journal

Reactive Hot Pressing of Titanium Nitride-Titanium Diboride Composites at Moderate Pressures and Temperatures

Lingappa Rangaraj and Canchi Divakar

High Pressure Laboratory, Materials Science Division, National Aerospace Laboratories, Bangalore 560017, India

Vikram Jayaram*

Department of Metallurgy, Indian Institute of Science, Bangalore 560012, India

Dense composites in the Ti-B-N system have been produced by reactive hot pressing of titanium and BN powders. The effect of the addition of a small amount of nickel (1-3 wt%) on the reaction kinetics and densification of TiN–TiB_2 (40 vol%) composite has been studied. Composites of ~99% of theoretical density have been produced at 1600°C under 40 MPa for 30 min with 1% nickel. The hardness and fracture toughness of these composites are 24.5 ± 0.97 GPa and 6.53 ± 0.27 $MPa \cdot m^{1/2}$, respectively. The microstructural studies on samples produced at lower temperatures indicate the formation of a transient liquid phase, which enhances the kinetics of the reaction and densification of the composite.

I. Introduction

REFRACTORY transition-metal borides, carbides, and nitrides are candidates for applications that require hardness and wear resistance, especially at elevated temperatures. One of the attractive systems, by virtue of the stability and hardness of the constituents, is the TiN–TiB_2 system, which is the focus of the present work. Titanium-based ceramics (borides, carbides, and nitrides) are an outstanding group of refractory materials with high hardness, elastic modulus, and abrasion resistance, good high-temperature strength, and moderate high-temperature oxidation resistance. Titanium-based ceramics possess good electrical and thermal conductivity compared with those of alloyed metals; thus, they can be electrical discharge machined. Because the melting temperatures of TiN and TiB_2 are extremely high, pressureless sintering of these materials, in monolithic and composite form, requires high temperatures. High-temperature sintering studies that have yielded moderate to high relative densities include those of Shobu and Watanabe[1] on $Ti(C_{0.5}N_{0.5})$–30% TiB_2, $Ti(C_{0.5}N_{0.5})$–60% TiB,, and TiN–30% TiB_2 composites at 1900°C, Watanabe *et al.*[2] on Ti(CN)–30% TiB_2 at 1700°–2000°C, Shobu *et al.*[3] on hot pressing of TiN–(20%–80%) TiB_2 at 1800°–1850°C, and Graziani *et al.*[4] on hot pressing and sintering of TiN–20% TiB_2 with 1–1.5 wt% nickel at 1700°-2150°C.

To circumvent the high sintering temperatures needed, reactive processing methods have been evolved to enable the achievement of high density at reasonable temperatures. Zhang and co-workers[5,6] studied the reactive hot pressing (RHP) of TiH_2 + BN + B_4C (with 2 wt% nickel as an additive) at 1850°C and 25 MPa to yield TiB_2 and $Ti(C_{0.5}N_{0.5})$ and that of TiH_2 + BN with 0-5 wt% nickel as an additive. In the latter case, the reaction kinetics showed the formation of TiN at 1000°C, TiB_2 at 1200°C, and the reaction completing at 1600°C to yield a stoichiometric mixture of TiN and TiB_2. The composites hot-pressed at 1850°C under 30 MPa for 30 min without nickel showed 98% relative density (RD), whereas the addition of 1 wt% nickel increased the RD to 99.9% and further addition of nickel (2 wt%) appeared to decrease the RD to 99.2%, Tomoshige *et al.*[7] produced TiB_2–TiN (10–60 mol% TiN) composites by combustion synthesis using titanium, boron, and BN powders. Lee *et al.*[8] used field activation to produce nanocrystalline TiB_2–TiN composite starting with titanium, boron, and BN powders followed by densification up to 90%–97% RD.

The reactive hot pressing of titanium and BN mixtures with substantial nickel additions has been studied by several processes, including thermal explosion and high-pressure consolidation.[9–11] The 3Ti-2BN blends with the stoichiometric ratio for full conversion to TiN and TiB_2, treated at 1100°C, showed incomplete reaction, and compositions with nickel addition showed very fine microstructures of TiN and TiB_2, with substantial amounts of nickel and Ni_3Ti. The significant densification of such a stoichiometric blend with large amounts of nickel at 1200°C for 20 h resulted in full conversion of reactants to products with final RD of ~92%, but with substantially decreased hardness, compared with the metal-free composite, because of the large amount of retained nickel. High RD values (99%) were obtained when pressure-assisted thermal explosion at 1000°–1100°C was used. The morphology of the phases showed that TiN was most probably formed by interfacial reaction between BN and liquid Ti_2Ni, whereas TiB, was formed by a dissolution and reprecipitation mechanism.

Our point of departure is to address the relative luck of attention paid to the conditions under which a predominantly ceramic composition can be produced by simple hot pressing, i.e., in the absence of explosions and high pressure, and also with the least addition of nickel, which otherwise is deleterious to the hardness of the composite. In the presence of nickel, transient liquid phases can persist below the melting point of nickel because of the presence of deep eutectics in the Ni–Ti system. Such a liquid is undoubtedly the cause of rapid densification and reaction when large amounts (25-30 wt%) of nickel are added. However, the situation can be markedly different when this amount is decreased to ~1%. The present investigation accordingly has been undertaken to establish the conditions for reaction kinetics and mechanisms of densification in stoichiometric mixtures of titanium and BN.

II. Experimental Procedures

The TiN–TiB_2 composite was produced by the reactive hot pressing of titanium and BN powders using the reaction

$$3Ti + 2BN \rightarrow 2TiN + TiB_2$$

Z. A. Munir—contributing editor

Manuscript No. 10381. Received July 11, 2003; approved April 28, 2004.
Based in part on the dissertation submitted by L. Rangaraj for the degree M.Sc. in Engineering, Indian Institute of Science, Bangalore, India, 2003.
*Member, American Ceramic Society.

