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Reactive Processing of Ceramic Composites at Moderate Temperatures

L. Rangaraj*[1], C. Divakar[1] and V. Jayaram[2]

[1]Materials Science Division, National Aerospace Laboratories (CSIR), Bangalore-560 017 017, INDIA
E-mail: *ranga@nal.res.in

[2]Department of Materials Engineering, Indian Institute of Science, Bangalore-560 012, INDIA
ranga@nal.res.in

ABSTRACT:

Dense TiN-TiB$_2$ and ZrB$_2$-ZrC composites were produced by using stoichiometric Ti-BN and Zr-B$_4$C powder mixtures with 1 wt% Ni at 40 MPa, 1600°C for 30 min. Addition of excess Ti-/Zr powder to stoichiometric Ti-BN-/Zr-B$_4$C powder mixtures yielded dense TiN$_x$-TiB$_2$ and ZrB$_2$-ZrC$_x$ composites at 1200°C. The densification mechanism in TiN-TiB$_2$ composites attributed to the presence of transient Ti-Ni liquid phase for long time. However, in case of ZrB$_2$-ZrC composites, plastic deformation of transient ZrC$_x$ grains during reactive hot pressing played a predominant role in densification without Ni. Further, ZrB$_2$-ZrC-SiC composite were produced by using Zr-B$_4$C-Si powder mixtures at 1600°C for 30 min. The relative density, hardness and fracture toughness of the composites are 99%, 20–22 GPa and 5–5.5 MPa.m$^{1/2}$ respectively.

Key-words: *Composites, Densification, Transient Liquid Phase, Plastic Deformation.*

1. INTRODUCTION

Group IV transition metal (Ti, Zr and Hf) borides, carbides and nitrides are considered for various engineering applications due to their high melting temperatures, high Young's modulus, high temperature strength, high hardness, good wear resistance etc.[1]. To specify a few, Ti-based boride (TiB$_2$), carbide (TiC) and nitride (TiN) are considered for cutting tool and wear resistant applications due to their high hardness and good wear resistance.[2–5]. On the other hand Zr-based (ZrB$_2$), carbide (ZrC) and nitride (ZrN) with silicon carbide (SiC) additions are considered for ultra-high temperature applications including nose-cone and thermal protection systems in reentry vehicles due to their high melting temperature (3000°C) and good chemical stability.[6–12].

At present, ceramic monoliths and composites have been produced by various methods including Pressureless Sintering (PS), Hot Pressing (HP), reactive hot pressing (RHP) etc., The PS required very high processing temperatures (1850–2200°C) in addition to Ni, Cr, Fe, MoSi$_2$ etc as sintering aids.[13–19]. These composites may deteriorate during the application due to exaggerated grain growth and liquid phase. The HP produces nearly fully dense composites at temperatures lower by 100–200°C than PS and also minimizes the amount of sintering aids.[9–11, 20–22]. In recent years, the RHP technique has been used to prepare various composites starting with reactant powder mixtures. This technique offered advantages like homogenous

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distribution of matrix and reinforcement, strong interfacial bonding between matrix and reinforcement, finer grain size distribution and hence better thermo-mechanical properties. The composites produced by RHP are: TiB_2-TiC [23], TiN-TiB_2 [3–5], ZrB_2-ZrC [24, 25], ZrB_2-SiC [24, 26–29], ZrB_2-ZrC-SiC [29] etc. The composites produced by RHP also adopted the similar conditions of HP. The densification mechanisms operating during RHP has not been well understood, except the fine grain size development in ZrB_2-SiC composites [27] and plastic deformation mechanism in TiB_2-TiC composites [23], however, these mechanisms were operative at high temperatures (1500°C and above).

