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Dense High-temperature Ceramics by Thermal Explosion Under Pressure

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Abstract

Near fully dense in-situ *particulate reinforced ceramic matrix composites (CMCs) were fabricated from fine Ti–B_4C, Ti–BN, Ti–Al–BN, Ti–SiC, Ti–B_6Si and Al–TiO_2 powder blends with or without the addition of Ni. Two reactive synthesis techniques were employed: thermal explosion/TE (SHS) under pressure, where the compacted reagent blend was placed and rapidly heated in a pressure die preheated slightly above the ignition temperature, and reactive hot pressing/RHP. In both approaches, the processing or preheating temperature ($\leq 1250°C$) was considerably lower than those typical of the current methods used for the processing of ceramic matrix composites. Partial to full conversion of reagents into products was achieved during TE, and a moderate external pressure of $\leq 150\,MPa$ was sufficient to ensure full density of the final products. Rapid cooling from the combustion temperature due to the 'heat sink' action of the pressure die resulted in the fine/micronsize microstructures of the* in-situ *composites synthesized. RHP processing yielded dense materials with even finer microstructures, however full conversion of reagents into products has not been achieved. © 1999 Elsevier Science Ltd. All rights reserved.*

Keywords: reactive hot pressing, thermal explosion, composites, borides, carbides, nitrides, silicides.

1 Introduction

Design and development of advanced materials for high performance applications and bringing these materials into use is one of the most challenging tasks of modern engineering. Refractory ceramic materials 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 ceramic 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 thermal diffusivity and high electric conductivity comparable with those of metal alloys. Good thermal diffusivity of a material is vital in many applications where heat transfer from the hot zone is required, e.g. cutting tools, parts working in friction, turbine blades, etc.

Ceramic–ceramic composites that successfully combine the advantageous properties of individual components are of special interest to the ceramic industry. For example, when TiC or TiB_2 is 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. The low electrical resistivity of TiC and TiB_2 can also make these materials suitable for electrical discharge machining. Toughening ceramics by incorporating submicron size hard particles is of considerable interest because of the dramatic improvements in their mechanical properties. Toughening by embedding ductile metal into the ceramic matrix, either as a continuos phase or in the form of dispersed particles, is another composite approach to improve mechanical properties of ceramics.[2] Particulate reinforced CMCs containing metal inclusions exhibit several advantages compared to single phase ceramics, e.g. high fracture toughness and strength, enhanced thermal shock resistance and high wear resistance.[3]

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Ultimately, the development of advanced CMCs into useful structural or functional materials depends not as much on our ability to demonstrate intrinsic properties, but on the availability of practical processing routes. Full density and fine microstructure are the basic requirements for high performance CMCs. 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, 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.

Self-propagating high-temperature synthesis (SHS), or combustion synthesis, is one of the rapidly emerging technologies used to synthesize refractory ceramic materials.[4–7] The principle of this technique is that initial reagents, when ignited, spontaneously transform into products due to the exothermic heat of reaction. The major advantages of this technique are very high reaction rates and the elimination of the need for high temperature furnaces used in conventional material fabrication due to self-generation of energy. An inherent limitation of combustion synthesis is the high retained porosity of the synthesized products. It has been demonstrated that application of pressure during or subsequent to the combustion step can considerably increase the product density.[1,7–16] Still, pressures of ~35 MPa typically applied during SHS processing are too low to obtain a fully dense ceramic material.

Displacement reaction synthesis is another example of reactive processing.[17] 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 effectiveness of displacement reaction synthesis can be improved if fully dense micron/submicron starting powders are used.[17] 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 one to obtain pore-free in–situ composites.

In this paper, the authors' experience with pressure-assisted reactive synthesis of dense in-situ CMCs from fine powder blends is reviewed. For the sake of integrity, the paper includes some results already reported in the earlier publications.[18,19]

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 $18\times18\times15$ and $18\times4{\cdot}5\times25$ 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 the $18\times18\times15$ mm compacts were high pressure consolidated[20] to full density at $P=3$ GPa and $T=300$°C yielding ~$18\times18\times12$ 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). Two different schemes of pressure-assisted TE were employed. In the first scheme, (Fig. 1), non-dense compacts $18\times18\times15$ mm 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 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 (Fig. 2)—a process that can be described as 'short distance infiltration' (SDI). SDI

Table 1. Phase composition and properties of selected in-situ CMCs synthesized

Starting blend	*Processing route*	*Phase composition of synthesized material*	*Density (% TD)*	*K_{1c}[a] (MPa$\sqrt{m}$)*
B_4C–3Ti	TE, 150 MPa, 1000°C	TiB_2, TiC	$\sim$99	6·8
B_4C–3Ti–0·95Ni	SDI–TE, 50 MPa, 1000°C	TiB_2, TiC, Ni	$\sim$99	10·8
B_4C–3Ti–0·95Ni + 0·3TiB_2	SDI–TE, 50 MPa, 1000°C	TiB_2, TiC, Ni	$\sim$99	9·8
B_4C–3Ti–0·95Ni + 2TiB_2	SDI–TE, 50 MPa, 1100°C	TiB_2, TiC	$\sim$97	8·4
2BN–3Ti	TE, 50 MPa, 1250°C	TiB_2, TiN	$\sim$99	—
2BN–3Ti–0·95Ni	SDI–TE, 50 MPa, 1000°C	TiB_2, TiN, Ni	$\sim$99	19·4
2BN–3Ti–0·95Ni + 0·3TiN_2	SDI–TE, 50 MPa, 1050°C	TiB_2, TiN, (Ni–Ni_3Ti)?	$\sim$99	14·2
2BN–3Ti–0·95Ni + 1TiB_2	SDI–TE, 50 MPa, 1100°C	TiB_2, TiN, NiTi?, Ni_3Ti?	$\sim$98	8·6
6BN–3Ti–6Al	SDI, 50 MPa, 900°C	Al_3Ti, Ti, BN	$\sim$99	—
6BN–3Ti–6Al	SDI–TE, 50 MPa, 1250°C	TiB_2, AlN, Ti_3Al	$\sim$99	—
3SiC–8Ti	TE, 100 MPa, 1100°C	TiC, Ti_5Si_3, Ti_3SiC_2	$\sim$99	7·3
3SiC–8Ti–2·53Ni	SDI–TE, 50 MPa, 1000°C	TiC, Ti_5Si_3, $Ni_{16}Si_7Ti_6$	$\sim$99	6·8
3Ti–Si–2C	TE, 100 MPa, 1100°C	Ti_3SiC_2, TiC, Ti_5Si_3, Ti	$\sim$99	—
3TiO_2–7Al	SDI–TE, 100 MPa, 800°C	Al_2O_3, TiAl, $TiAl_3$, Ti_3Al	$\sim$99	—
6B_6Si–14Ti	TE, 100 MPa, 1000°C	TiB_2, Ti_5Si_3	$\sim$99	—
B_4C–3Ti	RHP, 150 MPa, 1100°C	TiB_2, TiC, TiO_2	$\sim$95	5·9
B_4C–3Ti–1·5Ni	RHP, 150 MPa, 1100°C	TiB_2, TiC, Ni_3B	$\sim$99	6·8
2BN–3Ti	RHP, 150 MPa, 1100°C	TiB_2, TiN, Ti_2N, TiB	$\sim$99	6·4
2BN–3Ti–1·5Ni	RHP, 150 MPa, 1100°C	TiB_2, TiN, Ni_3Ti, TiB	$\sim$99	7·8
3SiC–8Ti	RHP, 150 MPa, 1100°C	TiC, Ti_5Si_3	$\sim$99	—
3TiO_2-7Al	RHP, 100 MPa, 800°C	Al_2O_3, TiAl, $TiAl_3$, TiO	$\sim$99	—

[a] Fracture toughness obtained from indentation crack measurements.