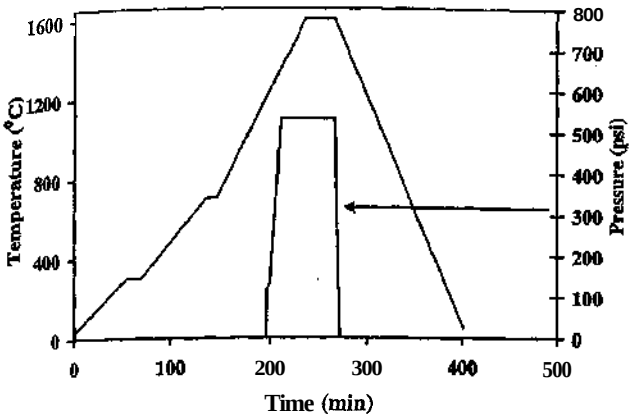

Fig. 1. Typical temperature–time–pressure cycle used to prepare composite at 40 MPa and 1600°C for 30 min. Oil pressure in the ram is shown. Load application was initiated at 1200°C and final pressure reached in 15 min.

(1) Materials and Process

The raw materials used were titanium powder ~99.5% pure and particle size ~10–15 μm (SPMS Powder Metal, France), BN powder ~99.5% pure and particle size ~5 μm (Alpha Chemicals, India), and nickel powder —99.5% pure and particle size ~4 μm (INCO, London, U.K.). The required amounts of titanium and BN powders (74.32 and 25.68 wt%) were mixed in a centrifugal ball mill (Model Pulverisette 6, Fritsch, Oberstein, Germany) for 24 h in hexane medium. The mixing was conducted at a ball:powder ratio of 10:1. The powder mixtures were dried at —100°C for ~5 h. Powder mixtures with various amounts of nickel also were prepared. The dried powder mixtures were hot-pressed in a high-density graphite die (internal diameter 25-30 mm and height 70 mm). To avoid direct contact between the powder and the die/punch assembly, flexible graphite sheet (0.2 mm thick) was used. The RHP experiments were conducted in a vacuum hot press (Materials Research Furnaces, Suncook, NH).

A typical reactive hot-pressing experiment involved the following steps. After the furnace was evacuated to 5 X 10^{-5} torr (6.5 mPa), the samples were heated to 300°C at 5°C/min, held for 30 min to remove gases present on the surface of the particles, and heated to 700°C at 6°C/min and held for 10 min. The samples were finally heated to the required temperature at 10°C/min and held for various times (1-30 min). The pressure of 40 MPa was usually applied within 15 min before reaching the final temperature, held for the required time, and released after 5 min during the cooling cycle. Oil pressure of 532-745 lb/in.^{2} (3.67-5.14 MPa) was generated to apply 40 MPa pressure on the sample. The assembly was cooled at 10°C/min. Typical time-temperature and time-pressure cycles are shown in Fig. 1.

Most of the experiments were conducted in the temperature range 1400°–1850°C for 30 min with and without nickel addition. The application of pressure was started at 1200°C and required pressure (40 MPa) reached in 15 min. The effect of an early application of pressure and nickel addition on the reaction kinetics and densification in the RHP experiments was studied in the temperature range 1100°–1475°C for 1-30 min. In these latter experiments, the application of pressure was started at 950°C and required pressure (40 MPa) reached in 15 min.

(2) Characterization

The top and bottom surfaces of reactive hot-pressed composites were ground and polished using SiC abrasive paper and diamond paste down to 1 μm, followed by ultrasonic cleaning with alcohol. X-ray diffraction (XRD) patterns were recorded (Philips, Eindhoven, The Netherlands), using Cu$K\alpha$ radiation with a graphite monochromator in the diffracted beam and a reflection geometry to identity phases present and determine the lattice parameter of TiN in the composite. Density and porosity measurements were conducted using the Archimedes method after boiling the samples in water for 1 h and cooling to room temperature. Vickers hardness measurements (Model HSV-20, Shimadzu Co., Kyoto, Japan)

Table I. Properties of Composites Produced without and with Nickel Addition†

Sample No.	Experimental conditions (MPa/°C/min) (with Ni addition)	Density (g/cm^3) (%RD)	Porosity (%)	Hardness (GPa)	Fracture toughness (MPa·m$^{1/2}$)
1	40/1400/30	3.9711 ± 0.0016 (78.5)	9.14		
2	40/1600/30	4.4975 ± 0.0025 (88.8)	2.08	16.8 ± 2.33	
3	40/1750/30	4.9420 ± 0.0008 (97.6)	0.6	24.0 ± 0.9	5.68 ± 0.28
4	40/1850/30	4.9718 ±0.0006 (98.2)	0.1	24.5 ± 0.72	6.03 ± 0.4
5	40/1400/1 (1%)	4.7151 ± 0.0105 (92.73)	0.75	17.2 ± 1.76	
6	40/1400/30 (1%)	4.9322 ± 0.0056 (97)	0.09	21.34 ± 1.6	
7	40/1550/1 (1%)	4.8559 ± 0.0036 (95.5)	0.77	19.6 ± 0.87	6.76 ± 0.18
8	40/1600/1 (1%)	4.9169 ± 0.0053 (96.7)	0.33	22.4 ± 0.77	5.35 ± 0.52
9	40/1600/15 (1%)	5.0085 ± 0.0043 (98.5)		23.4 ± 0.46	5.89 ± 0.52
10	40/1600/30 (1%)	5.0593 ± 0.0029 (99.5)		24.6 ± 0.97	6.53 ± 0.27
11	40/1750/30 (1%)	4.9627 ± 0.0026 (97.6)			
12	40/1400/1 (3%)	4.9446 ± 0.0049 (96.4)	0.565	16.9 ± 1.32	
13	40/1400/30 (3%)	4.9754 ± 0.0014 (97)	0.34	19.9 ± 0.93	
14	40/1600/30 (3%)	5.0266 ± 0.0014 (98)		22.7 ± 1.25	6.39 ± 0.15

†Pressure application was started at 1200°C.

were performed on a tester at a test load of 500 g (4.9 N) and a holding period of 15 s. An average of 10-15 readings was taken for each reported value. The indentation fracture toughness was determined by measuring the radial crack lengths on samples at a test load of 10-20 kgs (98-196 N). The equation derived by Niihara *et al.*[12] was used to calculate the fracture toughness (K_{IC}) of the composite. Microstructural observations of polished surfaces were made using optical microscopy and scanning electron microscopy (SEM; Model 440i, LEO Electron Microscopy, Fort Cambridge, U.K.) with energy-dispersive X-ray analysis (EDAX).

