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Hot pressed titanium nitride obtained from SHS starting powders: Influence of a pre-sintering heat-treatment of the starting powders on the densification process

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Abstract

Synthesis of titanium nitride (TiN) powders by the self propagating high temperature synthesis (SHS) process is economically appealing. This chemical reaction allows producing fine grains powders with a high specific surface area (12 m^2/g). After a thermal treatment above 1000 °C under argon atmosphere, the physical and microstructural characteristics of the powders are drastically modified: density increases and specific surface decreases. Powders morphology and heat treatment influence are investigated by transmission electron microscopy. Observations reveal a regular nanocrystalline layer, surrounding the particles. After heat treatment, this layer disappears from grains surface and powders undergo important morphological changes. The behavior of these special ceramic powders during the sintering stage by the hot press process is investigated. Bulk specimens obtained are characterized from a physical, microstructural and mechanical point of view and the beneficial effect of the heat treatment on starting powder is explained. Bulk specimens processed in the optimum conditions reach a relative density superior to 98%, a microhardness of 1790 Hv and a Young modulus of 430 MPa.

Keywords: SHS; Hot pressing; TiN

1. Introduction

Nitrides, especially those of transition metals, have received increasing attention in recent years because of their unique chemical and physical properties. Among them, TiN presents many advantages such as wear resistance, high hardness, good chemical and thermal stability, which make it interesting for some potential industrial applications. In addition, its electrical conductivity at room-temperature is high so that bulk specimens can be machined by the Electro Discharge Machining (EDM) process, which is a relevant technological advantage.[1] It is currently used as additives to other materials or as coatings[2] deposited by Chemical Vapor Deposition (CVD) or Physical Vapor Deposition (PVD). Due to its high melting point (2950 °C) arising from its strong covalent bonding, TiN is difficult to densify as a monolithic ceramic without additives help. Nevertheless, few papers report its sintering by conventional sintering,[3] hot isostatic pressing[4] or hot pressing (HP).[5,6]

Investigations about densification and properties of bulk TiN specimens revealed their attractive physical and mechanical properties but also underlined the drastic influence of starting powders on the final characteristics of dense specimens.[7,8] Indeed, the densification stage is dependent of the sintering process but also strongly of the initial starting powder grain size, stoichiometry and oxygen content.

Recently, nanocrystalline TiN powders offer the possibility to produce TiN bodies at sintering temperatures 500 °C to 600 °C below the powder sintering temperature for submicron and micron size particles.[9,10] However, these powders present an extreme oxygen affinity[10,11] and a high oxygen content is believed to delay the densification when sintering via consolidation techniques.

Besides the traditional method of direct reaction between titanium and nitrogen or ammoniac gas and synthesis by carbothermal reduction of titanium oxide, TiN could be synthesized by the SHS process. This process is based on systems able to

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react exothermally when ignited. The reaction sustains itself to form a combustion wave travelling through the heterogeneous mixtures of the reactants.[12] The temperature of the combustion can be very high (e.g. 4727 °C (5000 K)), as the rate of combustion (e.g. 25 cm/s). Grain size of the powders produced is usually fine. This is the reason why they stand as good raw material for a further sintering process.

Many studies concerning the efficiency of the SHS powder production method[12–14] have been carried out. First of all, high combustion temperatures, high synthesis rates, low energy consumption, and simplicity of special equipment suggest that the SHS production cost is much lower than that of the furnace technology. However the quality of SHS powders strongly depends on characteristics of the initial reactant, in terms of the green mixture preparation and completeness of the reaction process. It was reported[14] that the content of contaminant oxygen in the SHS powders is theoretically lower than that in their furnace analogs due to high temperatures associated to the combustion, as volatiles impurities could be expelled as the wave propagates through the sample. It will be demonstrated in the present paper that this statement is not always true.

The purpose of this study is first to characterize TiN powders synthesized by the SHS process and to correlate their physical properties with their microstructure. In a second part, powders are densified using a simple hot-pressing procedure. After an optimization of the hot-pressing temperature, the beneficial influence of the powders' heat treatment on the hot pressed compacts is studied and discussed on a micromechanistic perspective.

2. Materials and experimental procedure

TiN starting powders were supplied by La Céramique Plastique, France. The reaction to obtain the TiN powders is a solid-vapor type, highly exothermic:

$$2TiO_2 + Ca + Ca_3N_2 \rightarrow 2TiN + 4CaO$$

Synthesis is ignited by an electric arc and occurs under argon atmosphere. Finally, the mixture is chemically treated, washed and dried in order to eliminate lime.

Their chemical composition was determined by Inductively Coupled Plasma (ICP, Service Central d'Analyse, Solaize, France) analyses.

Particles size distribution was measured by the sedimentation method with a particle size analyser (Horiba Capa 700) and powder dispersion was done in ethanol.

DTA/TGA (SETARAM TMA 92/TGA 92) coupled with a mass spectrometer was carried out under helium atmosphere until 1500 °C, in an alumina crucible.

Chemical analyses were carried out by X-ray Photoelectron Spectroscopy (XPS, Escalab 200R-VG scientific). X-ray source is aluminium. Thickness analyzed here is around 2 nm from the surface of the TiN particles.

The microstructure and phase distribution/chemical composition of the powders and the pressed compacts were analyzed by X-ray diffraction (with Cu Kα radiation, graphite filtered, at 25 kV and 40 mA at a scanning speed of 2°/min), by scanning electron microscopy (SEM, JEOL 840) and by transmission electron microscopy (TEM, JEOL 2010F) equipped with an energy dispersive spectroscopy (EDS system).

