

# In situ synthesis of TiC–TiB<sub>2</sub>–hBN–SiC composites through SHS

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## Abstract

Ceramic composite powders with novel composition were synthesized in situ by the combination of two different reactions in one step.

The high exothermicity of a reaction previously investigated for the synthesis of TiC–TiB<sub>2</sub> powders was exploited to carry a second low exothermic reaction for the production of hBN–SiC composites in a self-propagation regime. The overall reaction exhibited sufficient exothermicity to self-sustain till completion.

The process yielded high purity powders with tailored compositions suitable for the fabrication of ceramic and cermet materials characterized by wear resistance and self-lubricant behaviour shown by the presence of hBN intimately dispersed into the hard ceramic matrix.

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## 1. Introduction

Self-propagating high-temperature synthesis (SHS) is a relatively novel and simple route for the synthesis of a great number of advanced ceramic composites and intermetallic compounds [1]. The process has recently received considerable attention as an alternative to conventional furnace technology within the efficient and energy saving technologies development now pursued.

In the typical thermite reaction, the reactants are usually fine powders that are mixed and pressed into pellets. Ignition through electrically heated graphite or tungsten wire supplies the initial energy, and the exothermicity self-sustains the reaction that carries on by combustion waves through the sample [2]. The high reaction temperature and the extreme rapidity allows obtaining high purity powders characterized by sub-micrometric particle size and homogeneity at atomic level [3,4]. The possible formation of metastable phases is based on the high thermal gradients and the rapid cooling rate associated to the reaction [5,6].

In comparison with the conventional ones, the TiC–TiB<sub>2</sub> based cermets show higher degree of hardness and chemical stability even at high temperatures making these ma-

terials good candidates for cutting and machining applications [7,8]. SHS synthesis of TiC–TiB<sub>2</sub> phase has been widely studied, achieving best results with the composition 60/40 wt.% TiC/TiB<sub>2</sub> [9].

A further improvement in powder production aims to obtain a mixture with self-lubricant properties. The addition of limited amount of hexagonal boron nitride to the ceramic phase has been under investigation.

Hexagonal boron nitride is a well-known solid lubricant and is generally prepared starting from compounds containing boron and nitrogen. Typical carriers of boron are boric oxide, boric acid, and boron trichloride while nitrogen is mostly supplied as ammonia gas or organic compounds such as urea, thiourea, and biuret [10,11].

hBN composites can be produced either by directly adding or by in situ synthesizing hBN particles into the ceramic matrix. Hot pressing is the common route to produce hBN composites as hBN shows poor sinterability. On the other hand, the synthesis of hBN through SHS has been carried out at high pressure; starting from boron powders in nitrogen atmosphere or through decomposition of borane hydrazine [12,13].

Aim of this work is the simultaneous synthesis of novel compositions of TiC–TiB<sub>2</sub> with small amounts of hBN and SiC through SHS. This way allows avoiding the high-temperature furnace technologies traditionally employed to produce hBN composites [14,15]. The addition of silicon

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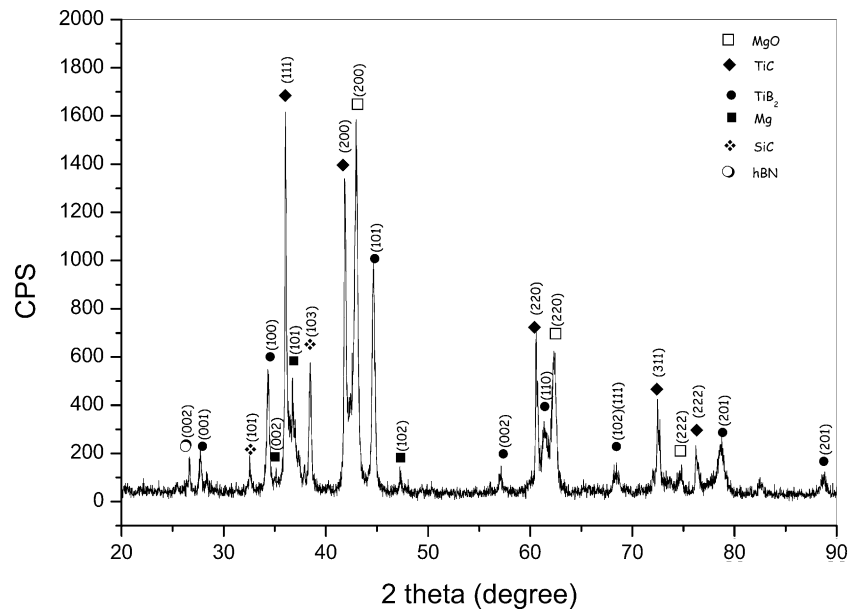


Fig. 1. X-ray diffraction analysis of the powders after SHS synthesis.

carbide which is an important ceramic for high-temperature applications represents a further improvement of the properties of the final composite material developed.

