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# Reactive synthesis of ceramic matrix composites under pressure

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**Abstract**

Near fully dense in situ ceramic matrix composites were fabricated from blends of fine Ti–$B_4C$, Ti–BN, Ti–SiC, Ti–$B_6Si$ and Al–$TiO_2$ powders without or with the addition of Ni. Two reactive synthesis techniques were employed: thermal explosion/TE (SHS) under pressure and reactive hot pressing/RHP. In both approaches, the processing or preheating temperature ($\leqslant 1100°C$) was considerably lower than those typical of current methods used for processing of ceramic matrix composites. Partial to full conversion of reagents into products was achieved during TE, and a moderate external pressure of 150 MPa was sufficient to ensure full density of the final products. RHP processing yielded dense materials with finer microstructures, however full conversion of reagents into products was not achieved. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

*Keywords:* In situ processing; Thermal explosion; External pressure

## 1. Introduction

Design and development of advanced high performance materials and bringing them into use is one of the most challenging tasks of modern engineering. Refractory ceramics, such as alumina ($Al_2O_3$), TiC, $TiB_2$, etc., are natural candidates for demanding applications due to their exceptional hardness and stability at very high temperatures. Alumina, $Al_2O_3$, is a well studied and universally used material possessing such attractive properties as excellent wear and oxidation resistance, good high temperature strength, etc. Ti-based ceramics (borides, carbides, etc.), although much less exploited in industry, also are an outstanding group of materials in that, in addition to high hardness and elastic modulus, they possess good electric and thermal conductivity comparable with those of alloyed metals. The latter features offer some unique shaping possibilities (e.g. electrical discharge machining) and widen the range of possible applications of these ceramics.

Ceramic matrix composites (CMCs) that successfully combine the advantageous properties of individual components are of special interest to industry. For example, when TiC or $TiB_2$ are combined with $Al_2O_3$, the composite, without a significant drop in hardness, has a better oxidation resistance and possesses superior mechanical strength and fracture toughness than TiC or $TiB_2$ alone [1]. Alumina/TiC composites show improved wear resistance and find application for cutting tools. Particulate reinforced CMCs containing hard ceramic or ductile metal/intermetallic inclusions exhibit several advantages compared to single phase ceramics, e.g. high fracture toughness and strength, enhanced thermal shock resistance and high wear resistance [2,3].

One of the major factors restricting the widespread use of composite ceramics for advanced structural applications is the difficulty and expense of producing dense components with fine-scale microstructure. Current methods of manufacturing dense particulate reinforced CMCs are liquid phase sintering, hot pressing or hot isostatic pressing (HIP). Long exposures at high temperatures typical of these techniques not only adversely affect the cost-effectiveness of materials produced, but also result in the coarsening of microstructure. Owing to the inability of current powder technology related methods to produce composite materials with the desired fine-scale or interpenetrating phase microstructures, in situ processing is becoming an increasingly important concept in composite synthesis. In situ composite is a material in which the matrix and the reinforcements have been formed during processing. The rationale for in situ synthesis is reduced cost,

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improved control of microstructure, and, therefore, improved properties. Three potentially attractive processing techniques that can be utilized for the reactive synthesis of in situ CMCs are self-propagating high-temperature synthesis (SHS), solid state displacement reactions and reactive infiltration.

SHS is one of the rapidly emerging cost-effective technologies used to synthesize monolithic and composite in situ ceramics [4,5]. The principle of this technique is that the initial reagents, when ignited, spontaneously transform into products due to the exothermic heat of reaction. The advantages of SHS synthesis are very high reaction rates and the elimination of the need for high temperature furnaces used in conventional material fabrication due to the immense energy release. The major problem to be overcome in the SHS processing of refractory ceramics is the high retained porosity of the synthesized products. Recent efforts aimed at achieving simultaneous SHS synthesis and densification of materials have demonstrated that application of pressure during or subsequent to the combustion step can considerably increase the product density [1,6–10].

Displacement reaction synthesis is another example of reactive processing [11]. Unlike the SHS process that utilizes the exothermicity of reactions, the reactions in this approach are accomplished via solid state diffusion at temperatures below the corresponding combustion temperatures. This gives the method the advantage of a better control over the microstructure and porosity in final products. Similarly to SHS, intrinsic pores are generated during displacement reaction synthesis, and some external pressure should be applied in order to obtain a fully dense material.

Recently, it has been suggested by the authors that the effectivity of displacement reaction synthesis can be improved if fully dense micron/submicron starting powders are used [12]. With fine starting powders, the short diffusion distances allow the synthesis of new phases to be completed over relatively short time periods thus preventing the undesirable coarsening of the microstructure. Reactive synthesis in fully dense powders coupled with the application of a moderate external pressure may allow the fabrication of pore-free in situ composites.

In this paper, pressure-assisted reactive synthesis of dense in situ CMCs from fine powder blends with and without the addition of a ductile Ni phase is discussed.