Powder density was measured with a helium pycnometer (ACCUPYC 1330, Micromeritics). Specific surface area measurements were done under krypton and argon atmosphere.

All thermal treatments were done using a graphite furnace, in a graphite crucible coated or not with boron nitride.

Specimens were densified by hot pressing. Powders were directly cold compacted in a graphite die in order to test the resistance of the die at room temperature. It was then inserted into the hot press. Degassing occurred up to 600 °C under vacuum, and after 600 °C argon atmosphere was maintained. A pressure of 50 MPa was applied through graphite punch and the temperature increased at a rate of 10 °C/min up to the dwell temperature (1400 °C, 1600 °C or 1800 °C), maintained for 1 h. Samples of 37 mm diameter and about 5 mm height were prepared. The ram displacement was recorded on-line during hot pressing and densification curves were then calculated.

Specimens were then rectified and mirror polished (until 1 μm) and the final density of the compacts was measured by the Archimedes' method.

Polished surfaces Micro Vickers hardness was measured by 15 points measurements under a 300 g load. Fracture toughness and flexural strength were determined by the four point method on bars (25 mm × 4 mm × 5 mm) with a crosshead speed of 0.5 mm/min. Young's modulus was measured by the ultrasonic method and electrical resistivity by the eddy current method.

3. Results and discussion

3.1. Starting powders characterization

The chemical composition of the as received TiN powder is given in Table 1. The amount of oxygen is rather high and impurities such as calcium and aluminium are present. Several chemical analyses have been performed on these powders and the amount of oxygen measured can vary drastically. Other measurements indicate an oxygen content of only 2.2 wt%. This powder has a very high oxygen affinity, explaining why this content can change and depends probably of the storage con-

Table 1
Chemical analyses of the TiN powders as received and after a heat treatment (1 h, 1300 °C in a graphite furnace)

	% Ti	% N	% O	% Ca	% C	% Al
As received TiN powders (wt%)	72.74	19.90	6.13	1.87	0.24	0.70
As received TiN powders (at%)	44.41	41.65	11.23	1.37	0.59	0.76
TiN heat treated (wt%)	72.85	19.05	5.25	1.65	0.36	0.67
TiN heat treated (at%)	45.95	41.20	9.94	1.25	0.91	0.75

ditions. Aluminium comes from impurities inside the initial SHS reactant (Ca_3N_2). Theoretically, calcium should have been eliminated totally during the chemical treatment but a parallel and incomplete reaction can also occur during the powders synthesis:

$$6TiO_2 + Ca + Ca_3N_2 \rightarrow 2TiN + 4CaTiO_3$$

This is why calcium could be present in a stable perovskite structure ($CaTiO_3$) form and because of the presence of various compounds no conclusion can be drawn concerning the TiN stoichiometry.

X-ray diffraction analysis (Fig. 1) indicates that the powder crystallized in a cubic face centered type structure with a lattice parameter of 4.2419 Å (JCPS 38-1420). A secondary phase, corresponding to a perovskite structure ($CaTiO_3$ – JCPDS 42-0423) is also identified in a very slight quantity, confirming that the secondary reaction given previously has occurred.

Particle size measurement results are presented in Fig. 2a. The white bars show particle size distribution for powder samples dispersed only in ethanol, and black bars for same samples subjected to ultrasonic agitation (15 s) to dissociate particles aggregates. A slight shift of the distribution for a powder submitted to ultrasonic agitation is observed. Indeed average grain size of a powder dispersed in ethanol is 2.3 μm while it moves to 1.9 μm when ultrasonically mixed: in this case, aggregates are

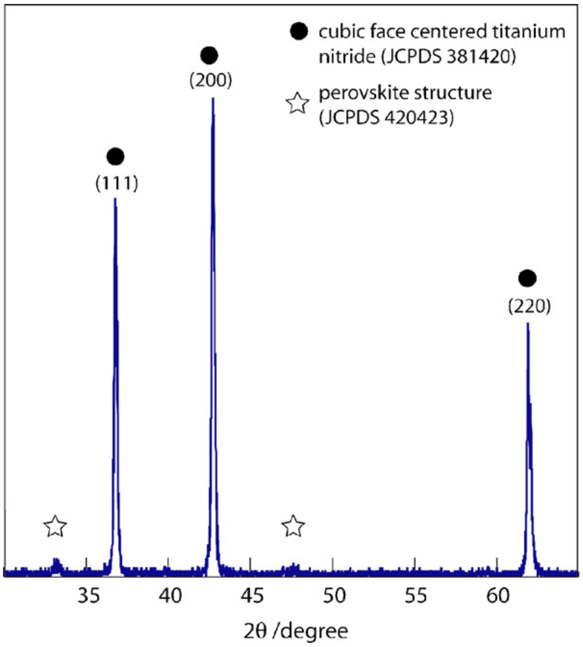

Fig. 1. X-ray diffraction spectrum of the as received TiN powder.

