

Simultaneous synthesis and densification of titanium nitride by high pressure combustion synthesis

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Abstract

Titanium nitride (TiN) has attractive physical and chemical properties such as hardness, chemical stability and electrical conductivity. It is a typical material with a wide range of stoichiometry. High-pressure combustion synthesis is a method which allows simultaneous synthesis and densification of titanium nitride. The composition and microstructures can vary with the experimental conditions especially with thermal treatment and nitrogen pressure. We have shown that for compaction pressure of 98 MPa, under a nitrogen pressure of 200 MPa, a maximum of atomic nitrogen content of 46.5% can be reached in dense titanium nitride. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The use of titanium nitride (TiN) in various fields of technology is constantly growing because of its excellent physical and chemical properties. Titanium nitride is extensively used as hard coating on machining tools owing to its wear resistance. It has a high melting temperature (2927°C), relatively low specific gravity and oxidation.¹ It is a typical material with a wide range of stoichiometry (TiN_{1-x} , $0 < x < 0.61$). As in other covalent compounds, limited atomic mobility prevents complete densification of pure TiN at reasonable temperatures.

Traditionally, these nitrides are synthesised by the direct reaction between metal and nitrogen gas or ammonia at temperatures near 1200°C for extended periods of time. Self-propagating high temperature synthesis (SHS) can also be used to synthesise nitrides by heating or igniting fine metal powders under high nitrogen pressure or by using sodium azide as a solid source of nitrogen.² This process is based on the self sustained propagation of a chemical exothermic reaction wave through a heterogeneous mixture of metal

and non metal powders.³ Due to the evolution of the high reaction heat, the process results in a significant and very rapid increase in temperature. Conversion of the reactants into the final product at such high temperatures occurs in a time scale of seconds, which complicates investigations of the combustion synthesis kinetics and mechanism.^{4,5} This combustion process results in nitride formation, though these reactions are often incomplete, leaving unreacted metal or lower nitrides in the product.

The purpose of this study is to use high-pressure combustion synthesis^{6–8} between titanium powder compact and nitrogen gas in order to obtain dense⁹ and stoichiometric titanium nitride.

2. Experimental

Combustion experiments are carried out in high pressure-high temperature equipment. Hydrostatic nitrogen pressures up to 1.5 GPa can be reached by means of a three-stage compressor, which is linked to a high-pressure vessel by a capillary.

Titanium powder (Aldrich Chimie, < 325 mesh) of 99.98% purity is used as initial substance. The grain size distribution is centred on an average diameter of 20 μm .

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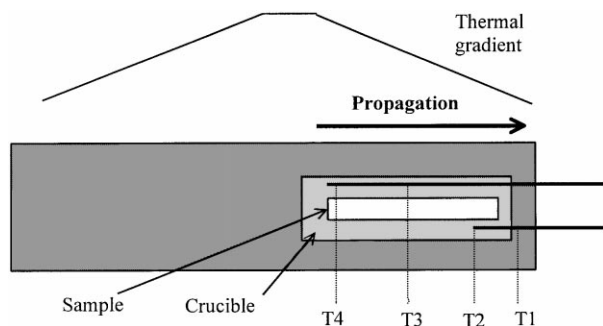


Fig. 1. Schematic representation of the location of the sample in the furnace.

A fixed mass of titanium powder, 0.85 g, is cold pressed uniaxially into parallelepiped compacts in a metal mold by applying pressure from 49 to 294 MPa. These compaction pressures correspond to relative green densities from 45 to 58%. The crucible containing the reactant compact (whose size is $27 \times 4 \times 5 \text{ mm}^3$) is introduced in a one heating zone furnace where temperature is controlled by means of four PtRh6%–PtPh30% thermocouples: one regulation thermocouple (T1) and three measurement thermocouples (T2–T4) as shown in Fig. 1. In this furnace, the existence of a thermal gradient which is about 100°C along the sample determines the ignition of the reaction.

