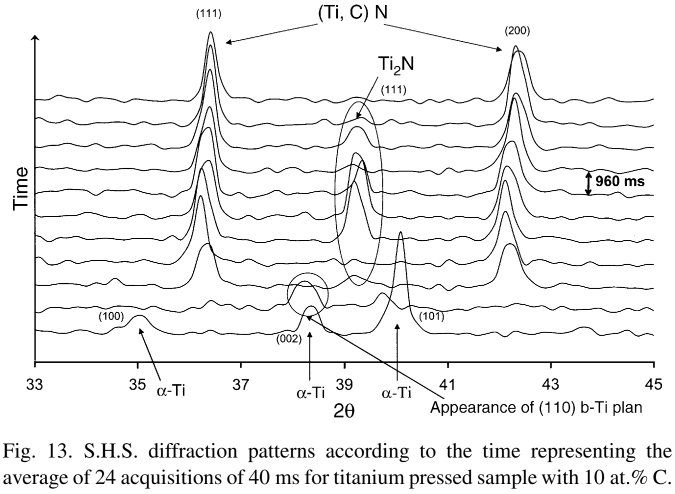


Fig. 13. S.H.S. diffraction patterns according to the time representing the average of 24 acquisitions of 40 ms for titanium pressed sample with 10 at.% C.

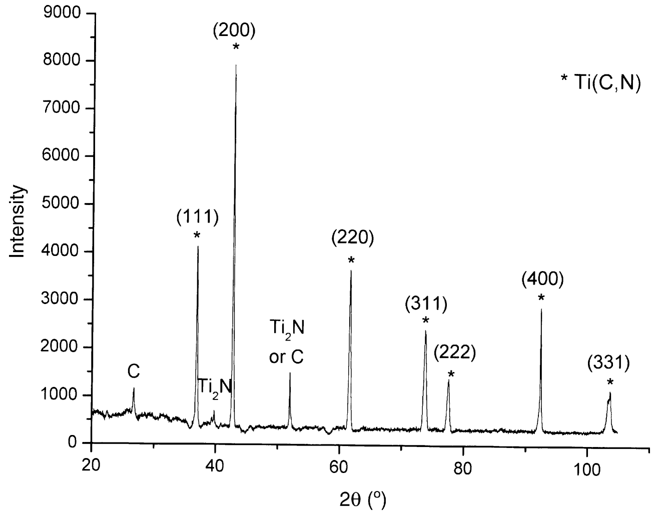


Fig. 14. Diffraction patterns realized after the synthesis from Ti + 10 at.% of C (the non-indexed peaks correspond to titanium carbonitride peaks).

after the initiation of the reaction. This XRD seems to correspond to either a secondary carbon peak, or a secondary Ti_2N phase peak (Fig. 14). At the end of the reaction, an additional peak appears and can be attributed to the Ti_2N phase.

We must take into account the fact that the XRD patterns correspond to phenomena occurring on the surface of materials, on a thickness of a few microns. Consequently, if a melting phenomenon happens in the bulk of the material, XRD patterns obtained during the syntheses would not evidence it.

Thanks to the infrared camera, from the images taken from the recordings, front velocities were determined. These images enabled us to monitor the whole sample but also the local ignition system, the heated carbon ribbon, which was represented on the right of the figure (Fig. 15). Thermal figures were produced from these recordings (Fig. 16) by representing the temperature profile on a line drawn on the sample (bottom of the figure) as a function of time. The front velocity was then calculated by determining the slope of the line joining the ignition and the end of propagation zones. The sample synthesized from titanium powder presents a front velocity of 6.5 mm/s whereas the sample with 10 at.% carbon has a front velocity of 2.4 mm/s.

This velocity is lower than the one evaluated during the syntheses in the laboratory, where it is supposed to be about a few cm/s. This difference can be attributed to the nitrogen pressure chosen during the syntheses, pressure varying between 6 and 200 MPa at the laboratory and being 0.115 MPa during the TRXRD syntheses.