## 2. Experimental

In the present work, fine Ni, Ti, Al, $B_4C$, BN, SiC, Si, $TiO_2$ and graphite powders (1–2 μm) from Cerac were used. Homogeneous powder blends of different compositions (Table 1) were prepared by high energy attrition milling. A low 2:1 balls-to-powder ratio was used for attrition milling in order to avoid mechanical alloying of powders. 70% dense compacts (18×18×15 mm) were prepared from the blends and heat treated in vacuum at 400°C in order to remove absorbed gases from the powder surface. After degassing treatment, part of

Table 1
Phase composition and properties of selected CMCs synthesized

| Starting blend | Processing route | Phase composition of synthesized material | Density (% TD) | $K_{1c}$[a] (MPa$\sqrt{m}$) |
|---|---|---|---|---|
| $B_4C$–3Ti | TE[b], 1000°C | $TiB_2$, TiC | ~99 | 6.8 |
| $B_4C$–3Ti–0.95Ni | SDI-TE[c], 1000°C | $TiB_2$, TiC, Ni | ~99 | 10.8 |
| $B_4C$–3Ti–0.95Ni + 0.3$TiB_2$ | SDI-TE[c], 1000°C | $TiB_2$, TiC, Ni | ~99 | 9.8 |
| $B_4C$–3Ti–0.95Ni + 2$TiB_2$ | SDI-TE[c], 1100°C | $TiB_2$, TiC | ~97 | 8.4 |
| 2BN–3Ti | TE[c], 1100°C | *No TE* | – | – |
| 2BN–3Ti–0.95Ni | SDI-TE[c], 1000°C | $TiB_2$, TiN, Ni | ~99 | 19.4 |
| 2BN–3Ti–0.95Ni + 0.3$TiB_2$ | SDI-TE[c], 1050°C | $TiB_2$, TiN, (Ni–$Ni_3Ti$)? | ~99 | 14.2 |
| 2BN–3Ti–0.95Ni + 1$TiB_2$ | SDI-TE[c], 1100°C | $TiB_2$, TiN, NiTi?, $Ni_3Ti$? | ~98 | 8.6 |
| 3SiC–8Ti | TE[d], 1100°C | TiC,$Ti_5Si_3$,$Ti_3SiC_2$ | ~99 | 7.3 |
| 3SiC–8Ti–2.53Ni | SDI-TE[c], 1000°C | TiC, $Ti_5Si_3$, $Ni_{16}Si_7Ti_6$ | ~99 | 6.8 |
| 3Ti–Si–2C | TE[d], 1100°C | $Ti_3SiC_2$ ,TiC,$Ti_5Si_3$, Ti | ~99 | – |
| 3$TiO_2$–7Al | SDI-TE[d], 800°C | $Al_2O_3$, TiAl, $TiAl_3$, $Ti_3Al$ | ~99 | – |
| 6$B_6$Si–14Ti | TE[d], 1000°C | $TiB_2$, $Ti_5Si_3$ | ~99 | – |
| $B_4C$–3Ti | RHP[b], 1100°C | $TiB_2$ ,TiC,$TiO_2$ | ~95 | 5.9 |
| $B_4C$–3Ti–1.5Ni | RHP[b], 1100°C | $TiB_2$ ,TiC,$Ni_3B$ | ~99 | 6.8 |
| 2BN–3Ti | RHP[b], 1100°C | $TiB_2$ ,TiN, $Ti_2N$, TiB | ~99 | 6.4 |
| 2BN–3Ti–1.5Ni | RHP[b], 1100°C | $TiB_2$ ,TiN, $Ni_3Ti$, TiB | ~99 | 7.8 |
| 3SiC–8Ti | RHP[b], 1100°C | TiC,$Ti_5Si_3$ | ~99 | – |
| 3$TiO_2$–7Al | RHP[d], 800°C | $Al_2O_3$, TiAl, $TiAl_3$, TiO | ~99 | – |

[a] Fracture toughness.
[b] 150 MPa.
[c] 50 MPa.
[d] 100 MPa.

the compacts were high pressure consolidated [13] to full density at $P = 3$ GPa and $T = 300$°C yielding ~18×18×12 mm samples.

The synthesis of ceramic matrix composites was accomplished via two different processing routes: thermal explosion under pressure (TE) and reactive hot pressing (RHP). For TE, non-dense compacts were placed in a rigid die preheated to $T_0 = 800$–1100°C and subjected to a moderate pressure of 50 to 150 MPa. [For each blend, $T_0$ was slightly higher than the SHS ignition temperature ($T_{ig}$) of the free-standing compact in a vacuum furnace.] For Al- or Ni-containing blends, $T_{ig}$ and, correspondingly, $T_0$ was typically higher than the the melting temperature ($T_m$) of one of the phases: Al ($T_m$≈660°C) or Ni–Ti eutectics ($T_m$≈940°C). Melting under pressure resulted in the squeezing of the micron-size liquid 'lakes' into the pores of a non-dense compact – a process that can be described as 'short distance infiltration' (SDI). [Compared to traditional melt infiltration, SDI has the advantage of the considerably shorter infiltration distances (microns vs. millimeters/centimeters)]. SDI leads to full densification of the compact, and it may or may be not followed by thermal explosion, depending on $T_0$ and on the exothermicity of the system. For the systems described in this paper, SDI was always followed by thermal explosion, and we'll refer to this route as SDI/TE.

To ensure that thermal explosion does not occur before the pressure is applied, samples were thermally insulated by $a$~0.2 mm thick coating of $Y_2O_3$ spray. Since the heating of the samples in the this scheme is realized via heat transfer from the die walls and the punches, the presence of the coating allowed to delay the onset of thermal explosion until the sample has been fully loaded. After the explosion, the sample was held under pressure for ~1 min and then unloaded and taken out of the die. The entire TE procedure was performed in open air.