Table 1: The Purity, Particle Size and Source of the Powders

Powder	Purity (%)	Particle Size (μm)	Source
Titanium	~99.5	~10–15	M/s Alfa-Aesar, USA
Boron Nitride	~99.5	~5	M/s Alpha Chemicals- India
Zirconium	98	2–10	M/s Yashoda special metals, Hyderabad
Boron Carbide	99	10–20	M/s Boron Carbide India Pvt. Ltd
Silicon	99	4	M/s Elkem, Germany
Nickel	~99.5	~4	M/s INCO – United Kingdom

Recently, our work has shown that the addition of 1 wt% Ni to the stoichiometric 3Ti-2BN powder mixture yielded 99.5% Relative Density (RD) 2TiN-TiB_2 composite at 1600°C for 30 min, whereas without Ni requires at least 1850°C to achieve 98.2% RD [5]. The densification mechanism was attributed due to the formation of a low temperature Ti-Ni liquid phase at ~942°C, which leads to higher densification due to the transient liquid phase sintering during the RHP. At the end (1600°C) it was identified that the Ni was present as isolated particles at the triple points. The present work deals with the reaction and densification of TiN-TiB_2 and ZrB_2-ZrC composites starting with stoichiometric and non-stoichiometric Ti-BN and Zr-B_4C powder mixture. The reaction and densification of ZrB_2-ZrC-SiC composites are also reported.

2. EXPERIMENTAL WORK

The composites were prepared according to the following reactions:

$$(3 + y)\ Ti + 2BN \rightarrow TiB_2 + (1+y)\ TiN_{1/(1+y)} \quad \ldots (1)$$

$$(3+y)\ Zr + B_4C \rightarrow 2ZrB_2 + (1+y)\ ZrC_{1/(1+y)} \quad \ldots (2)$$

$$2.5Zr + B_4C + 0.65Si \rightarrow ZrB_2 + 0.5ZrC_x + 0.65SiC \quad \ldots (3)$$

The value of 'y' is 0 to 0.5. The purity, particle size and source of the raw materials used in the present study are listed in Table 1.

2.1 Mixing of Powders

The mixing of required quantities of Ti and BN powders with 1 wt% Ni was carried out with a ball: powder ratio of 10:1 in a Fritsch Pulveresette centrifugal ball mill for 24 hrs in hexane medium. The required quantities of powders (Zr-B_4C or Zr-B_4C-Si) with 1 wt% Ni were mixed in a rotary ball mill using ZrO_2 (8 mol% Y_2O_3) milling media for 24 hrs in a polythene bottle containing ethanol medium with the ball: powder ratio of 3:1. Selected compositions without Ni were also mixed. The powder mixtures were dried at ~100°C for ~5 hrs. The weight loss of the ZrO_2 milling media after each mixing was ~2 wt%, indicating incorporation of impurity in the starting mixture.

~~**Table 1** The Purity, Particle Size and Source of the Powders~~

~~Powder~~	~~Purity (%)~~	~~Particle Size (μm)~~	~~Source~~
~~Titanium~~	~~~99.5~~	~~~10-15~~	~~M/s Alfa-Aesar, USA~~
~~Boron Nitride~~	~~~99.5~~	~~~5~~	~~M/s Alpha Chemicals- India~~
~~Zirconium~~	~~98~~	~~2-10~~	~~M/s Yashoda special metals, Hyderabad~~
~~Boron Carbide~~	~~99~~	~~10-20~~	~~M/s Boron Carbide India Pvt. Ltd~~

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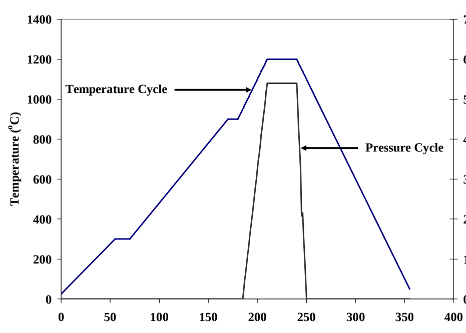
~~Silicon~~	~~99~~	~~4~~	~~M/s Elkem, Germany~~
~~Nickel~~	~~-99.5~~	~~-4~~	~~M/s INCO United Kingdom~~