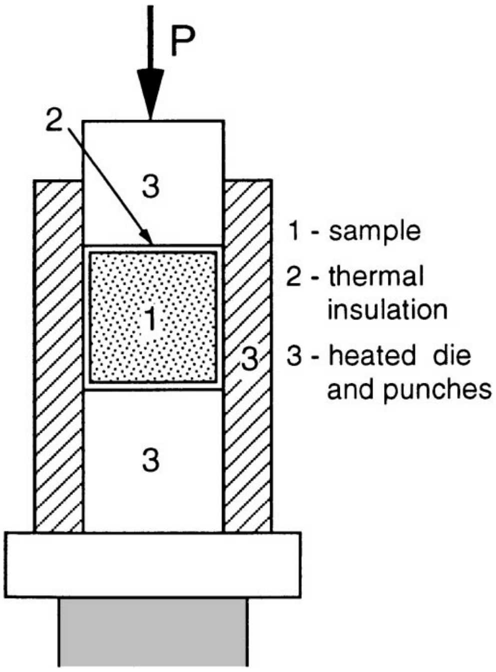


Fig. 1. Schematic of thermal explosion (SHS) under pressure in a preheated die.

under pressure can be obtained in any porous multi-component compact provided the processing temperature, T_0, is above T_m of at least one component, or above T_m of a eutectic phase that can be formed by any two components, and at least one component remains solid during processing. Compared to traditional melt infiltration, SDI has the advantage of the considerably shorter infiltration distances (microns versus millimeters/centimeters). SDI leads to full densification of the compact and, as will be discussed in the following section, it may or may not be followed by thermal explosion, depending on T_0 and on the exothermicity of the system. For the majority of the systems described in this paper, SDI was followed by thermal explosion, and we will refer to this route as SDI/TE. The pressure-temperature conditions for TE, SDI and SDI/TE processing routes of different in-situ composites studied in this work are shown in Table 1.

To ensure that thermal explosion does not occur before the pressure is applied, samples were thermally insulated by a $\sim$0·2 mm thick coating of an Y_2O_3 spray. Since the heating of the samples in 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. TE under pressure according to the scheme in Fig. 1 was performed for all the studied compositions.

In the other scheme of TE under pressure (Fig. 3), 18×4·5×25 mm compacts were put into a cold die and loaded to 150 MPa. TE was ignited using resistive heating by passing the electric current (DC) of 1000 to 1200 A/cm^2 through the sample for 2 s. Electric current-activated combustion synthesis was previously reported in Refs 21,22. The high current used ensured a very high heating rate and allowed to ignite the sample under the conditions of enhanced heat transfer into the cold die. To insulate the sample, the die walls were coated with a Y_2O_3 spray. In both TE schemes, the sample was held under pressure after thermal explosion for $\sim$1 min. and then unloaded and taken out of the die. The entire TE procedure was performed in open air. TE under pressure accord-

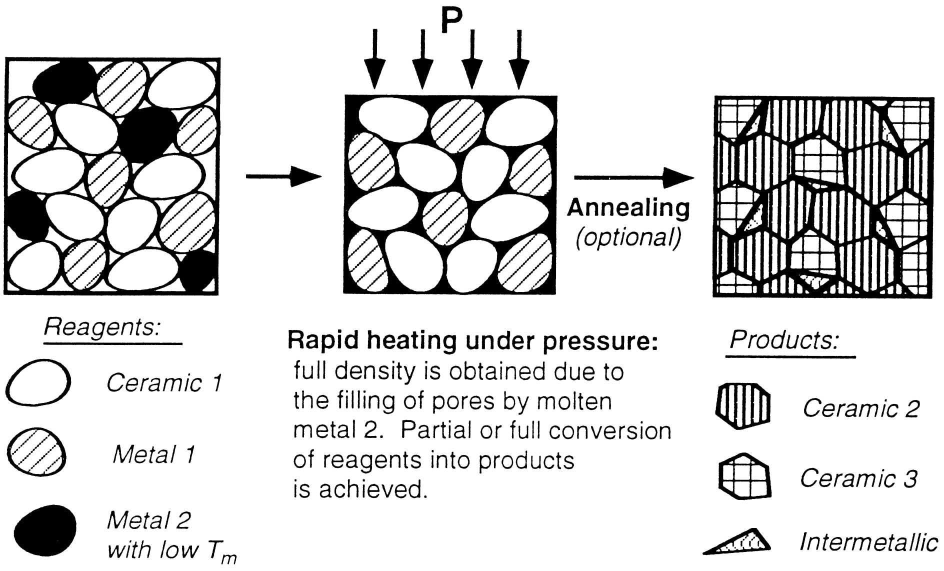


Fig. 2. Schematic of Short Distance Infiltration (SDI).

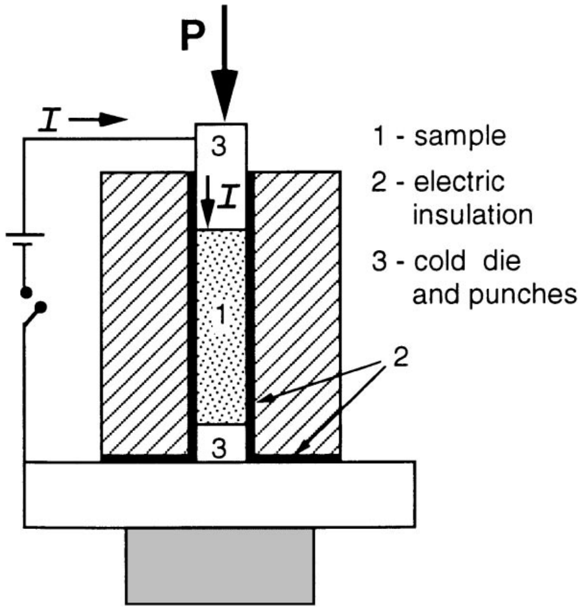


Fig. 3. Schematic of thermal explosion (SHS) under pressure ignited by passing electric current through the sample.

ing to the scheme in Fig. 3 was only attempted for B_4C–Ti–Ni and BN–Ti–Ni blends.