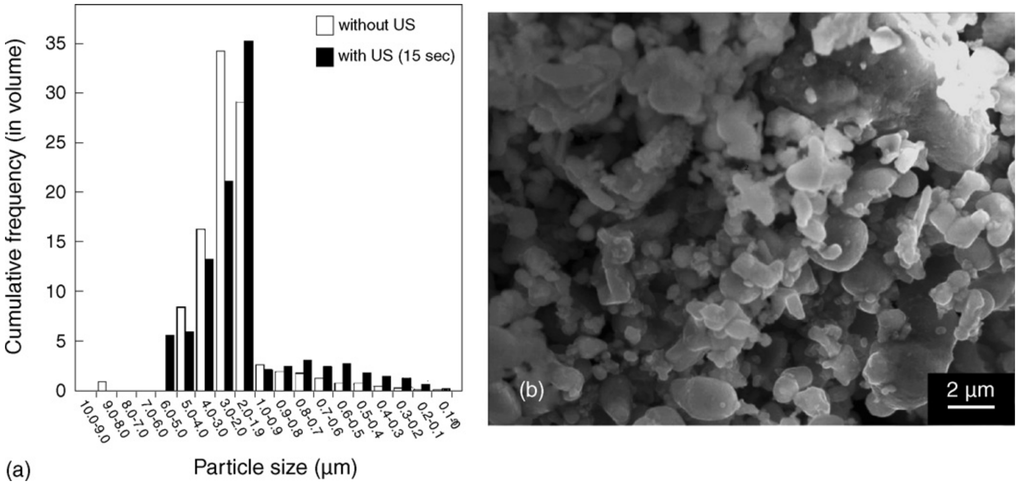

Fig. 2. (a) Particle size distribution of the as received TiN powder. (b) As received TiN powders observed by SEM.

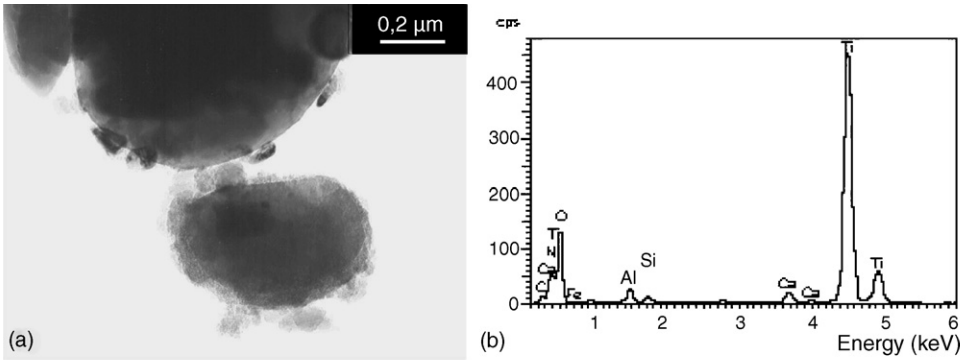

Fig. 3. (a) As received TiN powders observed by TEM. (b) EDX Chemical analyses spectrum corresponding on the micrograph.

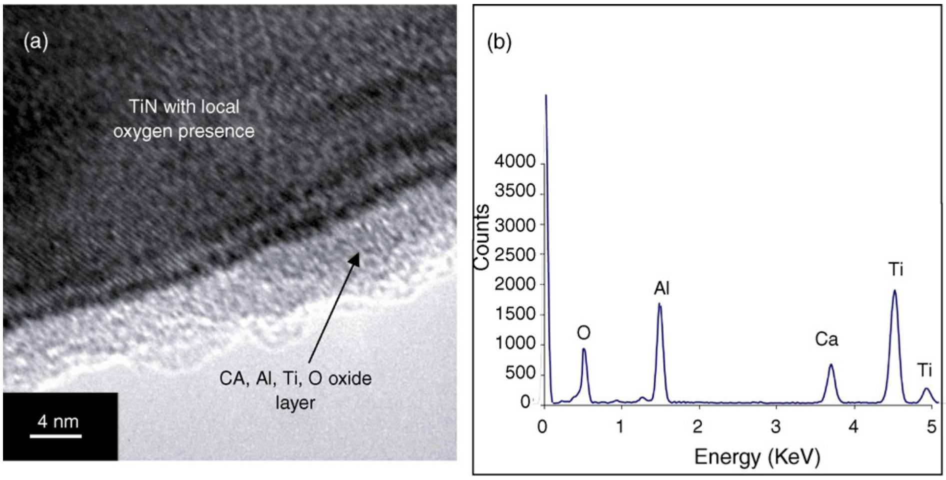

Fig. 4. (a) TiN powder observed by TEM. An amorphous oxide layer is observed on the surface. (b) EDX chemical analyses spectrum corresponding to the oxide layer.

dissociated. Another population, much finer, seems also present but not clearly determined by this method. SEM observations (Fig. 2b) confirm that a submicronic population is also observable.

Density value measured (5.06 g/cm^3) is 6% inferior to theoretical density (5.39 g/cm^3). Impurities could account for this phenomenon. Using the law of mixture, it is possible to evaluate the theoretical density of the investigated powder. Chemical analyses reveal 1.87 wt% of calcium. Actually, if considering the calcium to be present only in the perovskite structure, the quantity of $CaTiO_3$ could be estimated at 6.35 wt%, leading to a corrected TiN density close to 5.29 g/cm^3. Though still lower than the theoretical density, it remains much higher than the one measured by helium pycnometry.

From specific surface area measurements, an average value of 12 m^2/g is determined. Literature indicates that a TiN powder with an average grain size between 1 and 2 microns should have a specific surface of 1.7 m^2/g,[4] while nanocrystalline TiN powders should have a specific surface area between 20 and 250 m^2/g.[10] As a conclusion, the measured value is rather high considering particle size determination by the sedimentation method. Indeed powder characterized by this method would have a grain size between 2 and 3 microns. For such a grain size and considering literature data, its specific surface area is too high.