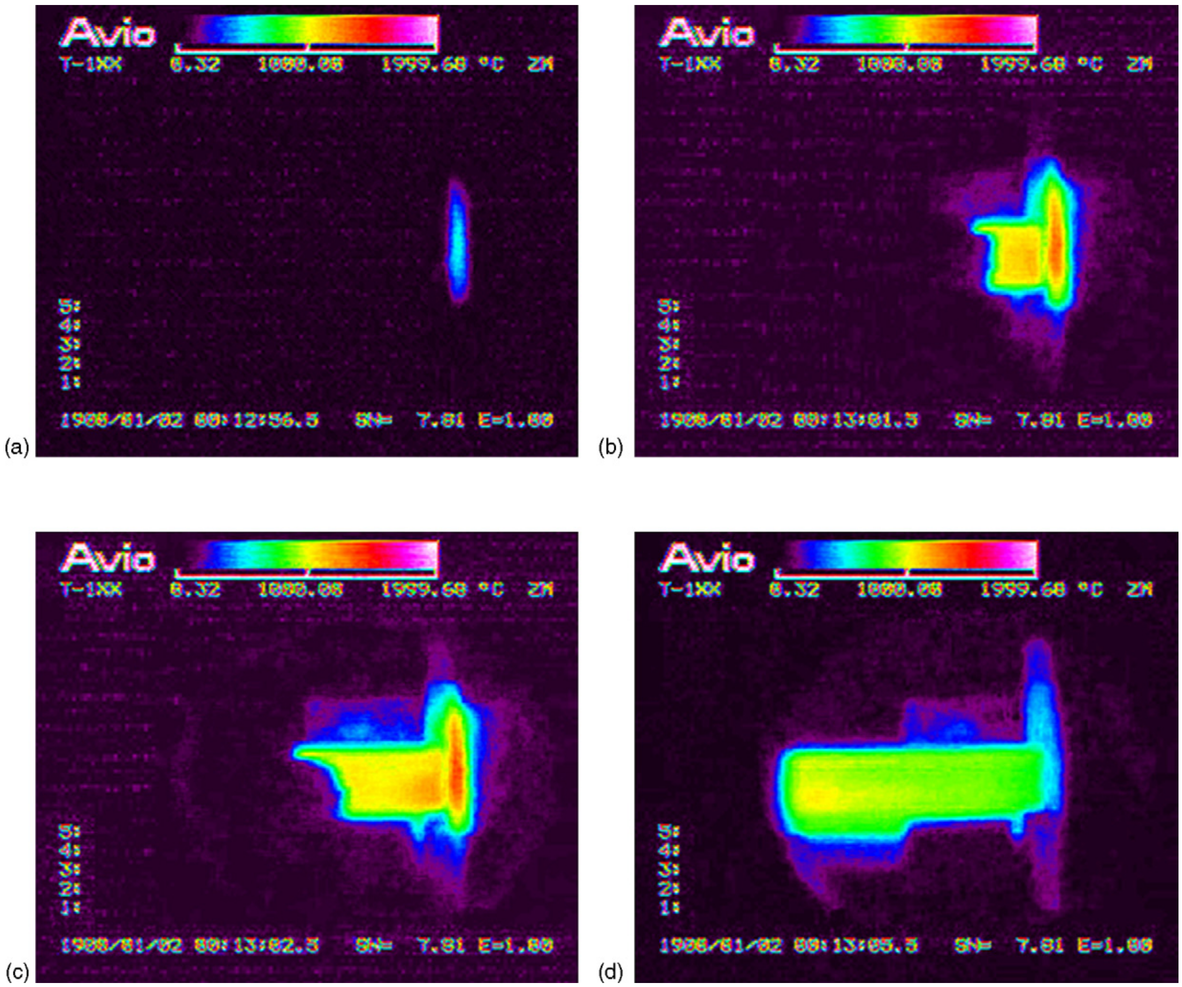


Fig. 15. Pictures of the reaction filmed by the infrared camera (a) during the carbon ribbon heating (8 s), (b) at the ignition of the reaction (13 s), (c) during the propagation of the reaction (14 s) and (d) at the end of the propagation (17 s).