III. Results

Initially, the results on the composites produced with and without nickel addition in the temperature range 1400°–1850°C for 1-30 min are presented. The role of nickel addition and effect of pressure application at lower temperature in the temperature range 1100°–1475°C for 1 min are described later. The experimental conditions and properties of the composites are presented in Table I.

(1) *High-Temperature Densification (1400°–1850°C)*

The XRD patterns of the pressed surface of the composites without nickel addition produced at 40 MPa and 1400°–1850°C for 30 min are shown in Fig. 2. At 1400°C, the strong peaks of TiN and TiB_2 with a weak signal of the BN 100% peak are evident. However, the BN peak does not appear on the surface parallel to the loading direction. The appearance of BN at the surface of the pellet may be due to the loss of some titanium in reaction with the graphite die. Density of the composite produced at 1400°C is only 78.5% RD. At ~1600°C, the reaction is completed and the density is 89% RD. The samples show an improvement of density as the temperature increases: 78.5% at 1400°C to 98.2% at 1850°C (Table I).

The addition of 1% nickel helps in the improvement of density to 97% (1400°C for 30 min) and 99.5% (1600°C for 30 min). The density-temperature plots of the composites produced with 1% nickel and without nickel for 30 min are shown in Fig. 3. The density of the composite with 1% nickel produced at 1600°C shows the increase in density from ~96.5 to >99.5% as the time increases from 1 to 30 min. At 1400°C, the corresponding increase in density is from 93% (1 min) to 97% (30 min).

The variation of density as a function of nickel content of the composite produced at 1400° and 1600°C under 40 MPa for 30 min is shown in Fig. 4. At 1400°C, the density increases from 78.5% to 97% with 1% nickel addition and does not improve with further addition of nickel (3%). At 1600°C, the density increases from 89% to 99.5% with 1% nickel, and further increase in nickel (3%) content decreases the density to 98%. The major role of nickel lies in its ability to complete densification by 1600°C and its impact at higher temperatures is marginal. Experiments conducted at 1400°C, which is lower than the melting point of nickel, demonstrate the dramatic role of nickel in enhancing densification, The addition of nickel in quantities as small as 1% enables near-theoretical densities (99.5%) to be reached at temperatures as low as 1600°C. Such a material possesses a hardness as high as 24.5 GPa, which is comparable with the hardness achieved without nickel in samples of similar RD that are produced at 1750°-1850°C (Table I). Typical optical micrographs of the composites produced without and with nickel at 1400°C for 30 min are shown in Fig. 5. The addition of nickel shows substantial decrease in porosity. Typical SEM micrographs of the composites with 1% and 3% nickel produced at 1600°C for 30 min are shown in Fig. 6. Residual nickel is shown as bright particles that are located at interphase boundaries.

TiN can form over a wide range of nonstoichiometric compositions with various N:Ti ratios.[13] The lattice parameter of TiN in composites without and with nickel addition is 4.2419-4.2439 A and 4.2439-4.2441 A, respectively, which is very close to the theoretical value 4.24193 A (Powder Diffraction File (PDF) No. 38-1420, International Centre for Diffraction Data, Newtown Square, PA). The lattice plane spacings are close to the values for monoliths of TiN and TiB, (PDF No. 35-0741) and are in agreement with those obtained by combustion synthesis.[7] These results indicate that stoichiometric TiN is produced in the composite (in solid-state reactions), unlike substoichiometric TiN in vapor-phase reactions.[13,14]

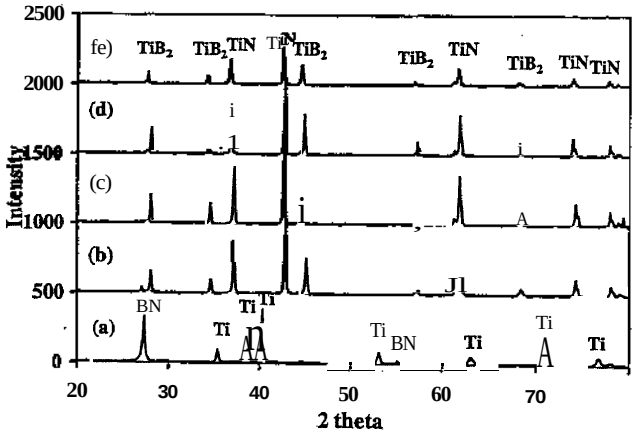

Fig. 2. XRD patterns of (a) powder mixture and the composite produced at 40 MPa for 30 min at (b) 1400°, (c) 1600°, (d) 1750°, and (e) 1850°C. Reaction is completed at ~1400°C and the only identified phases are TiN and TiB_2.

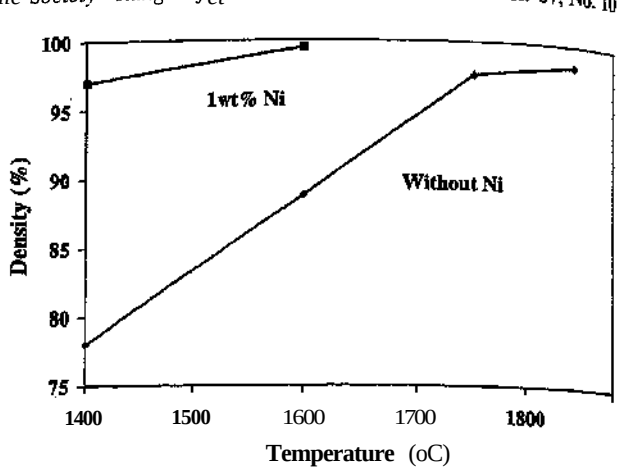

Fig. 3. Density versus temperature plot of the composite produced at 40 MPa for 30 min without and with 1% nickel addition. Improvement of density with nickel addition is evident.