In order to correlate these various results, especially density and specific surface area values, with powder microstructure, TEM observations are carried out. High specific surface area can be easily explained by the presence of nanometric grains around the submicronic or micronic particles (Fig. 3a). A chemical analysis (Fig. 3b) of the area revealed the presence of TiN, but impurities such as aluminium and calcium are also identified. Moreover, oxygen content is rather high. Using a high resolution imaging, element repartition can be more clearly assessed and a nanocrystalline layer is observed at particles surfaces (Fig. 4a). It is very thin (close to 4 nm) and as confirmed by EDX technique using a nanometric electron beam size, it is composed of calcium, aluminium, titanium and oxygen, embedding regularly each TiN grain (Fig. 4b).

As a partial conclusion, these TEM observations provide many interesting information. Whilst TiN with an oxygen partial presence is the main compound, an oxide nanocrystallized layer is also present at grain surfaces.

At this stage, many singular powders characteristics have been identified. Moreover, the perovskite structure ($CaTiO_3$) has not been observed by TEM; its presence is probably punctual. Two different oxide phases are present and could be possibly deleterious in regards of a further sintering process. Therefore, powders thermal treatments (from 700 °C to 2000 °C) are considered and heat treated powders characterized.

Thermal treatments are done in a graphite furnace. Samples are degassed until 600 °C under vacuum. The end of the temperature cycle is done under argon atmosphere, and dwelling temperature maintained for 1 h. Fig. 5 shows the density evolution as a function of heat treatment temperature. After heating at 1000 °C the density is 5.26 g/cm^3, while heating at 1300 °C

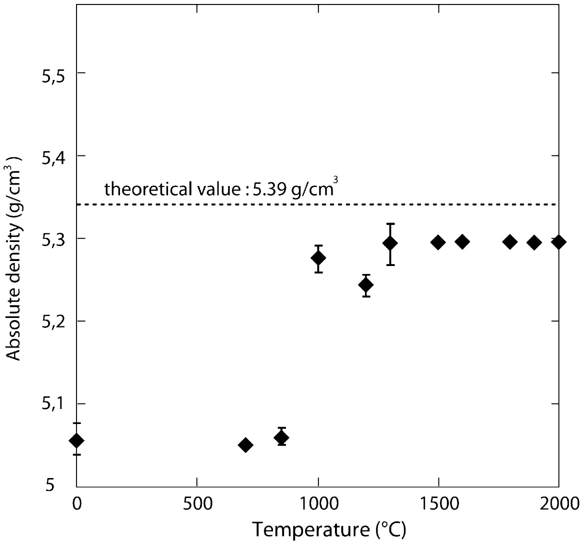

Fig. 5. Density evolution of the powder as a function of the heat treatment temperature.

Table 2
Comparison of the physical characteristics for a powder heat treated or not

	As received TiN powder	TiN powder heat treated
Density (g/cm^3)	5.06	5.29
Specific surface area (m^2/g)	12	1.3
Lattice parameter (Å)	4.2419	4.2433

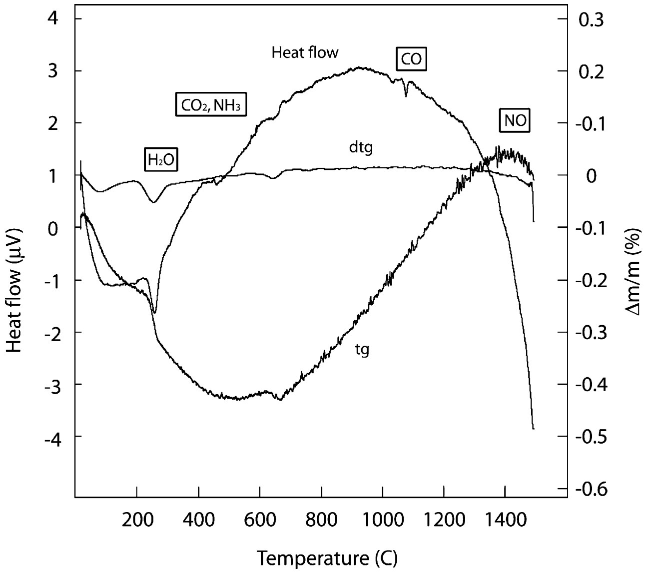

Fig. 6. DTA/TGA coupled with a spectrometer on the as received TiN powder under helium atmosphere.

for 1 h it increases and reaches its maximum at 5.29 g/cm^3. This value corresponds to the one previously calculated with the law of mixture and taking into account the perovskite presence. Over 1300 °C, density decreases. X-ray and chemical composition analyses indicate that, due to graphite presence, a titanium carbonitride solution is formed. The density of TiCN is lower than that of TiN ($\rho_{TiC_{0.3}N_{0.7}} = 5.25\,g/cm^3$, JCPDS 42-1488). Others treatments were performed in BN coated crucible at temperatures above 1300 °C. The carburation of the powders has been avoided and density presents a constant value of 5.29 g/cm^3. As a conclusion concerning density evolution versus temperature, if the second part of the curve (Fig. 5) is clearly explained, the first part, leading to density increase, is still obscure.

Table 2 gives a comparison between the density, specific surface area and lattice parameter for a powder treated or not. The specific surface area of a powder thermally treated 1 h at 1300 °C decreases drastically and reaches 1.3 m^2/g. The evolution of the lattice parameter is not significant, with respective values of 4.2419 Å and 4.2433 Å for as received and heat treated powders.