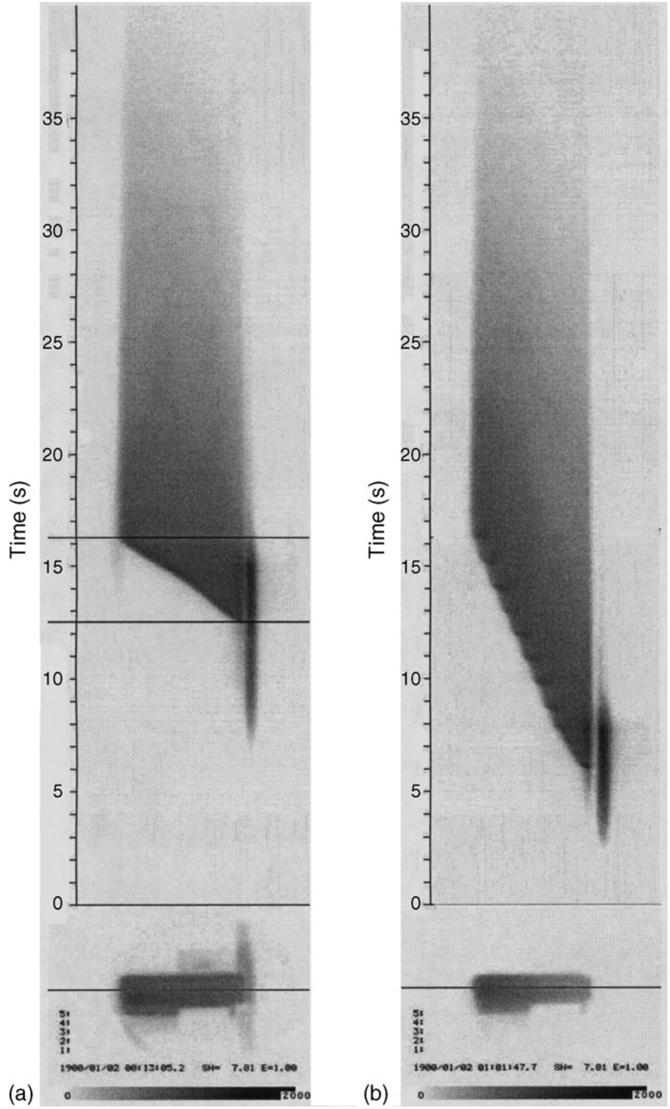


Fig. 16. Thermal figures showing the propagation of the combustion wave according to time for (a) a titanium compact (b) a titanium compact with 10 at.% of carbon; the lower part of the figure represent a capture of the compact with the carbon ribbon at its right side before the ignition.

4. Discussion

The syntheses of titanium nitride, titanium carbonitride and titanium carbide by S.H.S. presented structural differences, which enabled us to determine the mechanisms of the reactions. The thermal profiles obtained for the three materials and the characterization by TRXRD were very interesting to comment on the reactions. First, we decided to determine the mechanisms of the formation of titanium nitride and titanium carbide. Then, thanks to our results and the literature, we determined the formation mechanism of titanium carbonitride by S.H.S.

As was assumed by Dubois et al. [15], the formation of titanium carbide by combustion synthesis may occur by two different mechanisms. The first is based upon a solution/precipitation model. The titanium is heated above its melting point and spread around the carbon particles. Thus the carbon dissolves in the molten titanium phase and TiC crystals precipitate when the saturation of the solution is reached, especially as the solution cools. The second model is based on solid state diffusion. In this model, titanium surrounds carbon particles and reacts with their outer surface. As the carbon diffusion is at least three orders of magnitude greater than the titanium one, it is the carbon that diffuses through the TiC layer to react with the unreacted molten titanium (emptying core model) in the case of the synthesis of titanium carbide by S.H.S.