In these experiments, the parameters which are varying are compaction pressure of the titanium powder, nitrogen pressure in the vessel and heating rate of the furnace. Considering previous results obtained for aluminum nitride synthesis¹⁰ nitrogen pressure is fixed to 100 MPa. In fact, for this pressure, the reaction is almost complete.

The first step of our study is to obtain simultaneous combustion synthesis and densification of titanium nitride. We will show that variations of heating rates can give rise to different mechanisms. In the second step compaction pressure and nitrogen pressure (10, 30, 100, 200, 300, and 400 MPa) are varied in order to ensure both SHS reaction and an increasing degree of conversion.

Identification of the phases is performed by X-ray diffraction and the densification of products is observed by metallographic methods [scanning electron microscopy (SEM)].

3. Results and discussion

3.1. Nitrogen pressure equal to 100 MPa

3.1.1. Variation of heating rates

Two types of behaviours are evidenced when different heating rates are used. For low heating rates ($30^\circ\text{C}/\text{min}$), during the thermal treatment, SHS reaction is not

ignited and a temperature of 1200°C is maintained during 1 h to ensure a conventional nitridation.

For high heating rates, ($90^\circ\text{C}/\text{min}$), a sudden rise in temperature occurs corresponding to the exothermic reaction between titanium powder and nitrogen gas (Fig. 2). The ignition occurs in an atmosphere of nitrogen and the reaction process propagates by the continued supply of nitrogen to the surface of the metal.

Figs 3 and 4 show the aspect of the samples obtained. Fig. 3 presents a reactant compact of titanium and a material synthesised at $30^\circ\text{C}/\text{min}$. The partial nitridation is evidenced along the sample by the gradual variation of colours from yellow, characteristic of titanium nitride to grey corresponding to the unreacted titanium.

The products obtained at $90^\circ\text{C}/\text{min}$ after SHS nitridation under different nitrogen pressures are presented in Fig. 4. They appear as fully dense materials. But, an important deformation is observed at the extremity of the sample corresponding to the maximum temperature of the thermal gradient.

Products are identified by X-ray diffraction.¹¹ The nitridation at the lower heating rate results in a mixture of Ti, $\alpha\text{Ti}(\text{N})$ and Ti_2N . At $90^\circ\text{C}/\text{min}$, these products consists of mononitride phase, TiN.

The micrograph in Fig. 5, obtained by SEM, shows the fractured surface of the samples corresponding to the lower heating rate, $30^\circ\text{C}/\text{min}$. It was a typical microstructure of a ceramic made by nitridation of titanium at high temperature, i.e. at 1200°C .¹² An important porosity is noticed, whereas in the case of experiments realised at high heating rate, $90^\circ\text{C}/\text{min}$ (Fig. 6), a fully dense structure with interlocked TiN crystals is observed.

In the following, only rapid heating rate will be used in order to ensure both ignition of the reaction and densification of titanium nitride.

3.1.2. Variation of compaction pressures

The compaction pressures are varying from 50 to 300 MPa for a fixed nitrogen pressure of 100 MPa.

In each case, the SHS reaction is observed. The products crystallise in the cubic rock salt (NaCl) structure. We can show that the lattice parameter is in agreement with that of titanium nitride solid solution reported in the literature.¹¹ The peaks of the X-ray diffraction pattern are labelled with their (hkl) values in order to determine the lattice constant (Fig. 7). By considering the evolution of lattice parameter with atomic percent nitrogen in titanium, the atomic percent dissolved in the metal lattice can be evaluated as a function of nitrogen pressure.

In Fig. 8, for compaction pressures from 50 to 200 MPa, the nitrogen content keeps constant and equal to 42.5% allowing for experimental incertitude. For pressures greater than 200 MPa, there is a linear decreasing of the content of nitrogen.