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^{-1}) 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^{-1}) heating result in the formation of strong interfacial barriers, preventing the reaction from becoming self-sustaining after T_{ig} has been reached. The pressure-temperature conditions for RHP processing route of different in-situ composites studied in this work are shown in Table 1.

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 Palmqvist[23] was used to calculate K_{1c}.

3 Results and Discussion

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 in-situ CMCs

3.1.1 Thermal explosion under pressure (TE)

Thermal explosion of B_4C–3Ti, 3SiC–8Ti and B_6Si–Ti blends in a pressure die at 1000–1100°C and 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 matrix composites, respectively, according to the following reactions:

$$B_4C + 3Ti \rightarrow 2TiB_2 + TiC;$$

$$3SiC + 8Ti \rightarrow 3TiC + Ti_5Si_3;$$

$$3B_6Si + 14Ti \rightarrow Ti_5Si_3 + 9TiB_2$$

Examples of the XRD patterns of the samples before and after combustion consolidation are shown in Fig. 4. For the 2BN–3Ti sample which, similarly to the above blends, could be ignited in a vacuum furnace at ~950°C, thermal explosion in the pressure die [with full conversion according to $2BN + 3Ti \rightarrow TiB_2 + 2TiN$, (Fig. 5)] occurred at a much higher temperature of $\geq$1250°C. This is believed to be a result of the enhanced heat transfer from the reaction zone to the die caused by the high thermal conductivity of BN. In spite of the presence of an insulating Y_2O_3 layer, thermal explosion of the 2BN–3Ti and B_4C–3Ti blends caused extensive melting of the pressure die, apparently due to the high exothermicity of the synthesis reactions (the calculated combustion temperature, $T_{comb} > 3000$ K). Representative microstructures of combustion synthesized in-situ CMCs are shown in Fig. 6. It can be seen that reasonably fine microstructures have been obtained for all the compositions with the grain size not exceeding several microns. Interestingly, the finest microstructure is observed in the sample explosively synthesized from the 2BN–3Ti blend, despite the highest preheating temperature.

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: $3Ti + Si + 2C \rightarrow Ti_3SiC_2$. 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.[24,25] 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. 7). 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 was dense with no residual porosity observed in SEM (Fig. 8). 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 concentration of C may allow one to obtain graphite-free dense $Ti_3SiC_2/Ti_5Si_3/TiC$ composites.

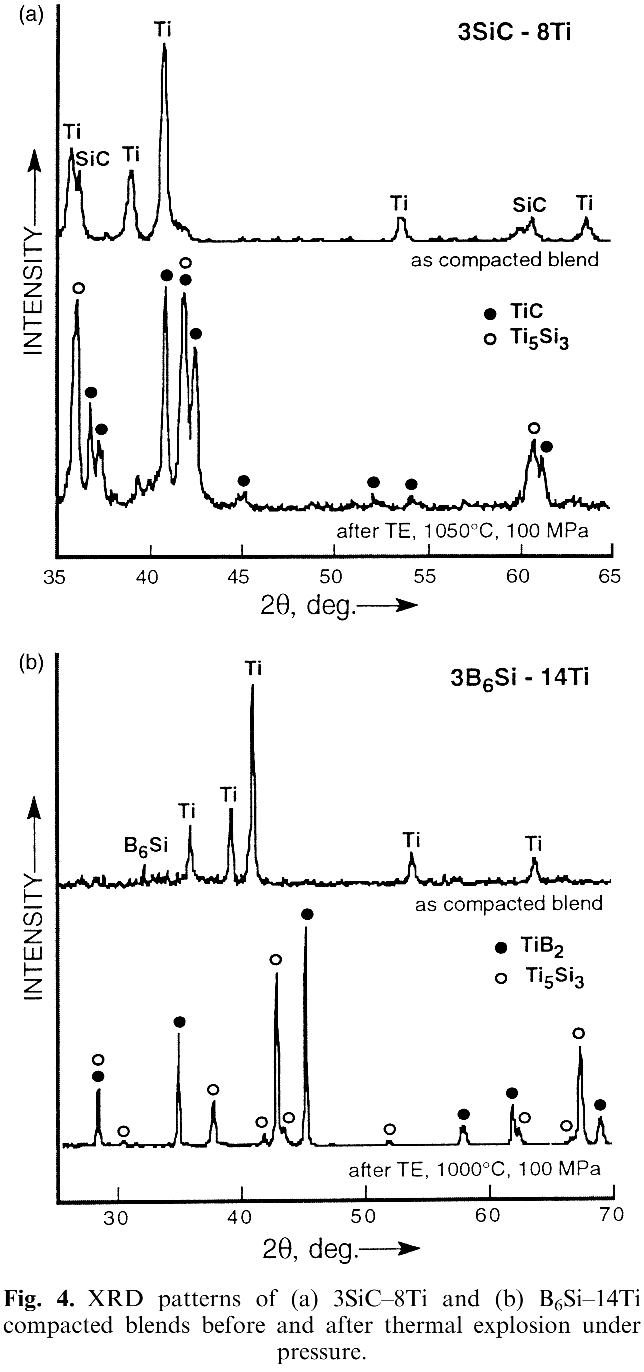


Fig. 4. XRD patterns of (a) 3SiC–8Ti and (b) B_6Si–14Ti compacted blends before and after thermal explosion under pressure.