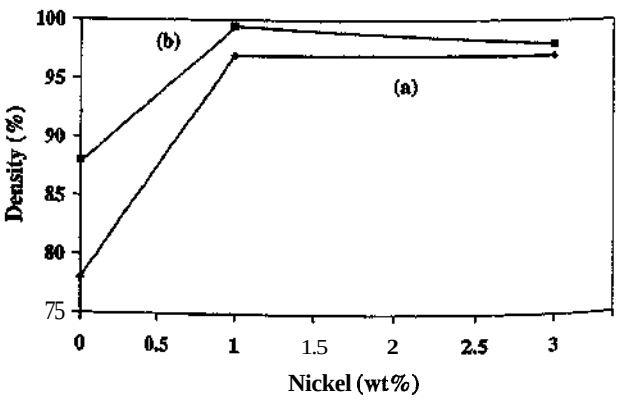

Fig. 4. Density versus nickel content plot of the composite produced at 40 MPa for 30 min at (a) 1400° and (b) 1600°C. Large increase in density (78%–97%) is observed at 1400°C with 1% nickel. Higher temperature (1600°C) is required to obtain samples with ~99.5% (theoretical density).

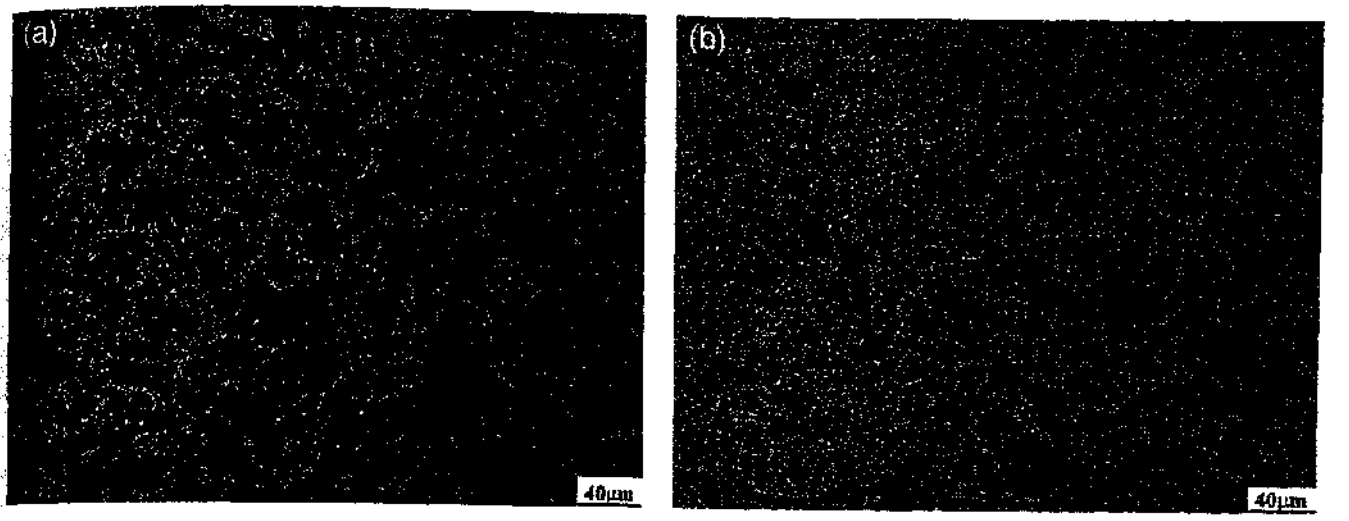

Fig. 5. Optical micrographs of the composite produced at 40 MPa for 30 min at (a) 1400° and (b) 1400°C with 1 % nickel addition. Dark regions are pores; decrease in porosity is evident with addition of nickel.

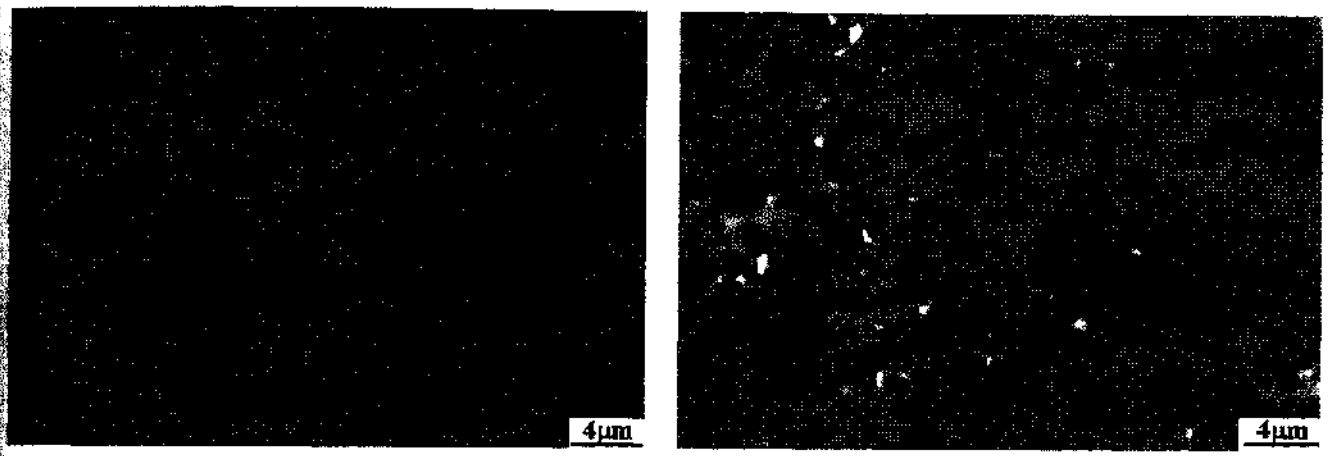

fig. 6. SEM micrographs of composite produced at 40 MPa and 1600°C for 30 min with (a) 1% and (b) 3% nickel. Light gray, dark gray, and bright particles are TiN, TiB_2, and nickel phases, respectively. TiB_2 phase is surrounded by TiN phase.