In our study, the mechanism which occurs during S.H.S. titanium carbide seems to be the solution/precipitation model due to the ignition temperature of the reaction (1600 °C), which corresponds to the melting temperature of titanium. This model can also explain the microstructure of the materials. This is in agreement with Dunmead et al. [16] who assumed that the solution/precipitation model is likely to occur at high temperature.

The synthesis of titanium nitride by combustion synthesis began with the allotropic transition of the α-Ti phase to β-Ti phase at 900 °C which seemed to be the initiation of the reaction. The sudden change of the specific volume of the titanium can lead to cracks in the oxide layer of the titanium surface, thus enabling the ignition of the titanium nitride synthesis. The β-Ti phase appeared for a very short time (320 ms) and the appearance of titanium nitride corresponded to the disappearance of the α-Ti titanium phase. The allotropic transition seemed to be the initiation point of the titanium nitride combustion synthesis.

Based on these experimental results and on the literature [17], the carbonitride formation mechanisms could be described. Surface titanium powders nitridation and carburation operated simultaneously during heating. The combustion reaction was initiated by the α-Ti(N) to β-Ti(N) transition undergoing the formation of titanium carbonitride solid solution on the surface of the sample. This could explain that the ignition temperature was lower than the melting temperature of titanium (950–1050 °C). The surface combustion reaction made the bulk titanium melt due to its exothermicity. The molten titanium, which was then enriched in nitrogen, reacted with the carbon to form titanium carbonitride at the molten titanium/carbon interface in the bulk material. Then the carbon diffused to the molten Ti(N) phase through the carbonitride solid solution to get the synthesized material. Thermodynamic calculations on the relative stability of TiC and TiN were made as functions of temperature and nitrogen pressure [16]. The calculations were based on the following reaction:

$$\mathrm{TiN} + \mathrm{C} \Leftrightarrow \mathrm{TiC} + \tfrac{1}{2}\mathrm{N}_2 \qquad (2)$$

According to these calculations and to the above experimental conditions (nitrogen pressures ranging from 6 to 50 MPa, maximum temperatures between 1350 and 1550 °C), we could suggest that the formation of the titanium nitride phase was thermodynamically favoured if equilibrium conditions were achieved. The titanium nitride formation would then be an intermediate step between the combustion reaction initiation and the sample surface formation of the titanium carbonitride solid solution. The existence of this intermediate titanium nitride formation could explain that the combustion reaction could not be ignited for carbon ratios higher than 33 at.%. The initiation reaction would then be inhibited by the reduction of the titanium particles/nitrogen gas interfaces due to the presence of carbon.

The TRXRD experiment on carbon addition showed the difficulty for the nitrogen to react with the titanium to produce titanium nitride. In this case, nitrogen sub-stoichiometric phases like Ti_2N were synthesized and it illustrated the influence of the carbon on the reaction.

5. Conclusion

The synthesis of titanium carbonitride was realized by self-propagating high-temperature synthesis under high nitrogen gas pressures. A single phase Ti(C,N) was obtained for a carbon ratio under 15 at.%. The materials present a porous structure layer and a dense bulk structure. We have observed that the increase in the nitrogen pressure results in an increase in the atomic nitrogen percentage on the titanium carbonitride synthesized materials.

This increase also corresponds to a decrease in the combustion temperature from 1550 to 1400 °C, and to an increase in the ignition temperature from 950 to 1050 °C. These results allow us to suggest mechanisms for the synthesis of titanium carbonitride which could be presented as follows: during the pre-heating, the nitridation and the carburation of the titanium powder begin in the material. At the ignition, the synthesis of titanium carbonitride occurs at the surface with an intermediate synthesis of TiN. The exothermicity of this reaction results in the melting of the titanium in the bulk and then the diffusion of the carbon in nitrided titanium occurs to form titanium carbonitride. TRXRD experiments have enabled us to observe the appearance of the β-Ti phase at the ignition of the reaction on the surface and to observe a decrease in the front velocity with the carbon addition.

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