## 2. Experimental procedures

The raw materials used in this work were  $B_4C$  powders (H.C. Stark,  $<10\ \mu\text{m}$ ), 99.8% pure  $TiO_2$  powders (Riedel-de Haën,  $<10\ \mu\text{m}$ ), 99% pure Mg powders (Aldrich,  $<300\ \mu\text{m}$ ), TiC powders (H.C. Stark,  $<3\ \mu\text{m}$ ), 99.5% pure

C powders (Aldrich,  $<2\ \mu\text{m}$ ) and  $\alpha\text{-Si}_3\text{N}_4$  (H.C. Stark,  $<2\ \mu\text{m}$ ).

Reactants powders were milled with a planetary mill for 2 h in a grinding vessel of agate with ball-to-powder ratio (BPR) of 1:1. The powders were uniaxially pressed into green compacts showing a relative density of about 60%.

The reaction investigated for the synthesis of 60/40 wt.% TiC/TiB<sub>2</sub> was as follows:

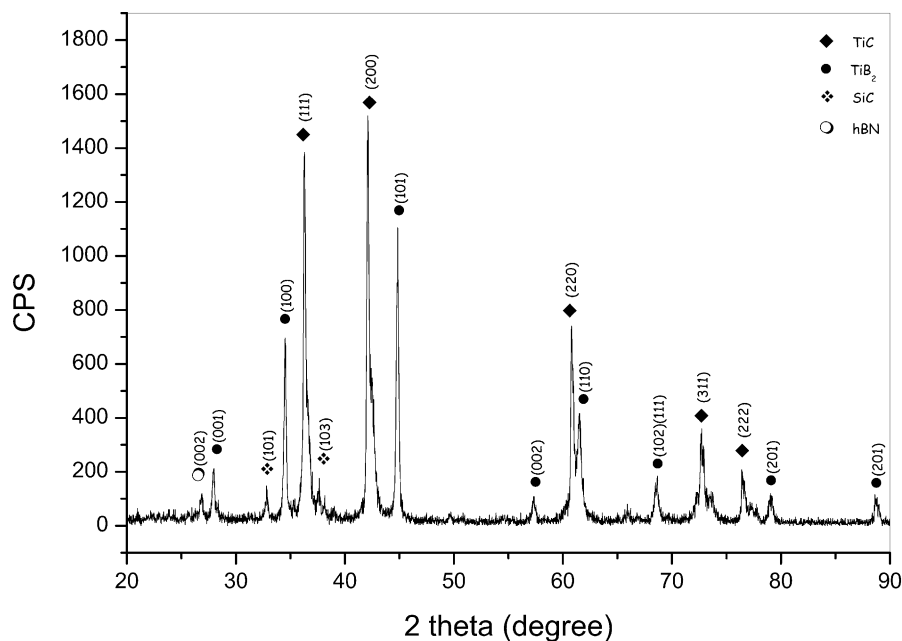
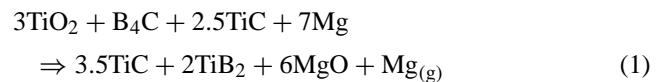
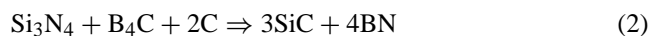


Fig. 2. X-ray diffraction analysis of the powders after leaching.

An excess of Mg is necessary to compensate the evaporation of this metal due to the high reaction temperature during synthesis. The reaction is highly exothermic ( $\Delta H = -3398$  kJ) and rapidly self-propagates once ignited [16].

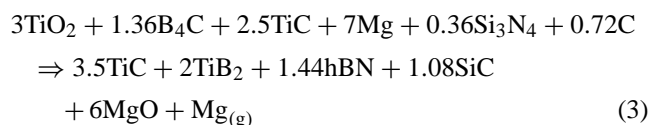
Different reactions have been considered for the formation of hBN. Best results were achieved through the following reaction:



This reaction is not self-sustaining due to its low adiabatic temperature ( $T_{\text{ad}} = 1200$  °C;  $\Delta H = -853$  kJ) [1–3,15].

However, once it is combined with the highly exothermic reaction (1), the heat released by the first reaction turns out to be sufficient to ignite reaction (2).