(2) Low-Temperature Densification (1100°–1475°C)

The results of reactive hot-pressing experiments at lower temperatures are now presented to understand the reaction kinetics and densification mechanisms involved. The role of nickel is not confined to aiding densification (Table II), but also in promoting the reaction between titanium and BN. The reaction is completed at 1200°C with 1% nickel and at 1100°C with 3% nickel (XRD patterns in Fig. 7). The presence of 1% nickel brings about a change in composite density from 86% to 97% when produced at 1200°–1475°C after 1 min and is higher than 78% density achieved at 1400°C after 30 min without nickel. Typical optical microstructural observations in samples containing 1% nickel

Table II. Properties of Composites with Nickel Addition†

Sample No.	Experimental conditions (MPa/°C/min) (with Ni addition)	Density (g/cm^3) (%RD)	Porosity (%)	Hardness (GPa)
15	40/1100/1 (1%)	3.5593 ± 0.03 (70)	6.2	
16	40/1200/1 (1%)	4.3729 ± 0.0009 (86)	2.06	12.21 ± 0.74
17	40/1300/1 (1%)	4.7288 ± 0.0029 (93)	0.12	21.48 ± 1.53
18	40/1475/1 (1%)	4.9627 ± 0.0017 (97)	0.02	21.59 ± 0.37
19	40/1475/30 (1%)	4.9475 ± 0.0006 (97.3)	0.01	22.18 ± 1.20
20	40/1100/1 (3%)	4.2059 ± 0.0184 (82)	6.75	
21	40/1475/30 (3%)	4.9703 ± 0.0016 (97.5%)		

†Pressure application was started at 950°C.

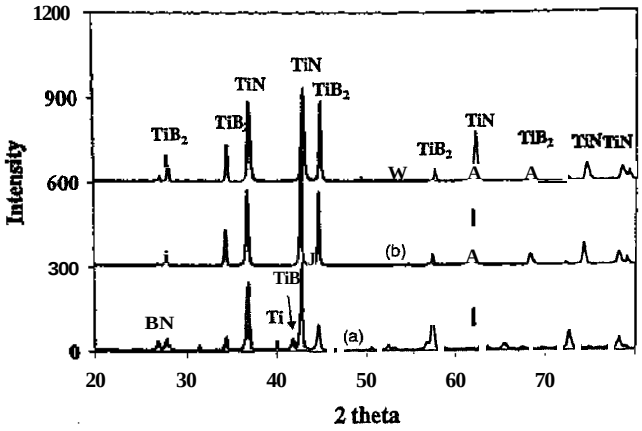

Fig. 7. XRD patterns of the composite produced at 40 MPa for 1 min with 1% nickel at (a) 1100° and (b) 1200°C and (c) 3% nickel at 1100°C. Load application was initiated at 950°C. Reaction is completed at ~1200°C with 1% nickel and at ~1100°C with 3% nickel.

reveal unreacted metallic phase at 1100°C for 1 min (Fig. 8(a)), whereas XRD observations indicate the presence of titanium. EDAX analyses in the SEM (Fig. 9) of regions optically identified as metallic in nature in the composite with 3% nickel (1100°C for 1 min) indicate the presence of intermetallic phases with compositions ranging from 27 to 88 at.% nickel.

A clear beneficial effect of the application of pressure at low temperature is shown by the final density (Table III). Increasing the amount of nickel from 1% to 3% results in acceleration of the reaction and of densification up to 1400°C but leads to a marginally lower density at 1600°C; i.e., the maximum density achievable seems to decrease even though it increases during the earlier stages.

IV. Discussion

The role of nickel addition on reaction kinetics and densification of the composites have been presented. We now examine the above results in relation to the phase diagram of Ti–Ni and earlier reports on liquid-phase-assisted reactive hot pressing. The following trends are clear:

(1) Up to and below 1600°C, nickel is beneficial in densification.

(2) The maximum density achieved below 1500°–1600°C does not reach theoretical density but falls short by ~3%, irrespective of the heating schedule used.

(3) Above 1600°C, the role of nickel is less significant.

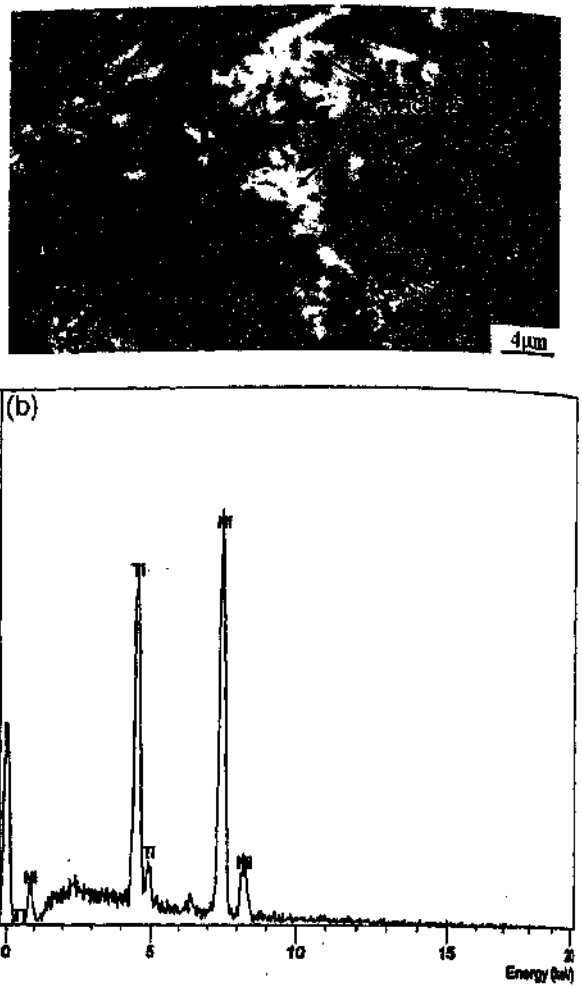

Fig. 9. (a) SEM micrograph and (b) EDAX analysis of the composite with 3% nickel produced at 40 MPa and 1100°C for 1 min (load application was initiated at 950°C). Nickel-rich phase is evident.