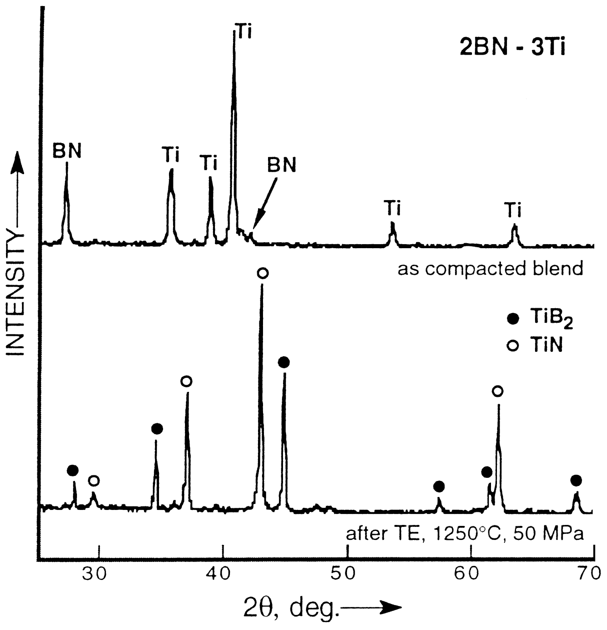
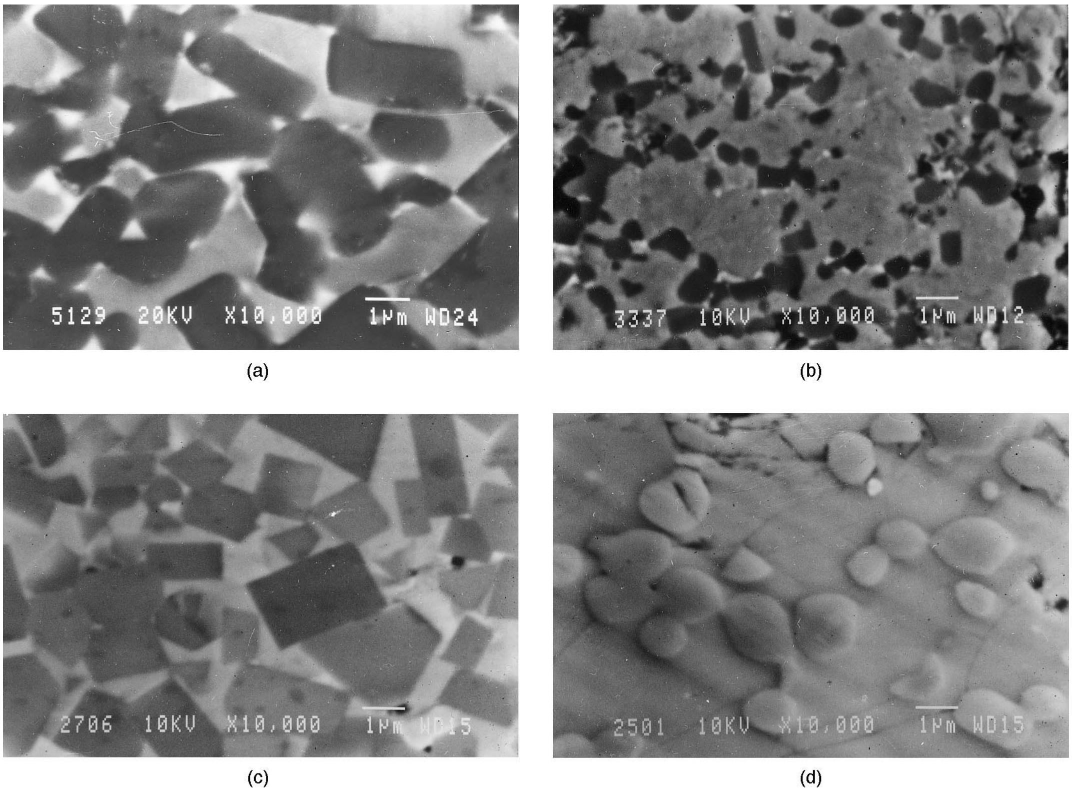


Fig. 5. XRD patterns of 2BN–3Ti compacted blend before and after thermal explosion under pressure.



(a) (b)

(c) (d)

Fig. 6. Representative microstructures of ceramic–ceramic composites synthesized via thermal explosion under pressure: (a) TiC–TiB_2; (b) TiN–TiB_2; (c) TiB_2–Ti_5Si_3; (d) TiC–Ti_5Si_3. SEM. The matrix phase is: (a) TiC, (b) TiN, and (c),(d) Ti_5Si_3; the particles are: (a)–(c) TiB_2, (d) TiC.

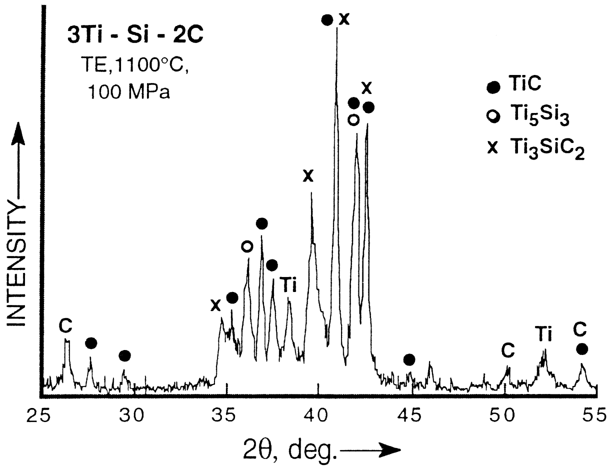


Fig. 7. XRD pattern of 3Ti–Si–2C compacted blend after thermal explosion under pressure.

3.1.2 Short distance infiltration/thermal explosion under pressure (SDI–TE)

In the SDI/TE route, thermal explosion was ignited by placing the sample into the die preheated above T_{ig} (Fig. 1), or by passing electric current through the sample (Fig. 3). The latter scheme was only attempted for B_4C–Ti–Ni and BN–Ti–Ni blends. For these compositions, similar final products were obtained by using either heating scheme. At the same time, extensive cracking of the materials synthesized via current-induced TE was observed, presumably due to the very rapid cooling of the sample in the cold die. It is believed that the problem can be overcome by preheating the sample together with the die to temperatures sufficiently low to prevent any solid state reaction from occurring prior to the onset of current-induced thermal explosion. In addition, the ignition of TE in such a preheated sample-die assembly will require a significantly lower current.

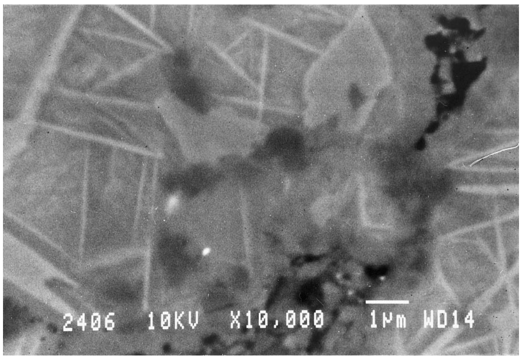


Fig. 8. A representative microstructure of the Ti_3SiC_2/Ti_5Si_3/TiC composite synthesized from 3Ti–Si–2C blend via thermal explosion under pressure. SEM.

The goal of adding Ni powder to the B_4C–3Ti blend (B_4C–3Ti–0·95Ni) 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. 9, full conversion of reagents into products was achieved according to the reaction: $B_4C + 3Ti + 0{\cdot}95Ni \rightarrow 2TiB_2 + TiC + 0{\cdot}95Ni$. The in-situ TiB_2–TiC–Ni composites synthesized had a fine microstructure with no residual porosity detected in SEM [Fig. 10(a),(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 at the periphery suggesting that the combustion temperature at the periphery was lower than in the center, 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, which is the calculated combustion temperature of the B_4C–3Ti–0·95Ni blend preheated

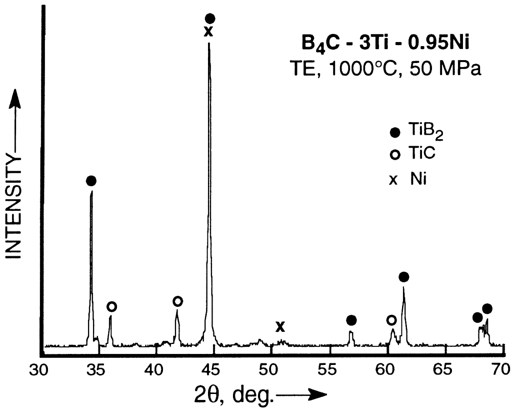


Fig. 9. XRD patterns of B_4C–3Ti–0·95Ni compacted blend after thermal explosion under pressure.