In Table 1 chemical analyses obtained by ICP analyses for a powder thermally treated or not are presented and compared. No important chemical evolution is observed. A very slight carburation occurred but weight carbon percentage evolution remains low. Oxygen and nitrogen contents decrease slightly. The decrease of the oxygen content corresponds to the elimination of absorbed water and to the reduction of oxides at the surface. The decrease of the nitrogen content is due to NO release. These phenomena have been confirmed by thermogravimetry analyses performed on as received powder (Fig. 6). Water is released between 100 °C and 300 °C. A slight release of NH_3 and CO_2 also occurs between 400 °C and 500 °C. Above 800 °C, a weight gain is observed, due to a powder oxydation. The oxygen affinity of the powder is high. The oxygen can come from the alumina crucible or from the presence of impurities, in spite of the helium flow. Around 1000 °C, a release of CO is observed, corresponding probably to the reduction of oxide at surfaces. Above 1400 °C, NO is also released, and can be associated to TiN decomposition.

In order to understand what happened during heat treatment stage, until 1300 °C, and to correlate physical evolution with microstructure, examinations by TEM of the powder thermally treated were performed. Particle morphology has drastically

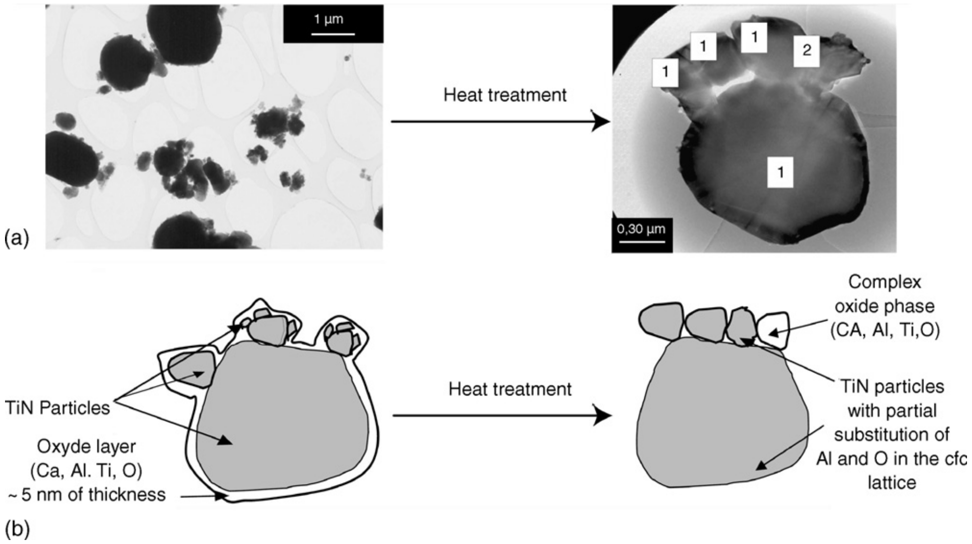

Fig. 7. Overview of heat treatment influence on powders morphology. (a) TEM micrographs of the powders before (left side) and after (right side) the heat treatment (zone 1 corresponds to a cfc phase and zone 2 is identified as a compound associated to a pseudo-cubic cell). (b) Schematic corresponding to the micrographs.

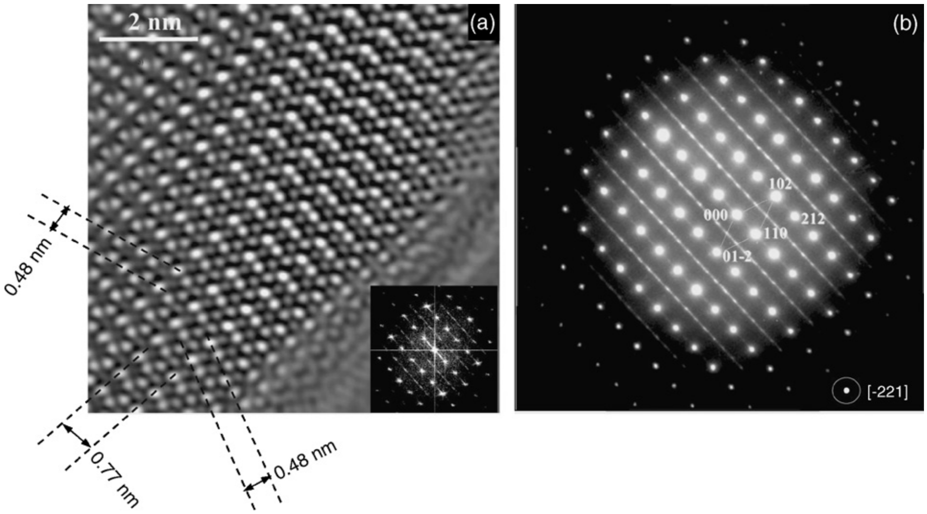

Fig. 8. (a) Pseudo cubic oxide phase observed by TEM in the high resolution mode. The inset shows the FFT of the micrograph. (b) Electronic diffraction picture of the same grain.

changed as shown in Fig. 7a. First of all, nanocrystalline particles have pre-sintered, explaining the important decrease of specific surface area. In addition, the nanocrystalline layer is not observed anymore and two different crystallographic zones are indentified. A first one (Fig. 7a, zone 1) was identified as a cubic face centered (cfc) similarly to TiN crystallographic cell and the second one (Fig. 7a, zone 2) possibly index-linkable as a pseudo cubic cell, with a lattice parameter of 10.46 Å from an indexing work of the fast Fourier transform of HREM micrograph (Fig. 8). In the titanium nitride phase, a partial diffusion of aluminium and oxygen has occurred. The second phase, corresponding to a pseudo cubic structure, is an oxide phase composed of calcium, aluminium, titanium and oxygen (Fig. 9).