(1) Effect of Nickel Addition on Reaction Kinetics and Densification

The Ni–Ti phase diagram[15] (Fig. 10) shows that, to obtain liquid phases in the powder mixture under equilibrium conditions. the metal content should be 12% (nickel) at 942°C. This value

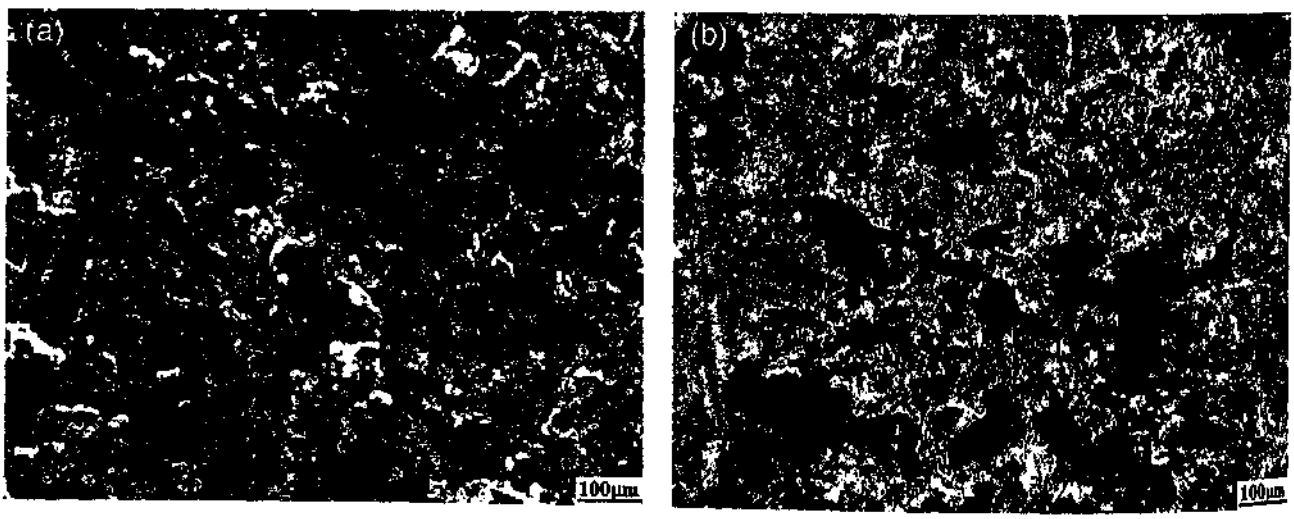

Fig. 8. Optical micr composite produced at 40 MPa and 1100°C for 1 min with (a) 1% and (b) 3% nickel addition (load application was initiated at 950°C). Bright regions in (a) are unreacted titanium particles.

Table III. Densities of Composites Produced with Nickel Addition at Various Temperatures†

Amount of nickel (wt%)	Temperature (°C)	Density of the composites (%)	
		Pressure application started at 950°C	Pressure application started at 1200°C
1	1100	70	
3	1100	82	
1	1200	86	
1	1300	93	
1	1400		92.7
3	1400		96.4
1	1475	97	
1	1550		95.5
1	1600		96.5
1	1475*	97.3	
3	1475*	97.5	
1	1600*		99.5

†At 40 MPa for 1 min. ‡For 30 min.

decreases to ~9% at 1200°C, but, in the present case, the amount of nickel is 1 wt% for the total mixture and 1.33 wt% with respect to titanium. Thus, for the formation of liquid under equilibrium conditions between the eutectic temperature and 1200°C, more than ~90% of the titanium should have first reacted with BN in the solid state. Such a scenario is unlikely, given the dominant role of nickel in promoting further reaction as well as densification. Thus, it is concluded that the onset of the reaction ($3Ti + 2BN \rightarrow 2TiN + TiB_2$) beyond 942°C leads to a local decrease of the Ti:Ni ratio in the vicinity of nickel particles, thereby leading to the formation of a low-temperature liquid. Such a liquid may then promote the dissolution of BN at a rate that is faster than that at which titanium from the solid particles diffuses into the liquid. Only then can the alloy composition be maintained sufficiently nickel-rich to remain partially molten and to continue its role in aiding sintering. Direct evidence for this lack of equilibrium has been presented in the simultaneous presence of solid phases with compositions that lie at opposite ends of the phase diagram (Fig. 10). Such a liquid phase is transient and metastable and is in striking contrast with earlier reports[9–11] of liquid-phase-assisted processing in which substantial amounts of nickel have been added (>25%). Addition of 3% nickel increases the volume of liquid and the rates of both processes that are driven by dissolution (reaction and densification), as is experimentally observed (Fig. 7 and Tables II and III).