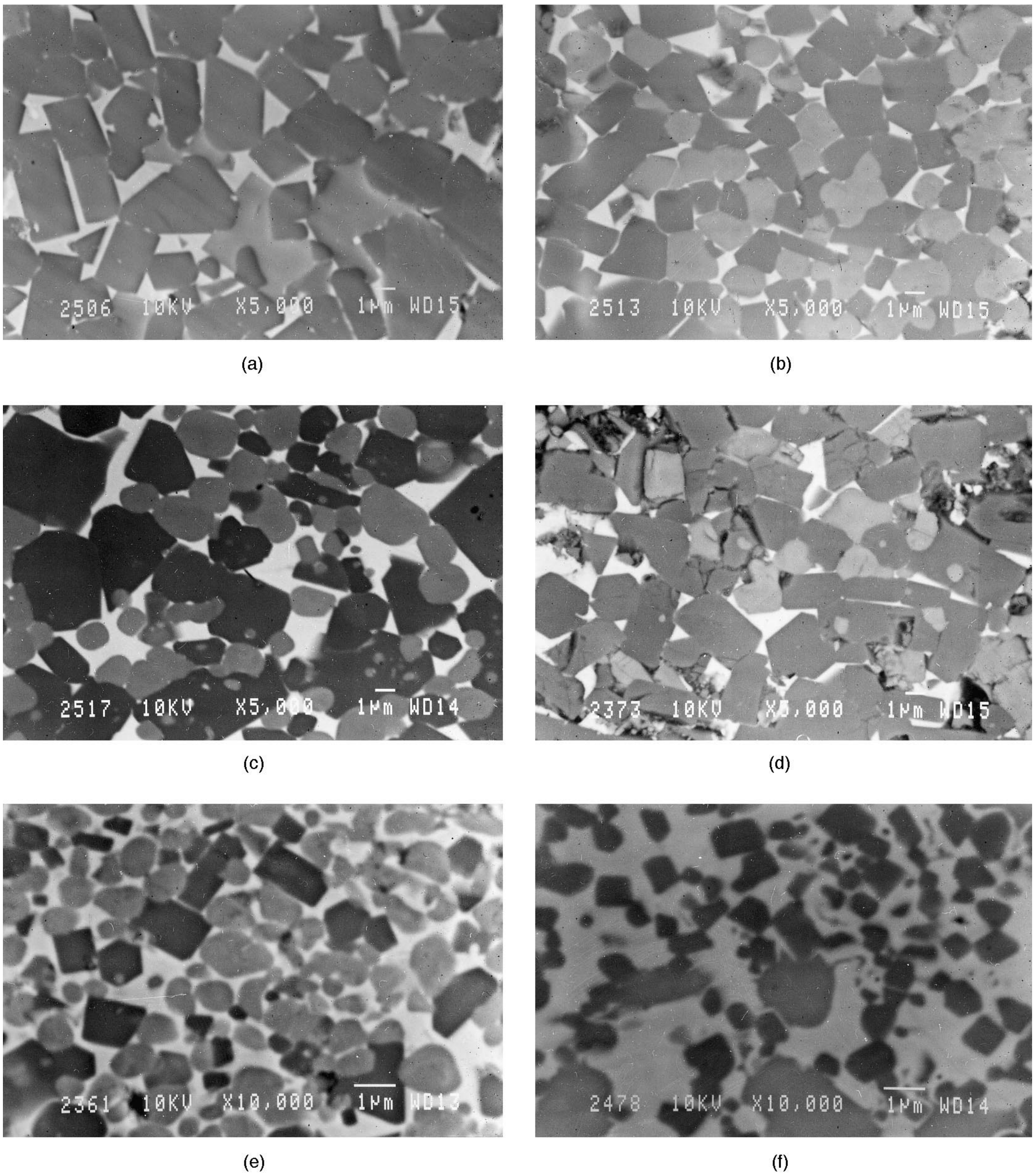


Fig. 10. Representative microstructures of Ni-toughened CMCs synthesized via thermal explosion under pressure: (a)–(d) TiB_2–TiC: (a) center and (b) periphery of the sample; (c,d) diluted with 0·3 and 2 moles of TiB_2, respectively; (e) TiB_2–TiN and (f) TiC–Ti_5Si_3. SEM.

to 1000°C. The high temperature, as well as the large amount of liquid during processing 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. 11(a)], 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 $(B_4C+3Ti+0{\cdot}95Ni)$ blend diluted with 8 wt% TiB_2 ($n=0{\cdot}3$) 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. 10(c), 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 $(B_4C+3Ti+0{\cdot}95Ni)$ blend diluted with 35 wt% (2 moles) TiB_2 is significantly lower than that of the undiluted blend (2721 versus 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.

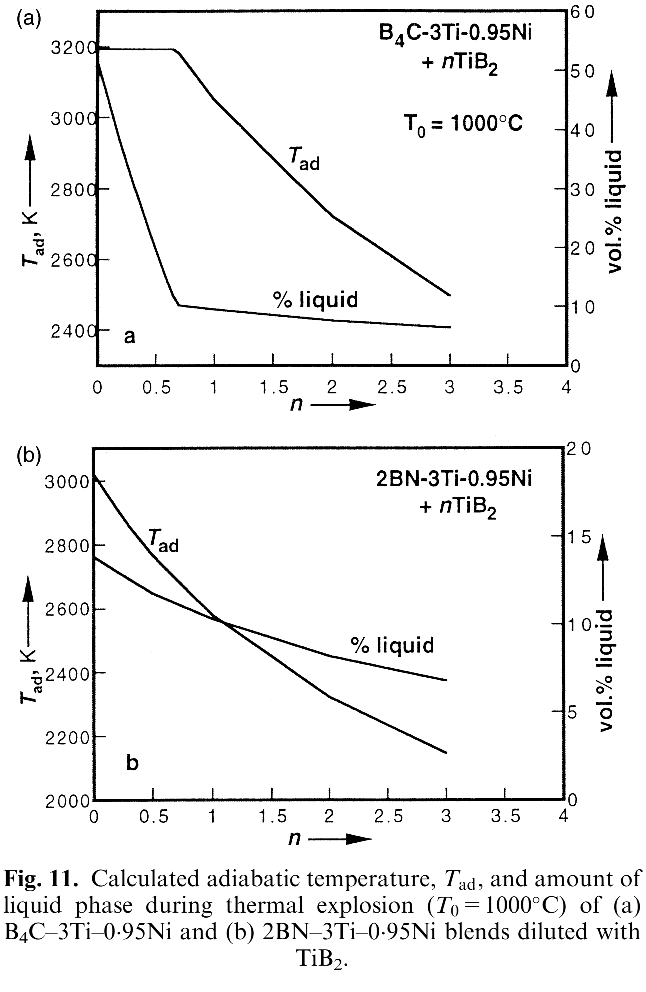


Fig. 11. Calculated adiabatic temperature, T_{ad}, and amount of liquid phase during thermal explosion ($T_0=1000°C$) of (a) B_4C–3Ti–0·95Ni and (b) 2BN–3Ti–0·95Ni blends diluted with TiB_2.