2.2 Reactive Hot Pressing

The dried powder mixtures were filled in a high-density graphite die (outer diameter 80 mm, internal diameter 25 mm and height 70 mm). The internal surface of the die was surrounded by flexible graphite sheet (0.2 mm thick) to avoid direct contact between the powder mixture and the die. Top and bottom graphite spacers were also protected by flexible graphite discs. The RHP experiments were carried out in a vacuum hot press (M/s Materials Research Furnaces, Suncook, USA). The RHP experiments were conducted at constant pressure (40 MPa) and different temperatures (1000–1600°C) for holding time ~5–30 min. Oil pressure of 540 psi was generated to apply 40 MPa pressure on the sample. In a typical experiment for producing TiN-TiB_2 composites, a vacuum of 5 × 10^{-5} torr was reached and the sample is heated up to 300°C at a rate of 5°C/min and held for 15 min to remove the gases and moisture in the chamber. The sample was further heated to 700°C at the rate of 6°C/min and held for 10 min, followed by heating up to the required temperature (1100–1850°C) at the rate of 10°C/min and held for required time (1–30 min). A typical temperature–time–pressure cycle of the composite produced at 40 MPa, 1200°C for 30 min is shown in ~~Figure~~Fig. 1.



~~Section 1.01~~ **Figure 1**The Typical Temperature–time–pressure Cycle of the Composites Produced at 40 MPa, 1200°C for 30 min.

For high temperature (1600 and 1850°C) experiments with (1 wt% Ni) and without Ni, the start of pressure application was at 1400/1600°C and the required pressure was reached in 25 min and maintained for the required time. For low temperature experiments (1100–1400°C), the start of pressure application was at 950 °C

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and again the final pressure was reached in 25 min and maintained for the required time. In both cases the pressure was released within 10 min during cooling. In case of ZrB_2-ZrC and ZrB_2-ZrC-SiC composites, the pressure application was started at 1000/1200/1400 °C and held for required temperature. The stoichiometric ZrB_2-ZrC composites have been produced at 1200–1600°C for 30 min and non- stoichiometric ZrB_2-ZrC_x composites have been produced at 1000–1400 °C for 30 min. ZrB_2-ZrC-SiC composites have been produced at 1400 °C and 1600 °C for 30 min.

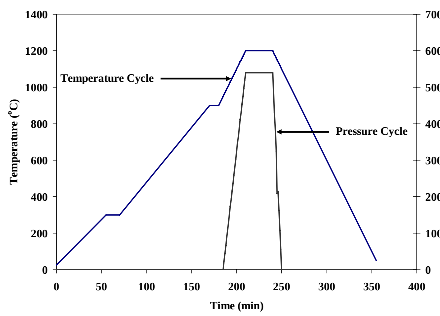

Fig. 1: The Typical Temperature-time-pressure Cycle of the Composites Produced at 40 MPa, 1200°C for 30 min

3.0 CHARACTERIZATION

The reactive hot pressed composites were recovered from the graphite die assembly after cooling to room temperature were ground by coarse silicon carbide (SiC) abrasive paper and final polishing using diamond pastes (1 and 0.25 μm) in an automatic polishing machine (Ecomet 4000 with Automet 2000, M/s Buehler, USA). The polished samples were cleaned with acetone in an ultrasonic cleaner. The density of the samples was measured by water immersion method. The relative densities (RD) of the composites are estimated using the measured bulk density and the calculated theoretical density according to rule of mixtures using the reactions (1) to (3).

The phase identification in the composites was carried out by recording the X-ray diffraction (XRD) patterns in the 2θ range of 20–80° with 0.1° step using A Philips x-ray diffractometer (Philips, Eindhoven, The Netherlands). The N/Ti and C/Zr and stoichiometry were studied by determining the lattice parameter (Å) of ZrC and TiN in the composites. The lattice parameters *a* and *c* of ZrB_2 and TiB_2 were also determined. The lattice parameter was calculated by recording the XRD patterns in the 2θ range of 80–156° with 0.02° step and using standard extrapolation functions ($\cos^2\theta/\sin\theta$) to determine the true lattice parameter at a Bragg angle of 90°.

Vickers hardness measurements (Model HSV-20, Shimadzu Corporation, Kyoto, Japan) were performed on the polished surfaces at a test load of 500 g (4.9 N) and a holding period of 15 seconds. An average of 15 readings was taken for each reported value. The indentation fracture toughness of the composites have been measured using 5 to 10 kg load calculated using the formula [30].