Reactive hot pressing (RHP) was performed at 1100°C and 150 MPa (800°C and 100 MPa for Al-containing blends). Dense cold sintered samples were placed into a cold die, loaded to 150 MPa and slowly heated (10°/min) to the synthesis temperature. (This is in contrast to the thermal explosion synthesis where samples were placed in an already heated die.) After the processing temperature has been reached, the samples were held in the hot press for one, 2 or 4 h. $Y_2O_3$ spray was used as a die lubricant to prevent the welding of the samples to the die walls.

The specific feature of reactive hot pressing is that the material is synthesized via diffusion controlled reaction. Thermal explosion should be avoided, which means that the processing should be performed below the corresponding $T_{ig}$. It has been shown, however, that no thermal explosion takes place when $T_{ig}$ is reached in the course of heating in a hot press. Apparently, solid state diffusion processes that take place during the slow (10°/min) heating result in the formation of strong interfacial barriers, preventing the reaction from becoming self-sustaining after $T_{ig}$ has been reached.

After processing, the microstructure and phase composition of the synthesized composites were characterized employing X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive analysis (EDS). Estimates of fracture toughness, $K_{1c}$, were obtained from indentation experiments using a Vickers diamond indentor with a load of 1 to 20 kg. An equation derived by Palmquist was used to calculate $K_{1c}$ [14].

## 3. Results

Phase composition, density and fracture toughness of selected composites reactively synthesized under pressure are given in Table 1.

### 3.1. Reactive processing of non-oxide CMCs

#### 3.1.1. Thermal explosion under pressure (TE)

Thermal explosion of $B_4C$–3Ti, SiC–Ti and $B_6Si$–Ti blends at 1000–1100°C under the pressure of 100–150 MPa resulted in full conversion of reagents into products with the formation of near fully dense $TiB_2$–TiC, TiC–$Ti_5Si_3$ and $Ti_5Si_3$–$TiB_2$ (Fig. 1a) matrix composites, respectively. Representative microstructures of the synthesized CMCs are shown in Fig. 2a–c. In spite of the insulating $Y_2O_3$ layer, thermal explosion of the $B_4C$–3Ti blend caused extensive melting of the pressure die, apparently due to the high exothermicity of the synthesis reaction. The 2BN–3Ti sample which, similarly to the above blends, had been observed to thermally explode in a vacuum furnace at ~950°C, did not explode in the pressure die even at 1100°C. This is believed to be the result of the enhanced heat transfer from the reaction zone to the die caused by the high thermal conductivity of BN.

An attempt was made to synthesize the ternary $Ti_3SiC_2$ phase via thermal explosion at 1100°C under 100 MPa according to the reaction: $Ti_3SiC_2$ $Ti_3SiC_2$. The $Ti_3SiC_2$ compound has a layered (graphite-like) structure, and possesses a very attractive combination of machinability, strength, ductility and oxidation resistance at elevated temperatures. Thermal explosion was successful, however, in addition to the planned $Ti_3SiC_2$, significant amounts of $Ti_5Si_3$ and TiC have been formed (Fig. 1b). Full conversion of reagents into products has not been achieved, with the peaks of unreacted Ti and carbon present in the XRD pattern. The material synthesized is dense with no residual porosity observed in SEM (Fig. 2d). The typical needle-like morphology of $Ti_3SiC_2$ can be detected, as well as dark areas of unreacted C. Using starting Ti–Si–C blends with a lower

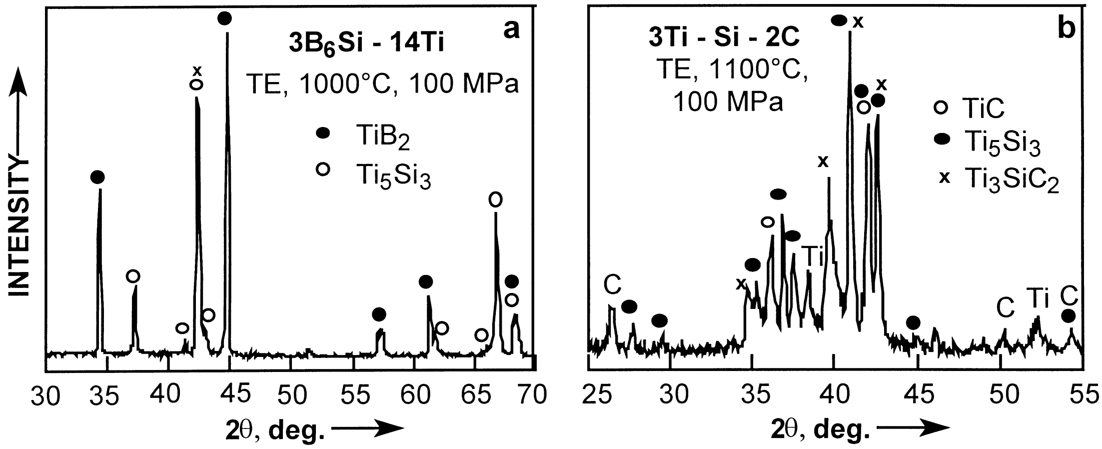
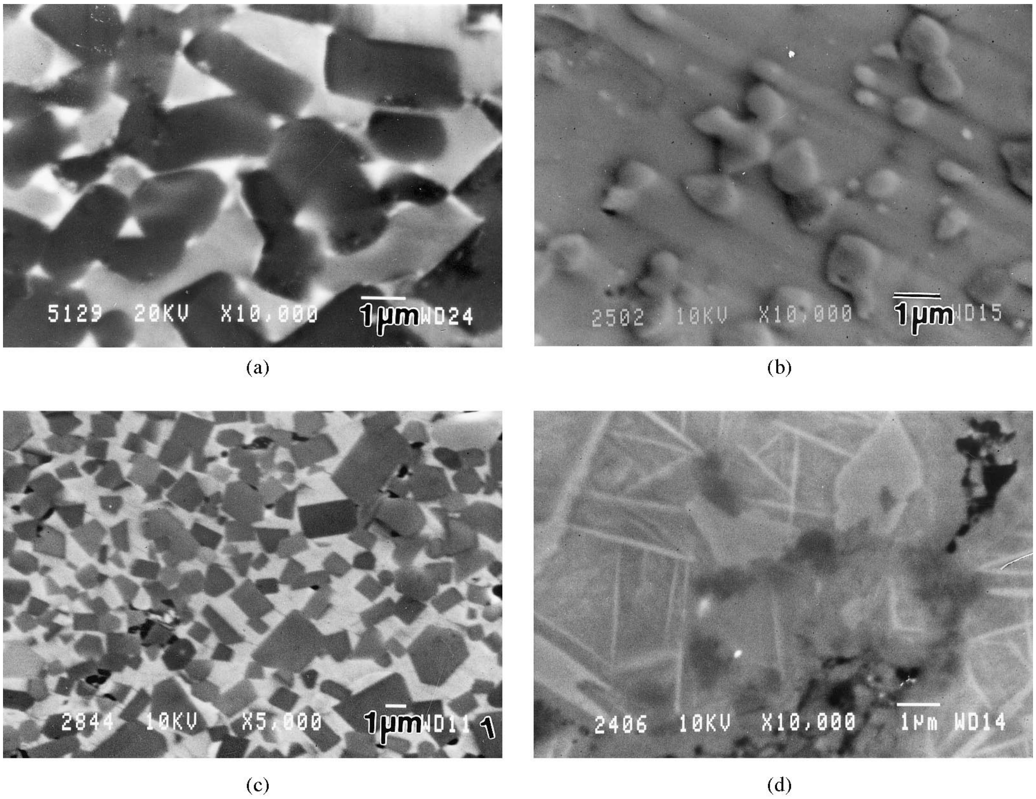