In the SEM micrograph [Fig. 10(d)], large colonies of TiB_2 diluent can be seen, cracked and 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 lower T_{ig} of thermal explosion under pressure which took place in the pure 2BN–3Ti blend only at ≥1250°C. With Ni added, thermal explosion occurred already at 1000°C and resulted in full conversion of reagents into products according to: $2BN+3Ti+0{\cdot}95Ni \rightarrow TiB_2+2TiN+0{\cdot}95Ni$. A representative microstructure of the sample after combustion consolidation is shown in Fig. 10(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 in-situ CMCs synthesized from the $(B_4C+3Ti+0{\cdot}95Ni)$ blend [Fig. 10(a) and (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 thermal explosion of the $(2BN+3Ti+0{\cdot}95Ni)$ blend [Fig. 11(b)], 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 in-situ CMCs. The synthesized TiB_2/TiN/Ni composite is very dense with practically no porosity observed in SEM. According to Fig. 11(b), dilution with only 8 wt% (0·3 mole) TiB_2 significantly lowers T_{comb} of the $(2BN+3Ti+0{\cdot}95Ni)$ blend. As a result, the diluted blend exploded at a higher temperature (1050°C), and full conversion has not been achieved.

Admixing various fractions of (2BN + 3Al) blend to the 2BN + 3Ti composition was aimed at promoting SDI/TE synthesis through the formation of a liquid phase (Al). It was expected, that, with the addition of n moles of (2BN + 3Al) to m moles of (2BN + 3Ti), the combustion product would be formed according to the reaction:

$$m(2BN+3Ti)+n(2BN+3Al) \rightarrow mTiB_2 \\ +2mTiN{+}nAlB2+2nAlN.$$

Thermodynamic calculations have shown, however, that, depending on the m/n ratio, products with different phase compositions should be obtained (Fig. 12). When Ti content in the starting blend is high ($m/n>0{\cdot}5$), a fully ceramic TiB_2–TiN–AlN product will be synthesized according to the reaction:

$$m(2BN + 3Ti) + n(2BN + 3Al) \rightarrow (m + n)TiB_2 + (2m - n)TiN + 3nAlN.$$

For $m/n = 0{\cdot}5$ ($n/m = 2$), the most thermodynamically feasible reaction will result in the formation of TiB_2 and AlN only according to:

$$(2BN + 3Ti) + 2(2BN + 3Al) \rightarrow 3TiB_2 + 6AlN.$$

It can be seen that all the available boron is bound by Ti, apparently due to the very high affinity of Ti for boron. For higher Al contents ($m/n < 0{\cdot}5$ or $n/m > 2$), thermodynamics predicts that, at T_{comb}, the reaction product will contain, in addition to TiB_2 and AlN, Al metal, free boron and AlB_{12} in different combinations. It is worth noting, that since the combustion product for $n/m > 2$ is partially liquid at T_{comb} [Fig. 12(b)], its phase composition can change on cooling to T_{room}. Thus, liquid Al can react with B and even with AlB_{12}, and a fully ceramic final product consisting of TiB_2, AlN and AlB_2 may be formed according to the reaction:

$$m(2BN + 3Ti) + n(2BN + 3Al) \rightarrow 3mTiB_2 + 2(m + n)AlN + 2(n - 2m)AlB_2.$$

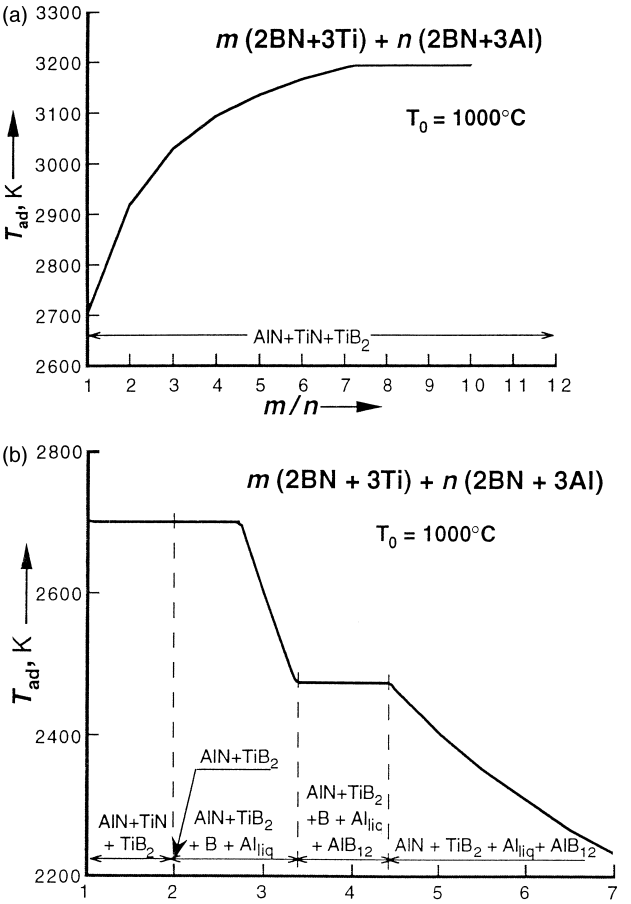


Fig. 12. Calculated adiabatic temperature, T_{ad}, during thermal explosion ($T_0 = 1000°C$) of m (BN + 3Ti) + n(BN + 3Al) blend for (a) $m/n \geq 1$ and for (b) $m/n \leq 1$ ($n/m \geq 1$).