As a partial conclusion, Fig. 7 summarizes the influence of a heat treatment on the powders. Three mains phenomena have occurred: first, nanoparticles have pre-sintered. Secondly nanocrystalline layer is not observed anymore; it has partially diffused into the TiN lattice. Finally, a new oxide phase (Ca, Al, Ti, O) is punctually present, stuck on major TiN particles.

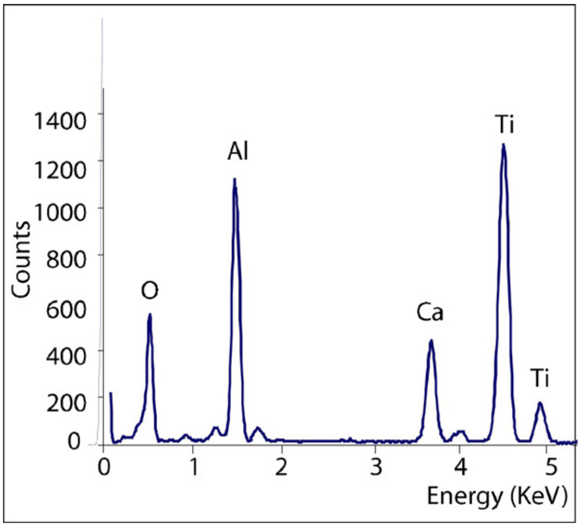

Fig. 9. Chemical analyses of the oxide phase (Fig. 8a) indexed as pseudo cubic cell.

Complementary to punctual TEM examinations, XPS analysis were carried out in order to obtain global information on as received and heat treated powders. Table 3 compares content of elements at surfaces, measured by XPS, for a powder treated or not. Many phenomena can be noticed and correlated with TEM observations. First, an important decrease of oxygen content is observed, corresponding to the layer disappearance. Secondly, titanium content increases. It can be correlated to TiN cleaning at grain surfaces. It is important to underline here that XPS signal comes from only few nanometers of thickness. Particles are hence cleaned from impurities. Finally, calcium content increases while aluminium content decreases. Chemical analyses shown in Table 1 indicate that their global content does not change with heat treatment. As surfaces analyses give different results, it can be concluded that their volume global repartition have been modified. Aluminium has diffused into titanium nitride lattice. Calcium is present in two specific phases: in a punctual perovkite structure ($CaTiO_3$ – JCPDS 42-0423) and in the pseudo cubic phase described before (Fig. 8).

Finally, all these microstructural changes can be correlated to the density value increase. First, nanocrystalline layer initially present does not seem to have a perfect structural organization and might be partially porous. Secondly, it is strongly possible that the starting powders, due to the rapid rate of the SHS process, are not completely crystallographically arranged. Heat treatment will favour diffusion phenomenon, in particular of aluminium and oxygen. This atomic reorganization will be responsible for a density increase.

Table 3
XPS analyses: influence of the heat treatment

	% O	% Ti	% N	% Ca	% Al
As received TiN powders (at%)	72.3	13.9	3.6	2.7	7.5
TiN heat treated (1300 °C) (at%)	51.3	22.0	17.5	4.3	5

3.2. Temperature influence on hot pressed bodies characteristics

Physical and mechanical properties have been studied as a function of the sintering temperature (1400 °C, 1600 °C and 1800 °C) under a constant 50 MPa pressure in a previous study:[15] powders have been initially thermally treated (1300 °C for an hour) in order to increase their density. Temperature influence on relative density and Young modulus is shown and at 1400 °C, specimens are not densified at all. The density of the samples increases with temperature. At 1600 °C, the relative density is greater than 98% and reaches 99.6% at 1800 °C. Young modulus varies in the same manner since it is very low at a sintering temperature of 1400 °C and increases to reach 430 ± 10 GPa at 1600 °C. At 1800 °C it remains stable.

Micro hardness and flexural strength vary differently than density and Young modulus with temperature. Indeed, both of them reach a maximum value at a sintering temperature of 1600 °C and then decrease at 1800 °C. The maximum Micro hardness 1790 ± 225 Hv is reached at a sintering temperature of 1600 °C and then decreases to 1600 ± 70 Hv when sintering temperature increases. Flexural strength reaches also a maximum value of 232 ± 15 MPa at 1600 °C and then falls down to 140 ± 15 MPa at 1800 °C.

In order to understand this decrease of mechanical properties, fracture surfaces of specimens sintered at 1600 °C and 1800 °C are observed and their average grain size is determined by image analysis. It is measured to be 2.1 ± 0.7 μm at 1600 °C as compared to 3, 3 ± 1.9 μm at 1800 °C. At 1600 °C grains are regular and fine. At higher temperature (1800 °C), TiN grains grow quickly and in an irregular way. This notable grain growth can account for the decrease of mechanical properties.

Fracture toughness was also measured for specimens sintered at 1600 °C and 1800 °C. For a TiN hot pressed at 1600 °C under a 50 MPa pressure, it reaches $3.5\,\mathrm{MPa}\sqrt{\mathrm{m}}$, while when sintered at 1800 °C, it falls down to $2.7\,\mathrm{MPa}\sqrt{\mathrm{m}}$. According to these results and to the observations of fracture surfaces of both samples, it can be concluded that at 1800 °C, fracture is mainly transgranular.