Fig. 1. XRD patterns of $B_6Si$–14Ti (a) and 3Ti–Si–2C (b) compacted blends after thermal explosion under pressure.



(a) (b)

(c) (d)

Fig. 2. Representative microstructures of TiC–$TiB_2$ (a), TiC–$Ti_5Si_3$ (b), $TiB_2$–$Ti_5Si_3$ (c) and $Ti_3SiC_2$/$Ti_5Si_3$/TiC (d) composites synthesized via thermal explosion under pressure.

concentration of C could, probably, allow to obtain graphite-free dense $Ti_3SiC_2$/$Ti_5Si_3$/TiC composites.

### *3.1.2. Short distance infiltration/thermal explosion under pressure (SDI-TE)*

The goal of adding Ni powder to the $B_4C$–Ti–0.95Ni blend was the toughening of the $TiB_2$–TiC ceramic product with a finely dispersed ductile metal phase. The chosen Ti-to-Ni ratio corresponded to the low melting 76Ti–24Ni (at%) eutectic ($T_m = 942°C$), with the expected volume fraction of metallic Ni in the final composite being 12.5%. The short distance infiltration/thermal explosion processing was performed in a die preheated to 1000°C under a pressure of 50 MPa. As illustrated by the XRD pattern in Fig. 3a, full conversion of reagents into products was achieved according to the reaction: $B_4C + 3Ti + 0.95Ni \rightarrow 2TiB_2 + TiC + 0.95Ni$. The in situ $TiB_2$–TiC–Ni composites synthesized had a fine