The results of thermodynamic calculations in Fig. 12 were confirmed, at least for one composition, by performing thermal explosion in a 6BN–3Ti–6Al blend ($n/m = 2$). T_{ig} of such a blend was ~1050 and 1250°C in open air and in a pressure die, respectively. In both cases, the final combustion product consisted almost exclusively of TiB_2 and AlN (Fig. 13), which is quite in agreement with the thermodynamic predictions. A representative SEM micrograph of the TiB_2/AlN in-situ CMC explosively synthesized under a pressure of 50 MPa is shown in Fig. 14. The microstructure is fine with the dark matrix of AlN and bright TiB_2 particles easily distinguishable. It is worth noting that when the synthesis of a non-dense 6BN–3Ti–6Al compact was performed under pressure in the 800–1200°C temperature range, i.e. above T_m of Al but

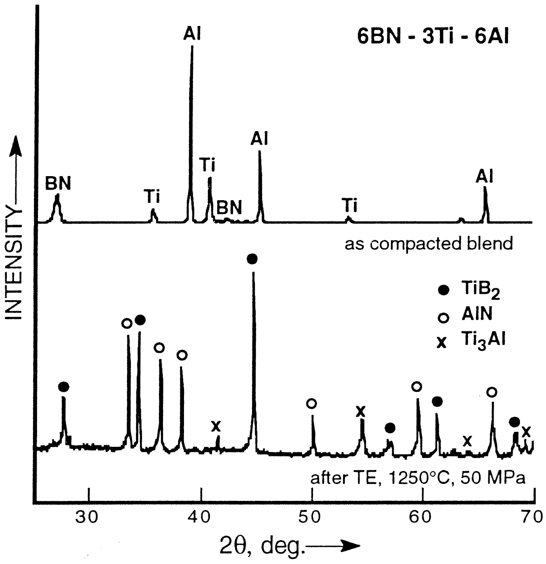


Fig. 13. XRD patterns of 6BN–3Ti–6Al compacted blend before and after thermal explosion under pressure.

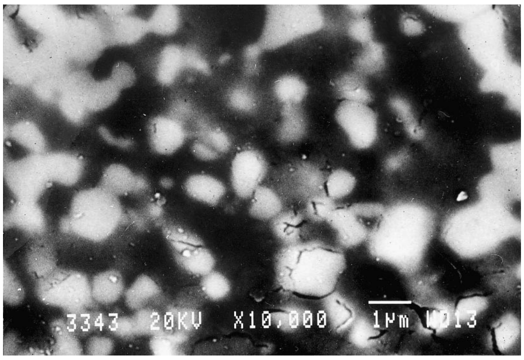


Fig. 14. A representative microstructure of the TiB_2/AlN composite ceramic synthesized via thermal explosion under pressure. SEM.

below T_{ig}, a fully dense material was obtained containing Al_3Ti, Ti metal and unreacted BN, but no traces of TiB_2 or AlN. Apparently, the temperature-pressure processing conditions allowed to achieve complete infiltration of liquid Al into pores accompanied by reaction between the Al melt and solid Ti, but were insufficient to ignite self-sustaining SHS reaction between BN and the metal powders. This suggests that in the 6BN–3Ti–6Al system, the conditions for SDI are different from those for TE, and SDI is not necessarily followed by thermal explosion. This is in contrast to the B_4C–3Ti–0·95Ni and 2BN–3Ti–0·95Ni systems, where T_{ig} is very close to T_m of the Ti–Ni eutectic, and SDI is practically always accompanied by TE.

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. 15. 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. 10(f)].

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.[26] 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 in situ CMC must be the result of its very fine microstructure. K_{1c} of the Ni-containing TiC/Ti_5Si_3 in situ 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.

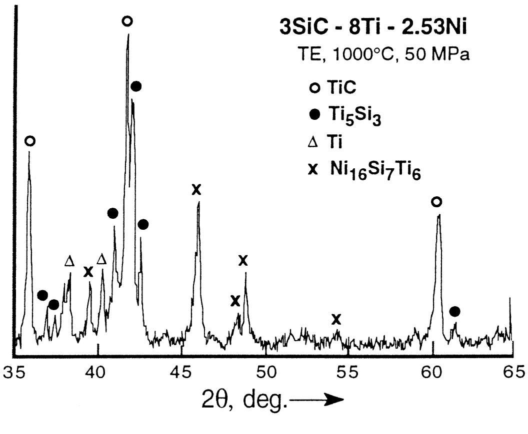


Fig. 15. XRD pattern of 3SiC–8Ti–2·53Ni compacted blend after thermal explosion under pressure.

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. 16(a)], 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. 17(a)], unreacted BN is still present after 4 h RHP at 1100°C, along with TiB_2, TiB, TiN and Ti_2N.

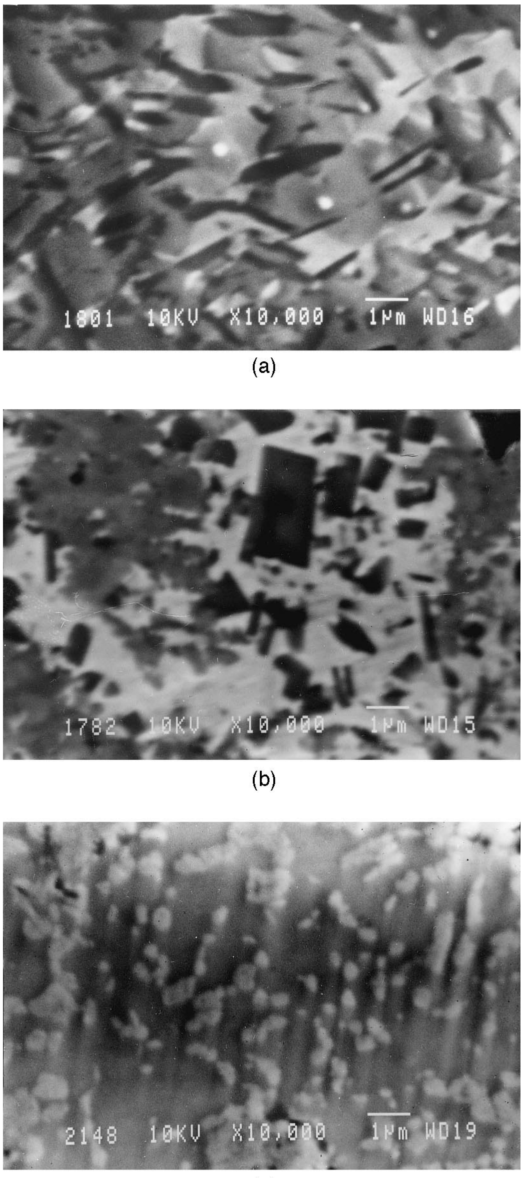


Fig. 16. Representative microstructures of CMCs synthesized via RHP: (a) TiB_2–TiC_{1-x} with residual B_4C; (b) TiB_2–TiN–Ni/Ni_3Ti; (c) TiC_{1-x}–Ti_5Si_3 with residual SiC. SEM.

With the addition of Ni, the RHP synthesis in the B4C–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. 16(b)].