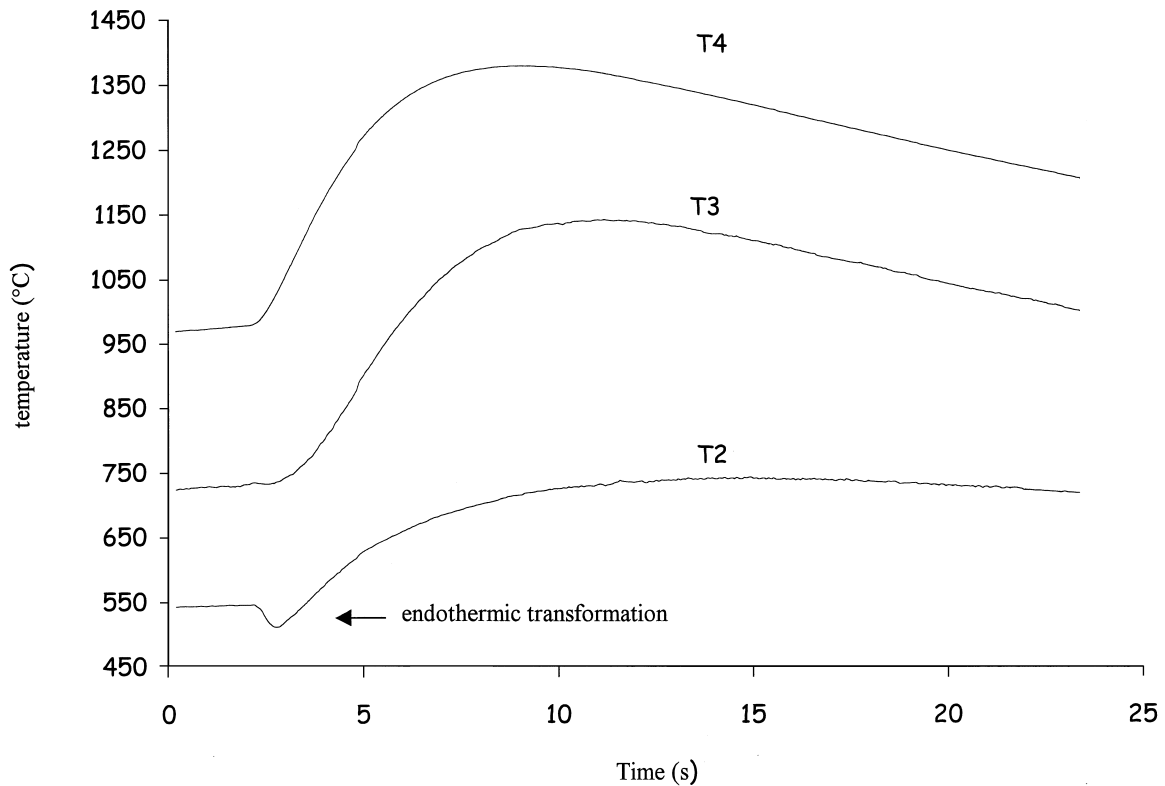


Fig. 2. Temperature–time profile obtained during combustion synthesis of titanium powder.

The explanation we can propose for this point is that for pressures less than 200 MPa, titanium is elastically deformed. So, after compression, it returns to an equilibrium state. Compaction has no influence on the conversion Ti/TiN. For pressures greater than 200 MPa, the elastic limit of titanium metal is exceeded and titanium

powder is plastically deformed to minimise the strains undergone. After compression, it keeps a permanent deformation which gives rise to a diminution of the accessibility of the gas towards the solid. This deformation increases with pressure. The conversion degree Ti/TiN is lowered. To control this hypothesis, we have made a study of the evolution of green density as a function of compaction pressures for titanium powder. Two behaviours are evidenced: the first one for pressures lower than 200 MPa with a rapid increase of green