(2) Effect of Early Application of Pressure on Reaction Kinetics and Densification

The beneficial role of early application of pressure also can be understood by the increase in coverage of the liquid as it is squeezed into the interparticulate porosity. The inability to obtain full density below 1500°C is striking and suggests that, as the reaction proceeds, once the metallic composition approaches the liquidus composition on the nickel-rich end of the phase diagram, the volume fraction of liquid is insufficient to complete densification, and solid-state transport becomes essential; i.e., higher temperatures are needed, typically 1550°–1600°C. This slowing in densification beyond 97% also is witnessed with *1%* and 3% nickel at 1475°C (Table III) and in the case where pressure is applied at a lower temperature; i.e., the measures that have been introduced to increase densification in the earlier stages fail below 1475°C, as expected, if the absence of sufficient volume fraction of liquid were the principal cause. A possible additional contributing factor is that molten nickel might not wet TiB_2 and TiN in the absence of titanium. Both these situations might be remedied by adding a small excess of titanium above the amount required for stoichiometric conversion of the BN to the ceramic products,

Microstructural observations and chemical analysis using SEM indicate that, as the reaction progresses, the nickel content of the metallic phase increases locally to form a nonequilibrium liquid phase that promotes further reaction and densification at temperatures as low as 1400°C (Fig. 8). Thus, the sequence of events is envisaged to be as follows:

(1) The addition of a small quantity of nickel is able to form a low-temperature liquid with the neighboring titanium. This liquid phase squeezes between the particles and enhances reaction and densification by providing a high-diffusivity path, thus enabling the completion of the reaction at ~1200°C.

(2) An early application of pressure, i.e., at low temperatures (950°C) during heating, promotes a uniform distribution of liquid and the formation of interparticulate contacts, thereby promoting reaction and densification.

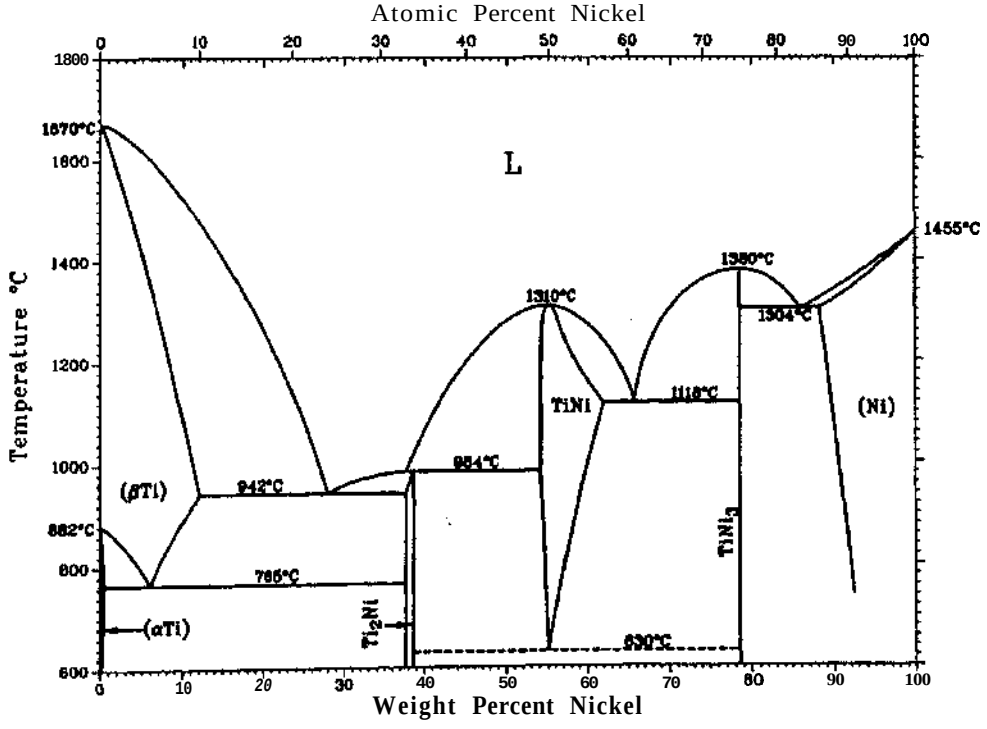

Fig. 10. Ni–Ti phase diagram.[15]

Table IV. Comparison of Results of TiN–TiB_2 Composites Produced Earlier† and Present Study

Material	Conditions (MPa/°C/min)	Density (%RD)	Hardness (GPa)	Fracture toughness ($MPa \cdot m^{1/2}$)
TiN–TiB_2 (20–80 wt%)[1]	20/1800/30	99	18	3
TiN-30 wt% TiB_2[2]	—/1700–2000/90	98	21	4
TiN + 20 wt% TiB_2	30/1700–1850/30	98.2	13.7	3.8
TiN + 20 wt% TiB_2 + 1.5 wt% Ni[4]	30/1700–1850/30	97.2	13.3	4.1
TiH_2–BN (0–5 wt% Ni)[6]	30/1850/30 (RHP)	98-99.9	20.5	6.2 ± 0.21
Ti–BN–1.5Ni[9–11]	~150–250/1100–1200/2–20 h (RHP)	~92–99	15-18	6.4–7.8
	Present study			
Ti + BN	40/1850/30	98.2	24.5 ± 0.72	6.03 ± 0.4
Ti + BN (1 wt% Ni)	40/1600/30	99.5	24.5 ± 0.97	6.53 ± 0.4
Ti + BN (1 wt% Ni)	40/1475/30	97.3	22.18 ± 1.2	

† Literature data.

(3) Even though the reaction is completed at lower temperature and substantial densification (—97%) is achieved at 1475°C, the final elimination of porosity requires higher temperatures (~1550°C) because of the gradual disappearance of the liquid and the need for solid-state diffusion within TiN and TiB_2.

The hardness achieved can be classified in two regions. The maximum density (99.5%) and hardness (~24 GPa) achieved at 1600°C with 1% nickel addition are similar to that fabricated at 1850°C without nickel addition. Significantly high hardness (~22 GPa) has been achieved at 1400°C. Fracture toughness seems to be relatively insensitive to processing conditions once the relative density exceeds ~95%.