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. 17(b)]. A SEM micrograph in Fig. 16(c) shows that the microstructure of the RHPed sample is much finer than that of thermally exploded one [Fig. 6(d)]. 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% versus−18·9% for $B_4C + 3Ti \rightarrow 2TiB_2 + TiC$, for example), that can be accommodated even under the relatively low applied pressure of 150 MPa.

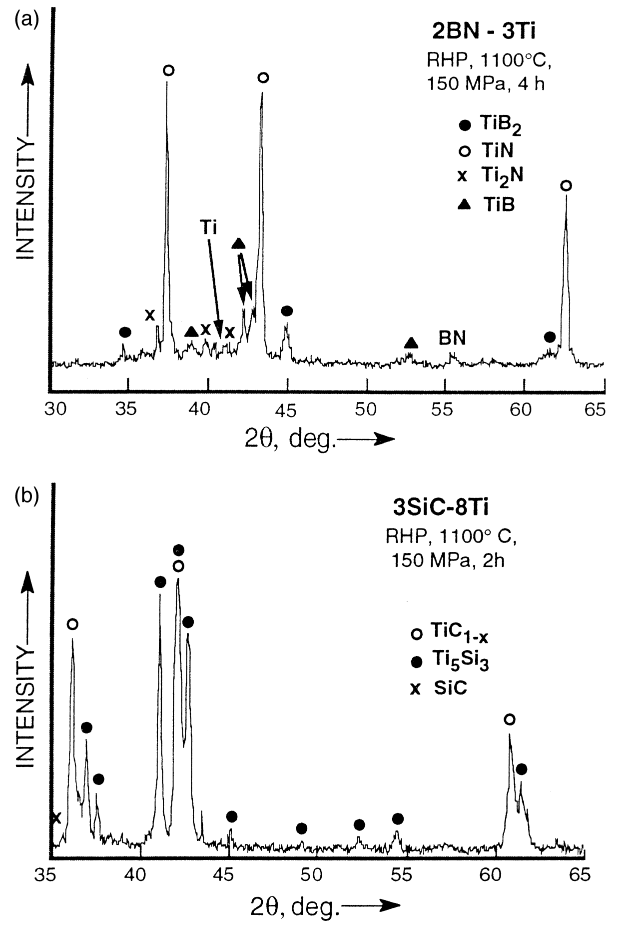


Fig. 17. XRD patterns of dense 2BN–3Ti (a) and 3SiC–8Ti (b) blends after reactive hot pressing.

3.2 Reactive processing of alumina-based in-situ 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. An example of the XRD patterns of a $3TiO_2$–7Al powder blend before and after TE at 950°C, 100 MPa is shown in Fig. 18. Thermal explosion was expected to proceed according to $3TiO_2 + 7Al \rightarrow 2Al_2O_3 + 3TiAl$. It can be seen that, indeed, all the available oxygen was bound by Al with the formation of Al_2O_3. Instead of TiAl, however, a mixture of TiAl, Ti_3Al and $TiAl_2$ was formed. The formation of intermetallics other than TiAl is, probably, due to partial oxidation of the starting Al powder, resulting in less Al available for the synthesis reaction. As can be seen in Fig. 19, combustion consolidation of the $3TiO_2$-7Al blend yields a composite material with fine microstructure consisting of the dark Al_2O_3 and the bright Ti–Al phases.

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.

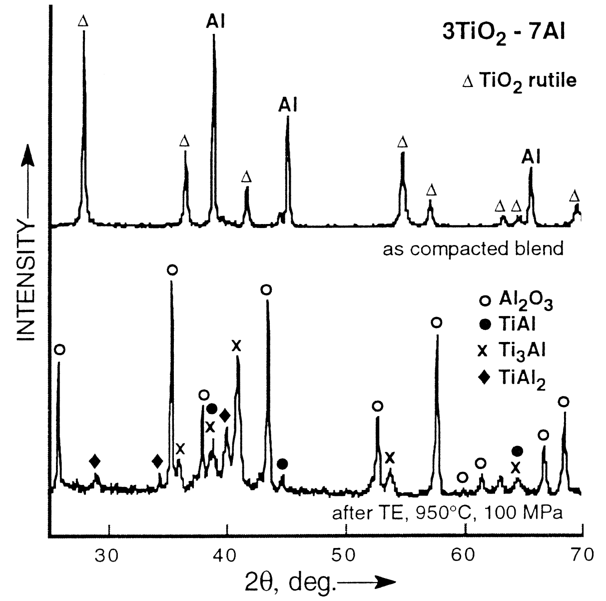


Fig. 18. XRD patterns of $3TiO_2$–7Al compacted blend before and after thermal explosion under pressure.

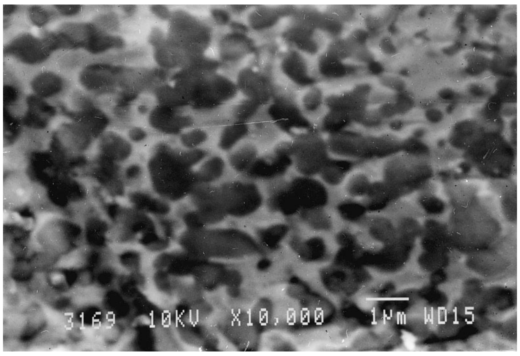


Fig. 19. A representative microstructure of an Al_2O_3–Ti_3Al composite synthesized via thermal explosion under pressure.

4 Conclusions

Various in-situ non-oxide and oxide ceramic matrix composites, based on TiB_2/TiC, TiB_2/TiN, TiB_2/AlN, TiB_2/Ti_5Si_3, Ti_5Si_3/TiC and Al_2O_3, were synthesized by pressure-assisted reactive processing. For a number of compositions, the brittle ceramic matrix was toughened with Ni metal or Ti-Al intermetallics. Near fully dense materials characterized by full conversion of reagents into products were fabricated via thermal explosion in a pressure die preheated to 1000–1250°C under a moderate pressure of ≤ 150 MPa. Such combustion-synthesized in-situ CMCs had reasonably fine microstructures with the grain size ranging from 1 to 5 μm. A remarkably fine submicron-scale microstructure was obtained in the TiB_2/TiN/Ni in-situ CMC combustion-synthesized from a 2BN–Ti–0·95Ni blend. For comparison, reactive hot pressing yielded composites with typically finer microstructures, however full conversion of reagents into products has not been achieved. 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. High fracture toughness values were measured in Ni-containing in-situ CMCs fabricated via thermal explosion under pressure, especially in those where Ni was present as a metallic phase. Thus, $K_{1c} = 20{\cdot}5$ and $11{\cdot}9\,\mathrm{MPa}\sqrt{m}$ were measured in the TiB_2/TiN/Ni and TiB_2/TiC/Ni composites, respectively, indicating the toughening effect of the finely dispersed ductile Ni phase. On the whole, thermal explosion under pressure is a potent technique for the in-situ processing of dense ceramic matrix composites of various compositions.

Acknowledgements

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