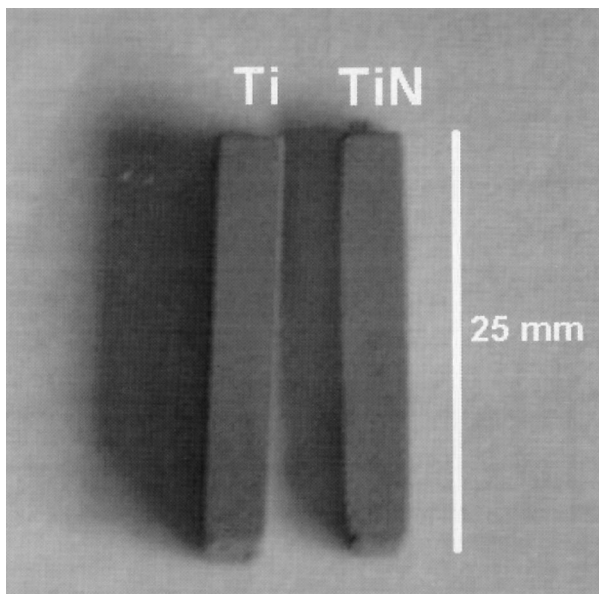


Fig. 3. Aspect of the materials obtained at 30 K/min: (left-hand side Ti compact; right-hand side TiN).

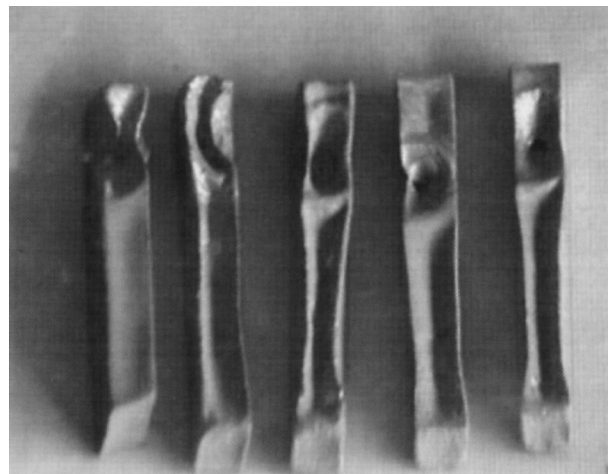


Fig. 4. Aspect of the materials obtained at 90 K/min. From left- to right-hand side, nitrogen pressure increases.

densities as a function of compaction pressures; the second is for pressures higher than 200 MPa where green density does not increase significantly as pressure increases.

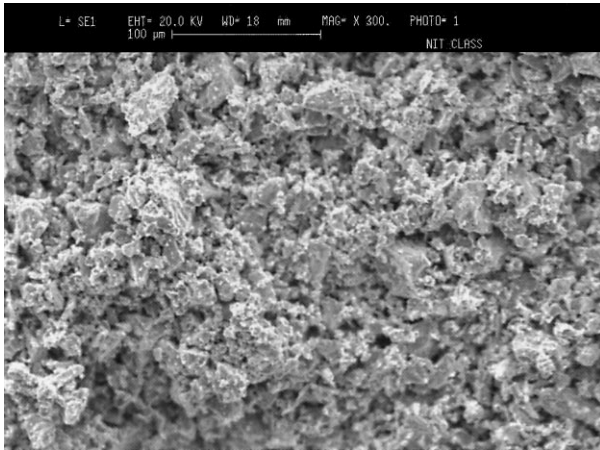


Fig. 5. SEM micrograph of a fractured surface obtained at 30 K/min ($\times 300$).

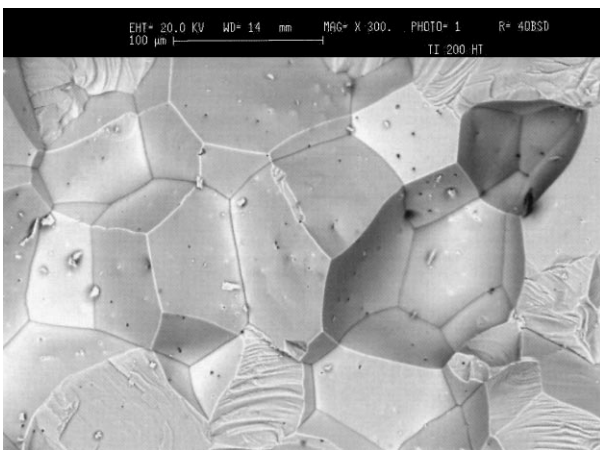


Fig. 6. SEM Micrograph of a fractured surface obtained at 90 K/min by combustion synthesis ($\times 300$).