Optimization of the combined synthesis (1) and (2) led to the set up of the following reaction:



This reaction allows the synthesis of TiC–TiB<sub>2</sub>–hBN–SiC compositions in situ.

The ignition of the reaction was performed through a graphite rod electrically heated under inert atmosphere of argon. The stoichiometry has been tailored in order to obtain 5–7% by weight of hBN in the final powders after the leaching step (for the elimination of undesired MgO phase and residual Mg).

The lixiviation has been executed using a solution of 6 M HCl at a temperature of about 90 °C for 15 min.

The reacted samples were milled in order to obtain fine powders. After every step, the powders were analyzed through X-ray diffraction (XRD) and scanning electron microscopy (SEM).

### 3. Results and discussion

Thermodynamic calculations about the reaction products (3) are shown in Table 1.

The data were calculated using software designed for thermodynamic equilibrium in complicated multicomponents heterophase systems.

Table 1  
Results of thermodynamic calculation

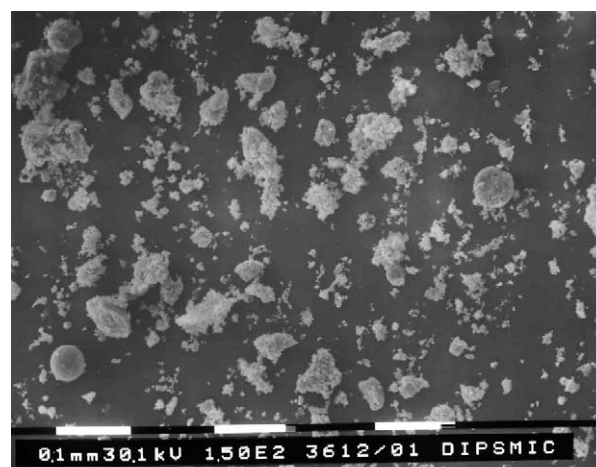
Product	Composition (wt.%)	
	Before leaching	After leaching
TiC	31.2	49
TiB <sub>2</sub>	22.3	35
hBN	4.6	7
SiC	5.5	9
MgO	36.4	–

$T_{\text{ad}}$ : 2035 K; gas amount (gaseous species formed during reaction): 1.4 mol.

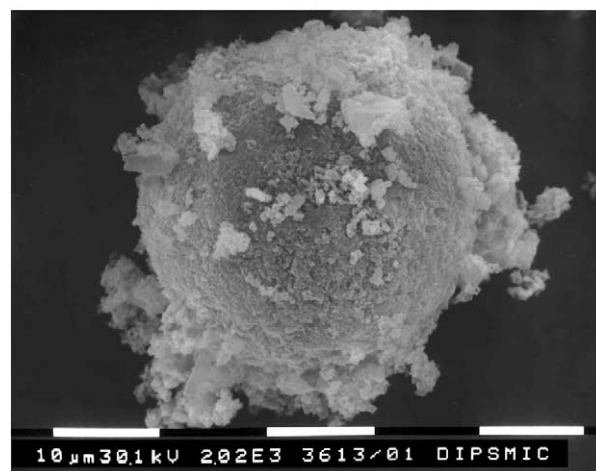
Dedicated database of thermodynamic properties for individual compounds was built on the basis of data published in well-known thermodynamic reference books [17–21]. The results of calculation are the equilibrium product composition (both condensed and gaseous), adiabatic temperature, and reaction enthalpy. Definition of thermodynamic equilibrium conditions is based on the procedure of minimization of thermodynamic potential (free energy) of system by taking into account the limitations connected to the mass conservation laws for chemical elements. The system under study is assumed to be chemically and thermally uniform, each particle of any component of the system is considered accessible for chemical interaction with the particles of the other phases, and the temperature is assumed uniform over the entire system volume. The calculation procedure consists of a cycle of iterations continued until the above mentioned criterion is satisfied.

In this case, the adiabatic temperature is higher than 2000 K and can give a self-sustained reaction.

The X-ray diffraction pattern of the reacted powders after milling in mortar is shown in Fig. 1. The final



(a)



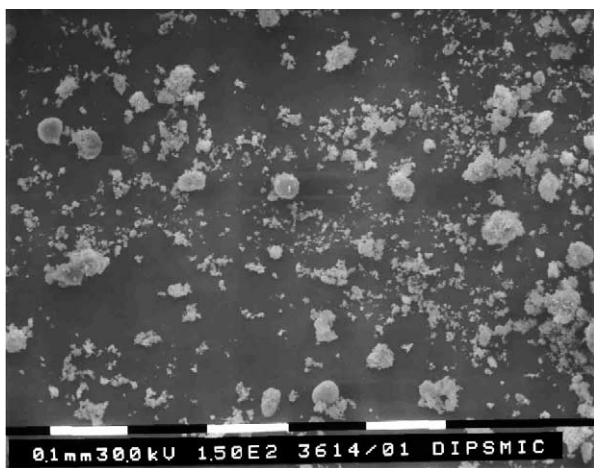
(b)

Fig. 3. SEM images of the powders before leaching: (a) general view; (b) spherical agglomerates.