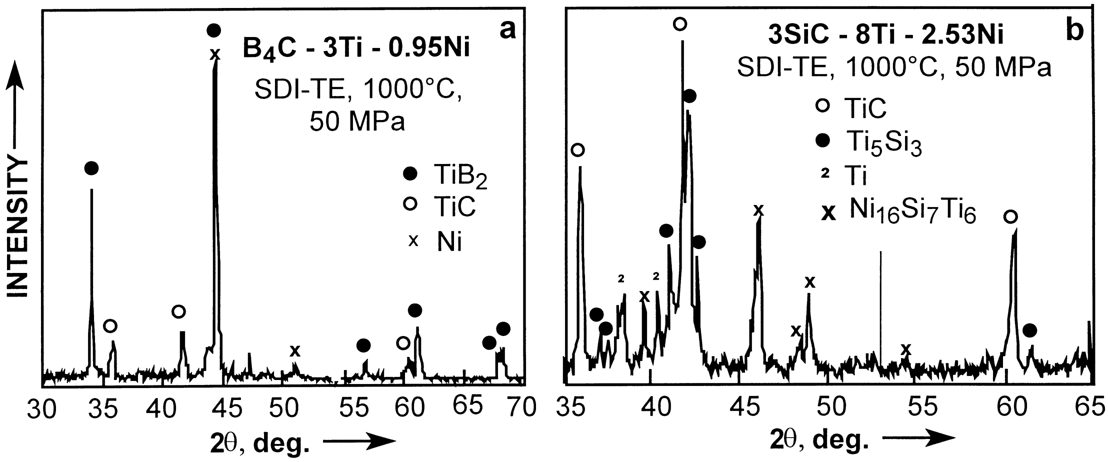


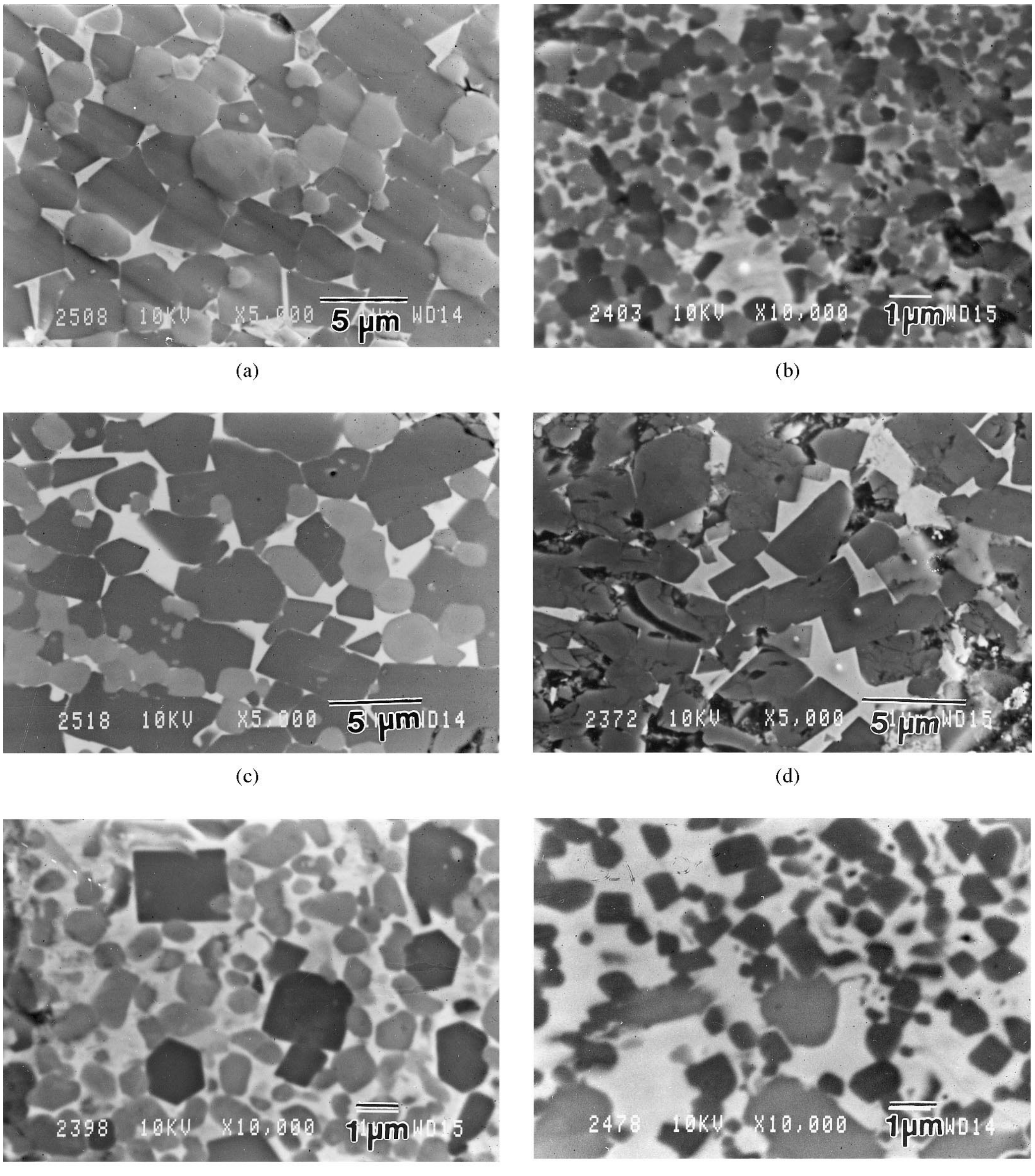
Fig. 3. XRD patterns of $B_4C$–3Ti–0.95Ni (a) and 3SiC–8Ti–2.53Ni (b) compacted blends after short distance infiltration-thermal explosion.

microstructure with no residual porosity detected in SEM (Fig. 4a and b). Dark gray $TiB_2$ platelets and bright gray equiaxed TiC grains can be distinguished with small islands of a bright Ni phase located in between. According to the results of EDS analysis, the Ni phase contains no more than 2 at% Ti. It can be seen that the microstructure in the center of the sample is coarser than that in the periphery suggesting that a higher combustion temperature was reached in the center during thermal explosion, apparently as a result of the enhanced heat transfer from the surface of the sample to the pressure die. The temperature in the center of the sample must have been close to 3200 K — the calculated combustion temperature of the $B_4C$–3Ti–0.95Ni blend preheated to 1000°C. The high temperature, as well as the large amount of liquid during processing have led to the partial melting of the inner surface of the die and to the welding of the sample to the die.

To avoid these undesirable consequences, the starting blend was diluted with one of the products, $TiB_2$. According to thermodynamic calculations (Fig. 5b), $T_{comb}$ is not affected by small additions of $TiB_2$, however the amount of liquid phase is drastically reduced. Larger amounts of $TiB_2$ significantly reduce $T_{comb}$. The ($B_4C+3Ti+0.95Ni$) blend diluted with 8 wt% $TiB_2$ ($n=0.3$) behaved very similarly to the undiluted blend, i.e. thermal explosion under pressure occurred at the same temperature of 1000°C. Both the phase composition and the microstructure (Fig. 4c), of the material synthesized was similar to that obtained in the undiluted blend. At the same time, less damage was caused to the die, apparently due to the lower amount of liquid during processing.