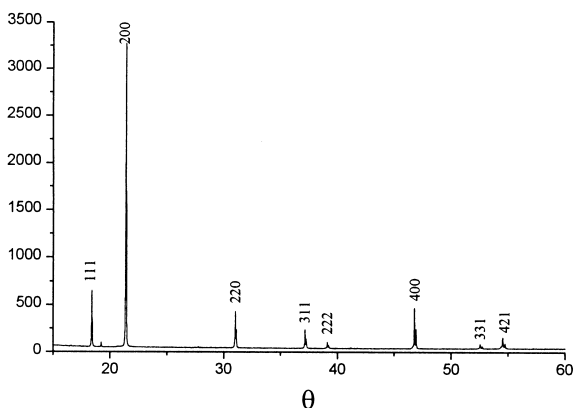


Fig. 7. X-ray diffraction pattern of SHS product.

3.2. Variation of nitrogen pressures

In these experiments, the compaction pressure is fixed to 100 MPa corresponding to a relative density of 50%. This value corresponds to the maximum value of the conversion degree according to Munir's results.^{3,13} Different nitrogen pressures 10, 30, 100, 200, 300, and 400 MPa are used in order to study the influence of gas pressure on the degree of conversion Ti/TiN.

Fig. 9 shows the variation of at.% nitrogen with nitrogen pressure.

Increasing nitrogen pressure up to 200 MPa leads to increase the conversion to TiN, up to 46.5 at.% of nitrogen, the permeation of gaseous nitrogen through the pores maintaining the local availability of nitrogen. Then the degree of conversion decreases and for pressures beyond 300 MPa, SHS reaction is no more ignited. An explanation for this phenomenon can be found if we consider that thermal conductivity of the gas increases twice from 10 to 600 MPa. Therefore, at high pressures, heat evacuation from the samples becomes very rapid and can lead to a complete extinction of the combustion synthesis.

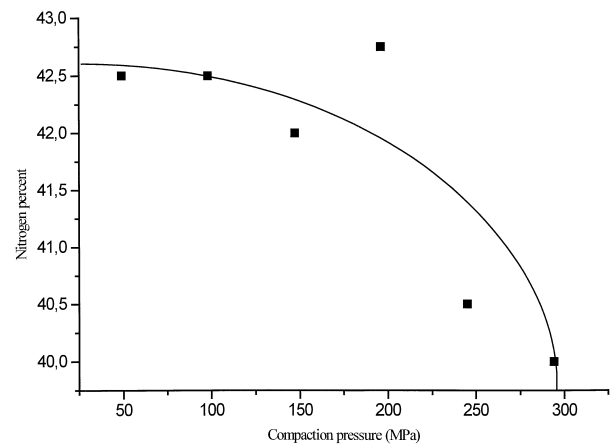


Fig. 8. Variation of at.% nitrogen with compaction pressure of titanium powder.

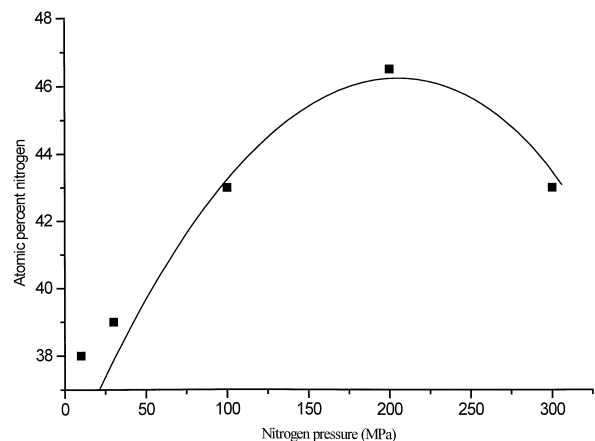


Fig. 9. Variation of at.% nitrogen with nitrogen pressure.