(3) Comparison with Earlier Work

Results of earlier work (literature) and present work are listed in Table IV. The temperature required for densification is high[1–4] when pure TiN and TiB_2 are used. Although the composites produced with larger amounts of nickel (23-25 at.%) and higher pressure during processing (~150 MPa) result in ~92%–99% density, the times required are longer (~2–20 h), and their hardness is significantly lower (14-18 GPa).[9–11] The densities of the composites in the present work are similar to those obtained by Zhang *et al.*[6] when the hot-pressing temperature is 1850°C. Thus, the present study leads to the conclusion that the addition of a small amount nickel (~1 wt%) can help decrease the densification temperature to as low as 1600°C with a hardness of ~24.5 GPa and fracture toughness of ~6.5 $MPa \cdot m^{1/2}$.

V. Conclusions

The present detailed investigations on the reactive hot pressing of titanium and BN powder mixtures have led to the following conclusions.

(1) The reactive hot pressing of TiN–TiB_2 without nickel addition is successfully completed by reacting titanium and BN powder mixtures at 40 MPa in the temperature range 1400°–1850°C for 30 min.

(2) The reaction is complete without nickel at a temperature of ≥1600°C, but the density achieved is only 88.8%.

(3) The addition of 1 wt% nickel produces 99.5% dense composites at temperatures as low as 1600°C after 30 min. The hardness and fracture toughness of the composites are ~24 GPa and ~6.5 $MPa \cdot m^{1/2}$, respectively.

(4) The role of nickel appears to be the formation of a low-temperature liquid as the neighboring titanium reacts with BN. This liquid phase provides a high diffusivity path, which enables the completion of the reaction at a temperature as low as — 1200°C.

(5) An early application of pressure during heating can bring about densities as high as 97% at a temperature as low as 1475°C. Even though the reaction is completed at a lower temperature and substantial densification is achieved at 1475°C, the final elimination of porosity requires higher temperature because of the gradual disappearance of the liquid and the need for solid-state diffusion within TiN and TiB_2.

Acknowledgment

The work that has been reported is a result of support from the Director of NAL, Head of Materials Science Division, and many colleagues in the Materials Science Division of NAL. The authors are indebted to P. M. Jaman and V. Babu for the assistance in hot-pressing experiments, S. Usha Devi for XRD measurements, M. A, Venkataswamy and Kalavati for SEM work, and K. V. Ramaiah for optical microscopy.

References

[1]K. Shobu and T. Watanabe, "Hot Pressing of TiN–TiB_2 System," *J. Powder Metall. Soc. Jpn.*, 32 [6] 215-18 (1995).

[2]T. Watanabe, H. Yamamoto, K. Shobu, and T. Sakamoto, "Factors Affecting the Porosity and Bending Strength of Ti(CN)–TiB_2 Materials," *J. Am. Ceram.Soc.*, 71 [4] C-202–C-204 (1987).

[3]K. Shobu, T. Watanabe, Y. Enomoto, K. Umeda, and Y. Tsuya, "Frictional Properties of Sintered TiN–TiB_2 and Ti(CN)–TiB_2 Ceramics at High Temperature." *J. Am. Ceram. Soc.*, 70 [5] C-103–C-104 (1987). "

[4]T. Graziani, C. Melandri, and A. Bellosi, "Fabrication of Monolithic TiN and TiN–20-vol%-TiB_2 Composites," *J. Hard Mater.*, 4, 29-36 (1993).

[5]G. J. Zhang, "Preparation of TiB_2–$TiC_{0.5}N_{0.5}$ Ceramic Composite by Reactive Hot Pressing and Its Microstructure," *Ceram. Int.*, 21 [1] 29–31(1995).

[6]G. J. Zhang, Z. Z. Jin, and X. Yue, "TiN–TiB_2 Composites Prepared by Reactive Hot Pressing and Effects of Ni Addition," *J. Am. Ceram. Soc.*, 78 [10] 2831-33 (1995).

[7]R. Tomoshige, A. Murayama, and T. Matsushita, "Production of TiB_2–TiN Composites by Combustion Synthesis and Their Properties," *J. Am. Ceram. Soc.*, 80 [3] 761-64 (1997).

[8]J. W. Lee, Z. A. Munir, M. Shibuya, and M. Ohyanagi, "Synthesis of Dense TiB_2–TiN Nanocrystalline Composites through Mechanical and Filed Activation," *J. Am. Ceram. Soc.*, 84 [6] 1209-16 (2001).

[9]F. Olevsky, P. Mogilevsky, E. Y. Gulmanas, and I. Gotman, "Synthesis of *in Situ* TiB_2/TiN Ceramic Matrix Composites from Dense BN-Ti and BN-Ti-Ni Powder Blends," *Metall Mater. Trans.*, 27A, 2071-79 (1996).

[10]I. Gotman, N. A. Travitzky, and E. Y. Gutmanas, "Dense *in Situ* TiB_2/TiN and TiB_2/TiC Ceramic Matrix Composites: Reactive Synthesis and Properties," *Mater. Sci. Eng.*, A244, 127-37 (1998).

[11]E. Y. Gutmanas and I. Gotman, "Reactive Synthesis of Ceramic-Matrix Composites Under Pressure," Ceram. *Int.*, 26, 699-707 (2000).

[12]K. Niihara, R. Morena, and D. P. H. Hasselman, "Evaluation of K_{IC} of Brittle Solids by the Indentation Method with Low Crack to Indent Ratios," J. *Mater. Sci. Lett.*, 1, 13-16 (1982).

[13]L. E. Toth, *Transition-Metal Carbides and Nitrides,* Vol. 7; p. 87. Academic Press, New York, 1971.

[14]S. Nagakura, T. Kusunoki, F. Kakimoto, and Y. Hirotsu, "Lattice Parameter of the Non-Stoichiometric Compound TiN_x," *J. Appl. Crystallogr.*, 8, 65-66 (1975).

[15]Alloy Phase Diagrams, *ASM Handbook,* Vol. 3; "p, 2.319. ASM International Materials Park, OH, 1992.