The calculated $T_{comb}$ (at $T_o=1000$°C) of the ($B_4C+3Ti+0.95Ni$) blend diluted with 35 wt% (2 mols) $TiB_2$ is significantly lower than that of the undiluted blend (2721 vs. 3193 K). It must be for this reason that thermal explosion under pressure of such sample occurred only at 1100°C. Nevertheless, no damage was caused to the pressure die. In the SEM micrograph (Fig. 4d), large colonies of $TiB_2$ diluent can be seen, cracked and are surrounded by pores. It is believed that if a finer $TiB_2$ powder is used for diluting the blend, there are more chances to avoid cracking and to obtain fully dense material.

For the 2BN–3Ti–0.95Ni blend, Ni was added to the starting blend not only to toughen the $TiB_2$/TiN matrix, but, more importantly, to promote thermal explosion under pressure which did not take place in the pure 2BN–3Ti blend even at 1100°C. With Ni added, thermal explosion occured already at 1000°C and resulted in full conversion of reagents into products according to: $2BN + 3Ti + 0.95Ni \rightarrow TiB_2 + 2TiN + 0.95Ni$. A representative microstructure of the sample after thermal explosion is shown in Fig. 4 e: dark gray $TiB_2$ platelets and bright gray equiaxed TiN grains can be distinguished surrounded by a bright Ni phase. The microstructure is much finer than that of the CMCs synthesized from the ($B_4C+3Ti+0.95Ni$) blend (Fig. 4a,b). The size of $TiB_2$ and TiN grains does not exceed 1 μm even in the middle of the sample, while at the periphery the characteristic grain size is submicron. The fine microstructure must be due to the low amount of liquid during SHS of the ($2BN+3Ti+0.95Ni$) blend (Fig. 5a), which does not lead to significant coarsening. Morphologically, the Ni phase in the material obtained can be described as an interconnected matrix in contrast to the separate islands in the $TiB_2$/TiC-based CMCs. The synthesized $TiB_2$/TiN/Ni composite is very dense with practically no porosity observed in SEM. According to Fig. 5a, dilution with only 8 wt% (0.3 mol) $TiB_2$ significantly lowers $T_{comb}$ of the ($2BN+3Ti+0.95Ni$) blend. As a result, the diluted blend exploded at the higher temperature of 1050°C, and full conversion has not been achieved.



(a) (b) (c) (d) (e) (f)

Fig. 4. Representative microstructures of Ni-toughened CMCs synthesized via thermal explosion under pressure: (a–d) $TiB_2$–TiC: (a) center and (b) periphery of the sample; (c) diluted with 0.3 mol and (d) with 2 mols of $TiB_2$; (e) $TiB_2$–TiN and (f) TiC–$Ti_5Si_3$.

Thermal explosion of 3SiC–8Ti–2.53Ni blend (Ti-to-Ni ratio corresponding to the Ti–Ni eutectic) at 1000°C under pressure resulted in the formation of a practically fully dense material. The phase composition of the material obtained is illustrated by the XRD pattern in Fig. 3b. The peaks of both $Ti_5Si_3$ and TiC are present; however, instead of the expected metallic Ni the peaks of a ternary $Ni_{16}Si_7Ti_6$ compound are easily detectable. In addition, small peaks of unreacted Ti are present. SEM observation of the material obtained revealed the presence of three phases: relatively large (1–2 μm) gray grains of $Ti_5Si_3$, much finer (0.25–0.5 μm) black grains of TiC, and a bright matrix with the EDS composition close to $Ni_{16}Si_7Ti_6$ (Fig. 4f).

As can be seen from Table 1, very high $K_{1c}$ values were measured in Ni-containing composites fabricated via SDI-TE from $B_4C$- and BN-based compacts, that are within the range of the highest fracture toughness numbers measured in tough ceramics with metal dispersions [15]. Apparently, $TiB_2$/TiN and $TiB_2$/TiC ceramic matrices are toughened by the finely dispersed ductile Ni phase effectively dissipating the energy of propagating cracks. The much higher toughness of the $TiB_2$/TiN CMC must be the result of its very fine microstructure. $K_{1c}$ of the TiC/$Ti_5Si_3$ CMC synthesized from the SiC–Ti–Ni blend is much lower, presumably due to the presence of a brittle $Ni_{16}Si_7Ti_6$ phase instead of the ductile metallic Ni.