The micro-structural observations of the surfaces of the composites were carried out using optical microscopy (Axiovert 200 M MAT, Carl Zeiss Light Microscopy, Goettingen, Germany). Polished ZrB_2-ZrC samples were etched using $HF:HNO_3:H_2O$ solution in the ratio of 2:3:95 for 10 seconds to distinguish ZrB_2 and ZrC grains. Scanning electron microscopy (SEM: FEI-Sirion, Eindhoven, The Netherlands) with energy dispersive x-ray microanalysis (EDAX, super-ultra-thin window, Genesis Spectrum, Mahwah, NJ07430, USA) was used to study the reaction and densification of composites. The average grain size of ZrB_2 and ZrC has been measured through image analysis of the SEM micrographs by the line intercept method by counting a minimum of 300 grains. The amount of unreacted B_4C present, porosity, amount of ZrB_2, ZrC, SiC, TiB_2, TiN in the composites were also estimated using optical and SEM micrographs

4.0 RESULTS AND DISCUSSION

4.1 TiN-TiB_2 Composites

4.1.1 *Reaction of Ti-BN Powder Mixtures*

Stoichiometric Ti-BN powder mixtures in presence of Ni led to completion of reaction at 1200ºC, whereas without Ni required at least 1400ºC. The RD of the composites without Ni increases from 78 to 98.2% as the temperature increases from 1400ºC to 1850ºC. The addition of 1 wt % Ni yielded 93 to 99.5% RD composites as the temperature increased from 1200 to

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1600°C. The composites produced at intermediate temperature (1100–1200°C) showed the formation of Ti-Ni liquid phase, which results in enhancement of densification.

Table 2: Experimental Conditions and Properties of the Composites

Composition	Experimental Conditions (MPa/°C/min)	Phases Present	Density –g/cm^3 (% Relative Density)	Hardness (Hv)	Fracture Toughness (MPa.m$^{1/2}$)
3Ti-2BN	40/1850/30	TiN, TiB_2	98.2	24.5	6.03
3Ti-2BN	40/1600/30	TiN, TiB_2	4.5 (89)	16.8	–
3Ti-2BN (1wt% Ni)	40/1200/30	TiN, TiB_2	4.71 (93)		
3Ti-2BN (1wt% Ni)	40/1600/30	TiN, TiB_2	5.06 (99.5)	24.6	6.53
3.25Ti-2BN (1wt% Ni)	40/1200/30	TiN, TiB_2	4.92 (97.8)	22	
3.5Ti-2BN (1wt% Ni)	40/1200/30	TiN, TiB_2	4.95 (99.9)	22	
3.5Ti-2BN	40/1200/30	TiN, TiB_2, TiB, Ti, BN	3.52 (70)	–	–

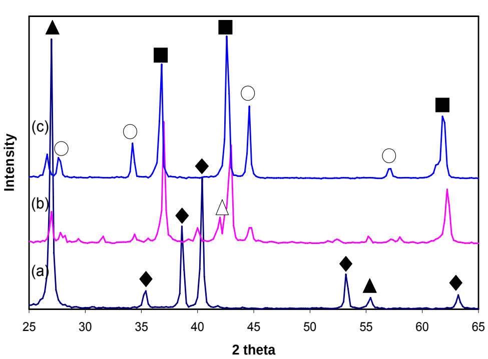

Fig. 2: The XRD Patterns of the Composites Produced with 1 wt% Ni at 40 MPa, for 1 min: (a) Starting Powder Mixture, (b) 1100°C and (c) 1200°C. (▲-hBN, ◆-Ti, ■-TiN, ○-TiB_2, Δ-TiB and ?- unidentified peak)

Non-stoichiometric Ti-BN powder mixtures (excess Ti) reactive hot pressed at 1100°C showed the incomplete reaction (Fig. 2 (b)) and the observed phases are TiN, TiB_2, TiB, Ti and BN phases. As the temperature was increased to 1200°C showed only phases corresponding to TiN and TiB_2 (Fig. 2 (c)). Since free Ti was not observed in XRD patterns and also the measured lattice parameter of TiN_x ($TiN_{x\sim1}$: 4.250 Å to $TiN_{x\sim0.8}$: 4.245 Å) in the stoichiometric and non-stoichiometric composites suggests the N/Ti ratio approaches to 1 to 0.8. Finally, it is concluded that the excess Ti was incorporated to form non-stoichiometric TiN_x, which can form N/Ti ratios from 0.65 to 1.1.[31, 32] The lattice parameter-N/Ti plot of TiN produced (TiN in the TiN-TiB_2 composites) in the present study is given in ~~Figure~~Fig. 3 and the values reported in literature are also shown. The measured lattice parameter of TiN is higher than the monolithic [33, 34] and lower than those reported for composite.[35] The lattice parameters of TiB_2 (a and c) are 3.029 ± 0.001 Å and 3.229 ± 0.001 Å respectively, which are in good agreement with the powder diffraction file (JCPDS: 35-0741; a = 3.0303 Å and c = 3.2295 Å) values. The experimental conditions, phases present, density and hardness of the composites are given in Table 2.