X-ray diffraction results of hot pressed bodies and powders are compared. No changes of phases are observed before and after the sintering process: the main phase is a cubic phase center TiN and the perovskite phase initially present in the powder remains stable. Concerning temperature influence, it can be concluded that the optimum sintering temperature, under a 50 MPa pressure, is 1600 °C, and the mechanical properties of samples elaborated in these conditions are comparable to literature data.

Powders used presently have been previously heat treated. For potential industrial applications, a thermal pretreatment of powders is not interesting from an economical point of view, so it should be interesting to study the influence of the thermal treatment on bulk specimens' properties. Hence, in the following part, the as received powders are densified at 1600 °C under 50 MPa and their physical and mechanical characteristics are discussed and compared to those obtained from heat treated powders.

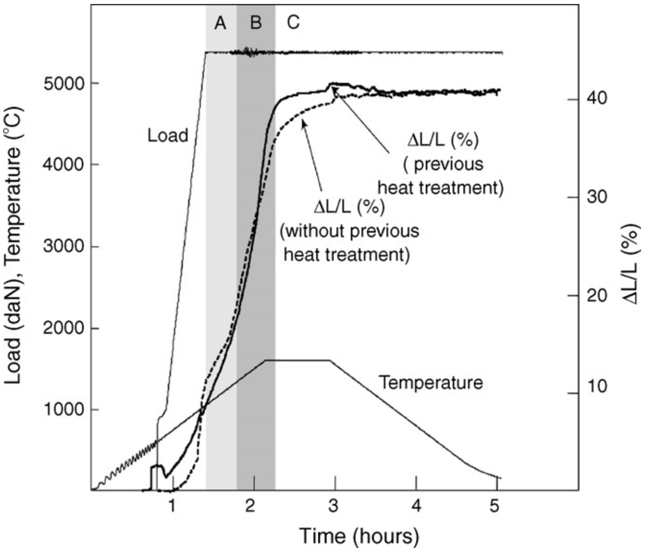

Fig. 10. Shrinkage curve recorded during the hot press cycle (1600 °C, 50 MPa, heating rate 10 °C/min) for powder with and without previous heat treatment.

3.3. Influence of thermal treatment and oxide presence

The shrinkage curves recorded during the hot press cycle (1600 °C, 50 MPa, heating rate 10 °C/min) for powders with and without a previous heat treatment are shown in Fig. 10. The two curves exhibit many differences. With no previous heat treatment the curve presents three stages: a first one (named A on the Fig. 10), from 1050 °C to 1300 °C, due to the pre-sintering of submicronics particles. A second one (B), from 1300 °C to 1600 °C, corresponds to the main sintering stage and a last one (C), from 1600 °C, where a decrease of sintering kinetic is clearly observed.

In the second curve, where a heat treatment has been previously performed, only two stages are observed since the first one, corresponding to the pre-sintering of submicronics particles has already occurred during the thermal treatment. In the last stage it can be observed that shrinkage is not completely achieved.

Table 4 allows comparing physical and mechanical properties of hot pressed specimens obtained with TiN powders heat treated or not. First of all, without a previous heat treatment, den-

Table 4
Comparison of physical and mechanical properties for specimens sintered at 1600 °C under a 50 MPa pressure from TiN powder heat treated or not

	Bulk TiN without previous heat treatment	Bulk TiN with a previous heat treatment	Literature value[16]
Density (g/cm^3)	5.11 ± 0.02	5.21 ± 0.06	5.4
Vickers micro hardness (Hv)	1570 ± 190	1790 ± 225	1800–2000
Young modulus (GPa)	385 ± 10	430 ± 10	250–460
4 points flexural strength (MPa)	213 ± 15	232 ± 15	250–550
Electrical resistivity (μΩ cm)	62 ± 3	34 ± 2	10–30

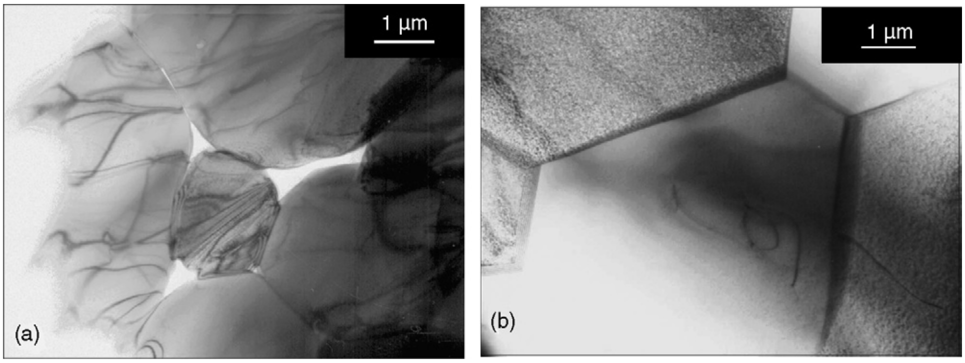

Fig. 11. TEM micrographs of hot pressed TiN (1600 °C, 50 MPa). (a) Without a previous heat treatment; (b) with a previous heat treatment (1 h, 1300 °C).