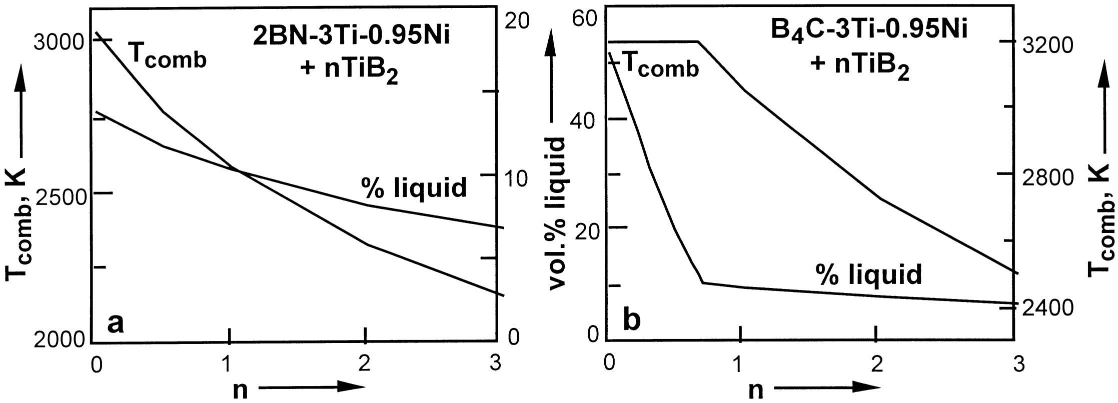
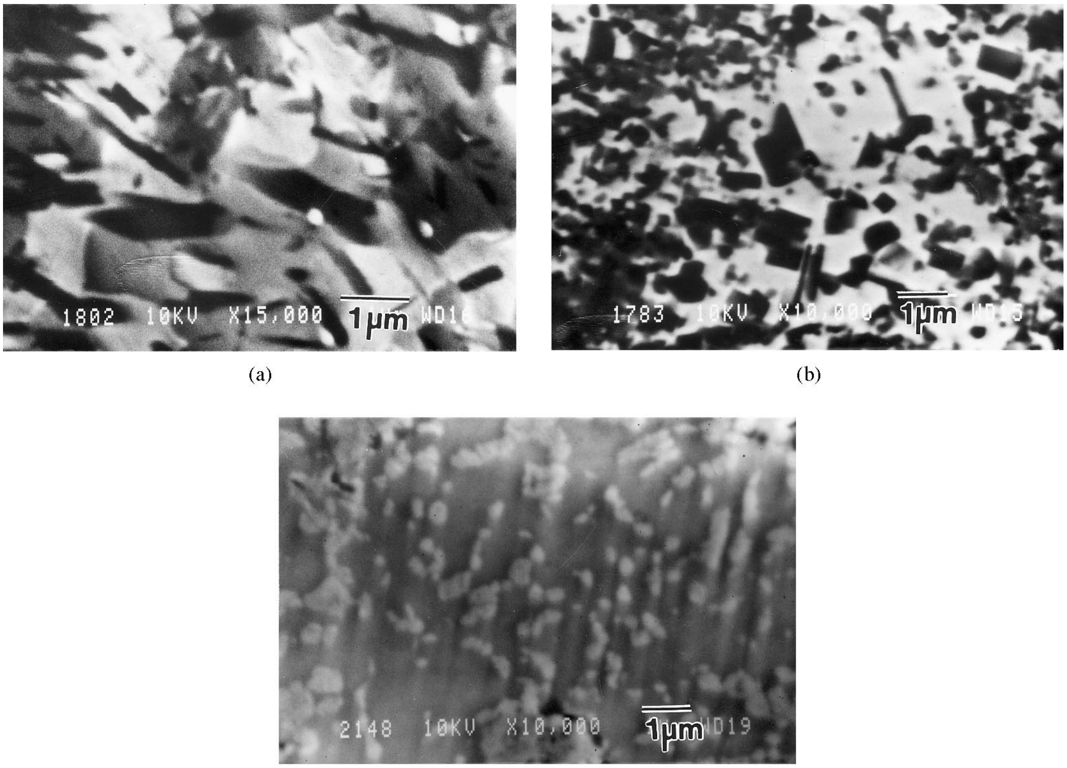


Fig. 5. Calculated combustion temperature, $T_{comb}$, and amount of liquid for thermal explosion at 1000°C of 2BN–3Ti–0.95Ni (a) and $B_4C$–3Ti–0.95Ni (b) blends diluted with $TiB_2$.

### 3.1.3. *Reactive hot pressing (RHP)*

Reactive hot pressing of the $B_4C$–3Ti blend at 1100°C for 4 h yielded a 94–95% dense material with very fine microstructure (Fig. 6a), comprising $TiB_2$, a Ti-rich carbide, $TiC_{1-x}$ and some unreacted $B_4C$. To achieve full conversion into $TiB_2$ and TiC, longer exposures could be required due to the low diffusivity of $TiC_{1-x}$. The synthesis reaction in the 2BN–3Ti blend proceeds even more slowly and, as can be seen in the XRD pattern (Fig. 7a), unreacted BN is still present after 4 h RHP at 1100°C, along with $TiB_2$, TiB, TiN and $Ti_2N$. With the addition of Ni, the RHP synthesis in the $B_4C$–3Ti blend starts with the formation of $Ni_3B$ which remains in the sample even after long (4 h) exposures at 1100°C. In the 2BN–3Ti–Ni blend, Ni reacts more readily with Ti forming a low melting $Ti_2Ni$ compound which later on transforms into $Ni_3Ti$. After 4 h RHP at 1100°C, the microstructure of the sample is very fine, and it contains, in addition to TiN and Ti borides, bright regions composed of Ni and $Ni_3Ti$ (Fig. 6b).



(a)

(b)

(c)

Fig. 6. Representative microstructures of CMCs synthesized via RHP: (a) $TiB_2$–$TiC_{1-x}$ with residual $B_4C$; (b) $TiB_2$–TiN–Ni/$Ni_3Ti$; (c) $TiC_{1-x}$–$Ti_5Si_3$ with residual SiC.