~~**Table 2**Experimental Conditions and Properties of the Composites~~

~~Composition~~	~~Experimental Conditions (MPa/°C/min)~~	~~Phases Present~~	~~Density –g/cm^3 (% Relative Density)~~	~~Hardness (Hv)~~	~~Fracture Toughness (MPa.m$^{1/2}$)~~
~~3Ti-2BN~~	~~40/1850/30~~	~~TiN, TiB_2~~	~~98.2~~	~~24.5~~	~~6.03~~
~~3Ti-2BN~~	~~40/1600/3~~	~~TiN,~~	~~4.5~~	~~16.8~~	~~-~~

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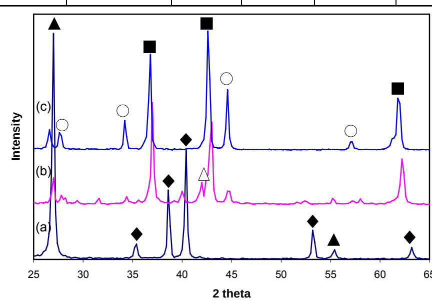
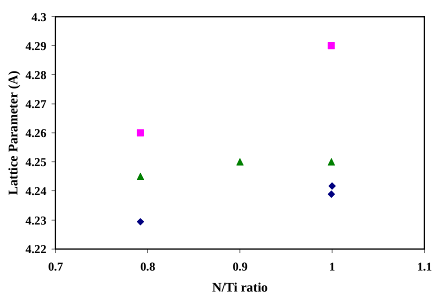
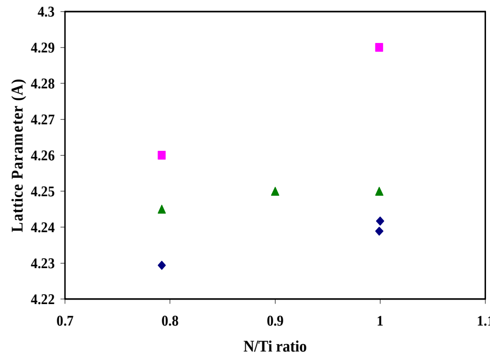
	0	TiB_2	(89)		
3Ti-2BN (1wt% Ni)	40/1200/30	TiN, TiB_2	4.71 (93)		
3Ti-2BN (1wt% Ni)	40/1600/30	TiN, TiB_2	5.06 (99.5)	24.6	6.53
3.25Ti-2BN (1wt% Ni)	40/1200/30	TiN, TiB_2	4.92 (97.8)	22	
3.5Ti-2BN (1wt% Ni)	40/1200/30	TiN, TiB_2	4.95 (99.9)	22	
3.5Ti-2BN	40/1200/30	TiN, TiB_2, TiB, Ti, BN	3.52 (70)	-	-





~~**Figure 2-** The XRD Patterns of the Composites Produced with 1 wt% Ni at 40 MPa, for 1 min: (a) Starting Powder Mixture, (b) 1100°C and (c) 1200°C. (▲-hBN, ◆-Ti, ■-TiN, ○-TiB_2, △-TiB and ?- unidentified peak).~~



~~Figure~~Fig. 3: Lattice Parameter- N/Ti Ratio Plot of the TiN: ▲-$TiN_{x\sim0.8-1}$ in the TiB_2-TiN Composites (present study), ■- $TiN_{x\sim0.8,1}$ in TiB_2-TiN Composites[35], ◆-monolithic TiN_x Produced by Gas Phase Reaction[33]