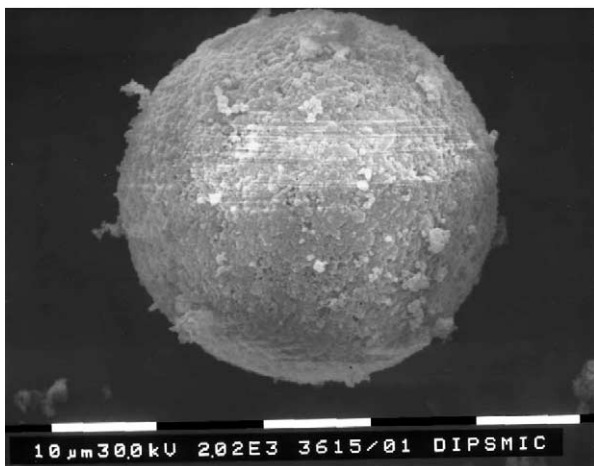
products detected are MgO, TiC, TiB<sub>2</sub>, hBN, SiC, and Mg.

The leaching step for the elimination of the high quantity of MgO formed and residual Mg was tailored to avoid the dissolution of the interesting reaction products. The XRD pattern after leaching is reported in Fig. 2. As can be seen, only MgO and Mg were leached out during the process. No loss of titanium diboride during leaching was confirmed by the absence of violet coloration of the leaching solution. Besides, no loss of hBN and SiC phases was noticed during the leaching.

SEM observation of the powders at every step were made after grinding in agate mortar. The results of SEM observations before and after leaching are reported in Figs. 3 and 4, respectively. The powders morphology before leaching (Fig. 3) is characterized by the presence of a large number of spherical agglomerates surrounded by loose powders. The EDS microanalysis detected titanium and silicon as main elements in the agglomerates and magnesium oxide as main constituent of the loose powders.



(a)



(b)

Fig. 4. SEM images of the powders after leaching: (a) general view; (b) spherical agglomerates.

SEM analyses after leaching (Fig. 4) show that the spheres are present in higher quantity than before leaching while the amount of loose powder highly decreases due to the elimination of MgO but a minimum amount of the loose powders are due to the fragmentation of the spheres of TiC/TiB<sub>2</sub>.

The phenomenological evolution can be explained considering the different steps of the SHS reaction.

In the first step, a high exothermic reaction due to the oxidation of magnesium and the formation of metallic titanium takes place. Then, the high temperature generated by the redox produces the melting of titanium with the formation of micrometric droplets surrounded by MgO. Molten titanium reacts with boron carbide causing its decomposition and promoting the formation of titanium carbide and boride intimately mixed. This reaction mechanism has been observed through Synchrotron radiation in a previous work [22].

Probably, the Si<sub>3</sub>N<sub>4</sub> decomposition takes place due to the high temperature reached, and the heat released by reaction (1) favors the occurrence of reaction (2) giving SiC and hBN.

#### 4. Conclusions

1. Self-propagating high-temperature synthesis was employed to synthesize in situ TiC–TiB<sub>2</sub>–hBN–SiC compositions starting from a compacted TiO<sub>2</sub>–B<sub>4</sub>C–TiC–Mg–Si<sub>3</sub>N<sub>4</sub>–C powder blend. The production of the powder was carried out combining two different reactions, the first acting as booster for the second one resulting in very pure final mixture with fine particle size.
2. Simultaneous synthesis of TiC–TiB<sub>2</sub> and hBN–SiC composites was achieved without the application of high pressure or high temperature.
3. Mg was used in the reactant mixture as reductant element. The undesired MgO phase resulting from the synthesis was chemically removed by HCl lixiviation. The hBN and SiC phases were not leached out by the HCl solution, and MgO-free powder was obtained after leaching.
4. The overall process yielded an intimately dispersed mixture of fine hBN powders into the hard TiC–TiB<sub>2</sub>–SiC matrix. The tailored composition has potential applications for the fabrication of intrinsically wear-resistant and self-lubricant bulk materials to be assessed by further densification and tribological testing.

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