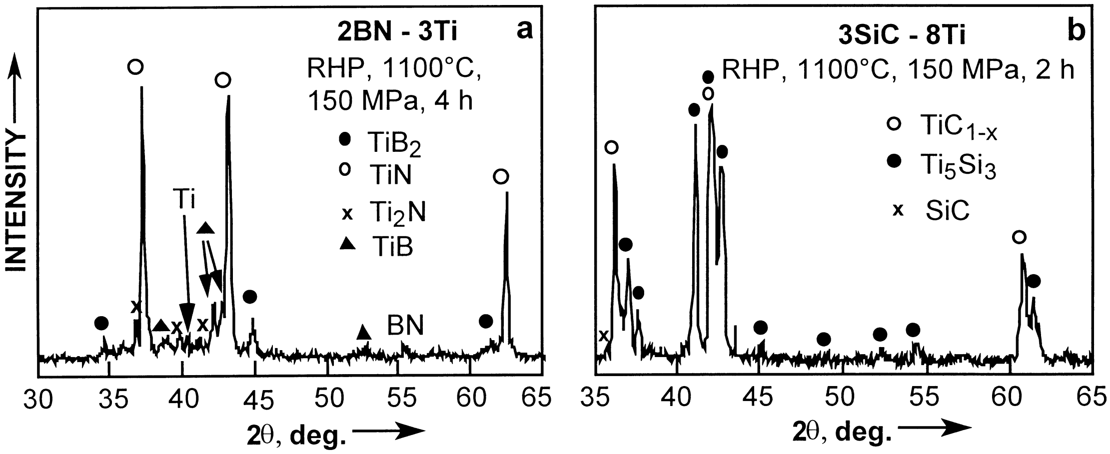


Fig. 7. XRD patterns of dense 2BN–3Ti (a) and 3SiC–8Ti (b) blends after reactive hot pressing.

Similarly to the $B_4C$–3Ti composition, RHP of the 3SiC–8Ti blend resulted in the formation of the Ti-rich $TiC_{1-x}$. Other phases detected after 2 h RHP at 1100°C are $Ti_5Si_3$ and some unreacted SiC (Fig. 7b). A SEM micrograph in Fig. 6c shows that the microstructure of the RHPed sample is much finer than that of thermally exploded one (Fig. 2b). The RHPed composite is dense with no pores observed in SEM. This must be due to the low volume change associated with the $3SiC–8Ti \rightarrow Ti_5Si_3 + 3TiC$ transformation (−8.6% vs. −18.9% for $B_4C + 3Ti2TiB_2 + TiC$, for example), that can be accommodated even under the relatively low applied pressure (150 MPa).

### 3.2. Reactive processing of alumina-based CMCs

Short distance infiltration followed by thermal explosion in preheated to 700–900°C dies under 100 MPa was attempted for various $TiO_2$–Al powder blends. The products of synthesis were fully dense and contained $Al_2O_3$ and Ti aluminides of different stoichiometry depending on the composition of the starting blend. A representative microstructure of such a composite synthesized via thermal explosion at 900°C is shown in Fig. 8. The composition of the bright matrix is close to $TiAl_3$, and the dark dispersions are $Al_2O_3$ (EDS).

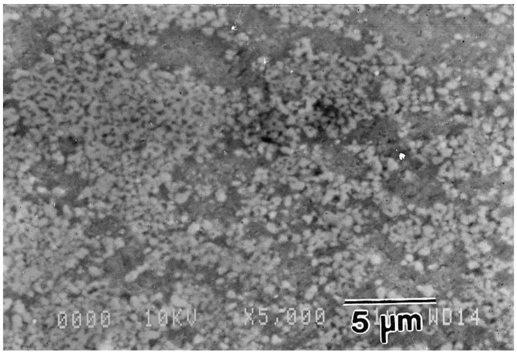


Fig. 8. A representative microstructure of $Al_2O_3$–TiAl based composite synthesized via thermal explosion/TE under pressure.

Reactive hot pressing of a $3TiO_2$–7Al composition at 800°C for 2 h under 100 MPa yielded a fully dense material, however full conversion of reagents into products according to the reaction: $3TiO_2 + 7Al \rightarrow 2Al_2O_3 + 3TiAl$ has not been achieved, and the sample contained, in addition to $Al_2O_3$ and TiAl, appreciable amounts of TiO and $TiAl_3$. The sub-micron microstructure of the material obtained gives grounds to belief that longer exposures at 800°C will result in full conversion without significant coarsening of the microstructure.

## 4. Summary

The authors' experience with pressure-assisted in situ reactive synthesis of dense particulate reinforced ceramic matrix composites (CMCs) has been reviewed. Two different processing routes have been discussed: thermal explosion in a rigid die under pressure–combustion consolidation, and reactive hot pressing. Combustion consolidation allowed the fabrication of near fully dense non-oxide and oxide-based CMCs under moderate applied pressures of $\leqslant 150$ MPa. Combustion-synthesized non-oxide in situ materials ($TiB_2$/TiN, $TiB_2$/TiC, $TiB_2$/AlN, $TiB_2/Ti_5Si_3$, $TiC/Ti_5Si_3$) had reasonably fine microstructures with grain size not exceeding 5 μm. A remarkably fine submicron-scale microstructure with correspondingly high mechanical properties was obtained in $TiB_2$/TiN matrix composite toughened with a few percent ductile Ni phase. Dilution of highly exothermic blends, e.g. $B_4C$–3Ti–0.95Ni, with the reaction product, e.g. $TiB_2$, resulted in a smaller amount of liquid during combustion and allowed to minimize the damage to the pressure die without changing the phase composition of the final product. Combustion synthesized oxide-based $Al_2O_3$/TiAl composite had a typical grain size below 1 μm. For comparison, reactive hot pressing yielded composites with even finer microstructures, however full conversion of reagents into products has not been achieved.

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