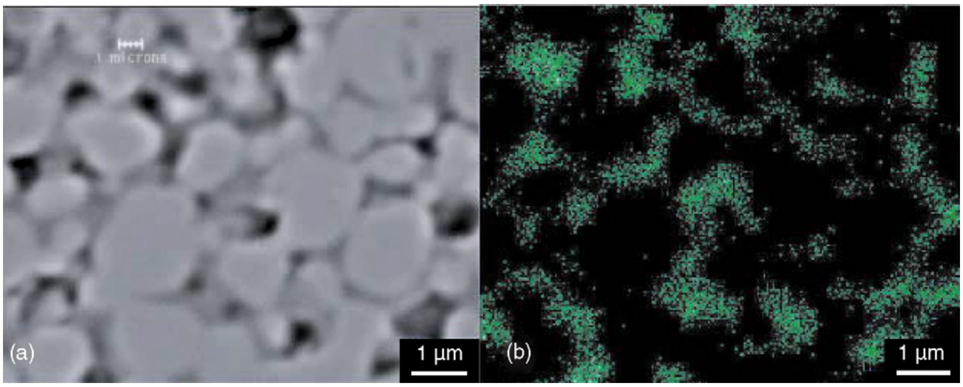

Fig. 12. (a) SEM micrographs of a TiN polished surface (1600 °C, 50 MPa, after a previous heat treatment) presenting some rooting up zones; (b) EDX cartography of the calcium corresponding to this area.

sification is not achieved and properties such as Vickers Micro hardness, Young modulus and four points' flexural strengths are lower. In addition, the low value of the electrical resistivity for a heat treated specimen is close to literature data.

X-ray diffraction results on both specimens do not reveal any difference between a densified body previously heat treated or not. TiN lattice parameter does not vary and the perovskite phase is also identified in both of them though in a very punctual manner.

TEM observations of both specimens show (Fig. 11) that heat treatment has a drastic influence on microstructure. When powder is not heat treated before, grains have a round shape, micro porosities are present at triple junctions and incomplete densification is observed. On the contrary, when powders have undergone a thermal treatment, the microstructure is different: grains have a polyhedrical shape; no porosity is found at triple junction and specimens are well sintered.

Fig. 12 shows an SEM micrograph of a TiN polished surface (1600 °C, 50 MPa) presenting some rooting up zones with the calcium EDX cartography corresponding to the same area. Calcium is present at grain boundaries and probably as a perovskite structure. TEM observations (Fig. 13) confirms this hypothesis and in both samples (heat treated or not), oxide inclusions of perovskite phase ($CaTiO_3$) are observed at grain boundaries in

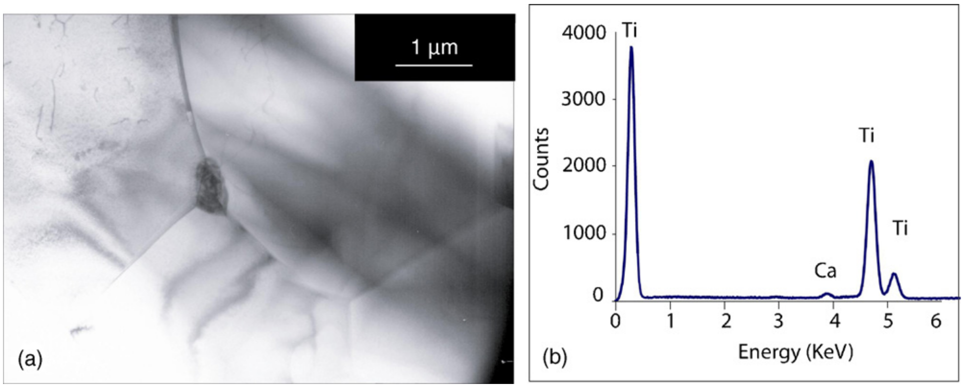

Fig. 13. (a) TEM micrographs of a hot pressed body previously heat treated (1600 °C, 50 MPa). A $CaTiO_3$ inclusion is observed at the grain boundaries. (b) Chemical analyses spectrum corresponding to the inclusion.

a punctual manner. Results presented in Table 4 show that the presence of this phase is not deleterious to physical and mechanical properties and could also be helpful to the sintering stage. Indeed this secondary phase acts as sintering aids as it allows decreasing the sintering temperature. To confirm this hypothesis, commercial powders (TiN Starck, grade C, 0.8–1.2 μm) of pure TiN have been hot pressed in the same conditions. It is clearly observed that at 1600 °C, specimens are not completely densified since a relative density of only 95% is measured and it is necessary to sinter at higher temperature (1800 °C) to obtain a good densification.

Concerning the second oxide phase identified on heat treated powders and composed of calcium, aluminium, oxygen and titanium, it is not observed anymore on hot pressed bodies. Aluminium, oxygen and titanium have probably diffused into the TiN lattice. Traces of carbon are also present because of graphite tools and die. Therefore, the final compound will be a TiN with partial substitutions in small amounts of aluminium, oxygen and carbon.

Finally, a previous treatment is highly favorable to the sintering stage: it permits to clean the surface of these particular powders. The oxide layer present at their surface is eliminated and the nano sized grains have already pre-sintered.

4. Conclusions

The aim of this work was to characterize TiN powders synthesized by the SHS process and to clarify the influence of a heat treatment on their microstructure and on a subsequent densification stage. The results obtained confirm that self propagating high temperature Synthesis allows to product fine powders in an easy and economic way. However some limits remain in the process regarding the purity of the obtained powders. This study also demonstrates that these original titanium nitride powders can be densified by hot pressing without additives and lead to materials with nearly full relative density. A previous thermal treatment on TiN starting powders has a beneficial effect on sintered products: the surface of the powder is cleaned from impurities and the oxide phase (perovskite, $CaTiO_3$), initially present, acts as a sintering aid. Mechanical properties are close to literature data and bulk TiN obtained from SHS starting powders have been sintered with attractive characteristics.

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