3.3. Interpretation of the formation and densification of TiN

These experimental studies have shown that the heating rate in the furnace has a great influence on SHS process and hence on the densification of the ceramics. The first step in the Ti + N₂ reaction has been shown to be the Ti (α) (h.c.) \rightarrow Ti (β) (cfc) transition, simultaneous with TiN_x formation.^{14–16} Two competing reactions are observed: an endothermic transformation Ti (α) \rightarrow Ti (β) at 885°C and an exothermic reaction corresponding to the formation of nitrides at 1000°C. The allotropic transformation is usually screened due to the highly exothermic reaction. However, in our experiments, the endothermic transformation can be evidenced at the level of T2 because of the weakening of the combustion wave along the sample (Fig. 2).

At 30°C/min, heating rate is low, so the supply of thermal energy in the system is, on the same way low. The reaction process in T4 can be divided in four stages: nitrogen diffusion in titanium α , allotropic transformation, nitrogen diffusion in titanium β vacancies, and formation of nitride as a layer around Ti grains. In this case, there is a low diffusion of nitrogen into titanium. Exchanges are very low and the nitridation of titanium occurs only by diffusion and by permeation of the gas into the titanium.

At 90°C/min, the quantity of energy supplied is more important. At the level of the thermocouple T4, owing to the high temperature associated with the important nitrogen diffusion in α -titanium,¹⁷ the amount of nitrogen supplied to α -titanium is extensive and then ignition of reaction appears as a thermal explosion. This thermal explosion is illustrated by the deformation observed at the hotter extremity of the materials (Fig. 4). Between T4 and T3, the thermal gradient acts as a reaction regulator and temperature decreases following the thermal gradient (Fig. 1). It contributes to the stabilisation of the combustion wave which shifts with a planar front along the sample.

The idea for densification is the same described by Shibuya et al.^{18,19} (Fig. 10). We have not measured the combustion temperature of the reaction between nitrogen and titanium but according to Yamada,⁸ the combustion temperature measured with a two-color pyrometer reached > 3300°C over the melting point (1660°C) of titanium. So, titanium melts during SHS process. As the nitrogen gas inside the closed pores reacts with the molten Ti, the gas pressure inside the pores should decrease. Consequently, the gas pressure outside the specimen becomes relatively higher during the time of nitridation inside. The pressure difference between the inner (P_i) and the outer (P_o) gases becomes a driving force for the simultaneous densification just after the SHS nitridation. In our case, whatever pressure value is used, the difference between inner (P_i) and outer (P_o) is sufficient to provide the same densified structure.

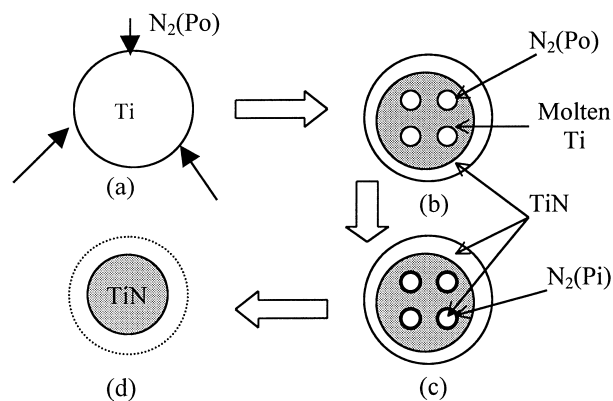


Fig. 10. Densification in SHS process:¹⁸ (a) titanium powder; (b), (c) intermediate stages Ti–N₂(P_o) \rightarrow TiN–N₂(P_i) P_o > P_i; (d) densification.

4. Conclusion

In this paper, investigations concerning high-pressure combustion synthesis and densification of titanium nitride are presented. The composition and microstructures can vary with the experimental conditions especially with thermal treatment and nitrogen pressure. At high heating rate, the intensity of heat exchange and its existence exerts a significant influence on the development of ignition. It results in a formation of a fully dense structure with coalesced TiN crystals.

Titanium nitride has a wide range of stoichiometry. So, the main objective in the synthesis of titanium nitride is to improve the stoichiometry. We have shown that for compaction pressure of 98 MPa, under a nitrogen pressure of 200 MPa, a maximum of atomic nitrogen percent of 46.5 can be reached in dense titanium nitride.

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