4.1.2 *Microstructural Observations and Densification of TiN-TiB2 Composites*

Relative densities of the TiN_x-TiB_2 composites produced without Ni and with 1 wt% Ni at 1200°C for 30 min are 3.52 g/cm^3 (70% RD) and 4.95 g/cm^3 (99.9% RD) respectively (Table 2). The substantial influence of non-stoichiometry (Ti: 0.0- 0.5 mol) on densification in the presence of 1 wt% Ni increases the RD from 93% (TiN-TiB_2) to 99.9% ($TiN_{x\sim0.8}$-TiB_2) at 1200°C. The densities of the TiN-TiB_2 and $TiN_{x\sim0.8}$-TiB_2 composites produced at 1100°C for 1 min are 3.56 g/cm^3 and 3.32 g/cm^3 respectively, whereas $TiN_{x\sim0.8}$-TiB_2 processed for 30 min showed a density of 3.98 g/cm^3. The reaction and densification of the composite with 1 wt% Ni does not complete below 1200°C.

The typical optical micrographs of the composites produced with 1 wt% Ni and without at 1200°C for 30 min is shown in ~~Figure~~Fig. 4. It is noticed that when Ni is absent, the RD for TiN_x-TiB_2 drops to ~70% as shown in Fig. 4 (a) and similar to what has been reported for stoichiometric composite at 1600 °C.[5]. Significant change in densification can be seen with non-stoichiometry and the addition of 1 wt% Ni (Fig. 4 (b)).

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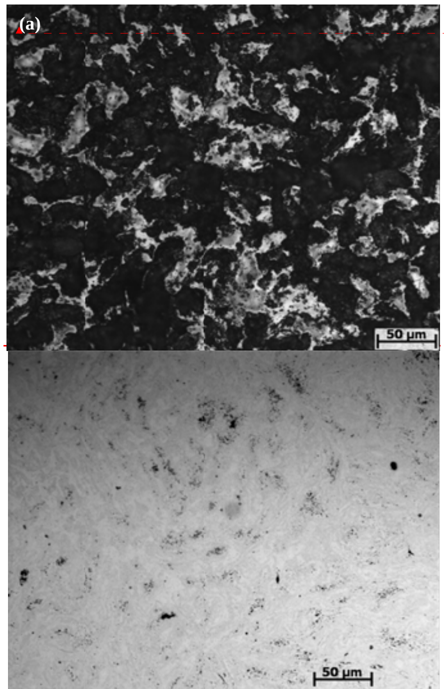

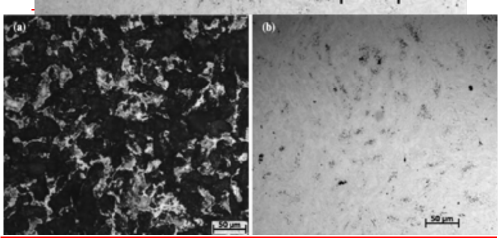

~~Figure~~Fig. – 4: Optical Micrographs of the Composites Produced at 40 MPa, 1200°C for 30 min: (a) TiN_x-TiB_2 without Ni (70% RD) and (b) $TiN_{x\sim0.8}$-TiB_2 with 1 wt% Ni (99.9% RD)

The role of excess Ti with the presence of Ni was observed after partial densification for 1 min at 1200°C. The partially dense regions with isolated Ni particles in the TiN-TiB_2 composite as shown in Fig.5 (a) are observed The large sizes of Ni-rich regions in TiN_x-TiB_2 composites are also observed and is shown in Fig. 5(b).The EDAX spectra (Fig. 5 (c) and (d)) of core and rim of a white region in Fig. 5 (b) reveal the core to be enriched in Ni relative to the rim. The core contains ~53 at% Ni, 37 at% Ti and 10 at% N and rim contains ~1.2 at% Ni, 65 at% Ti and 33.8 at% N. The compositional analysis suggests that Ti is being removed from the Ni-Ti metallic phase and added to the TiN matrix and further supported by the contrast of the rim similar to that of the TiN matrix, which surrounds the Ni-rich core.

The typical SEM micrographs at higher magnification reveal that after densification is complete in TiN_x-TiB_2 (Fig. 6 (a)), the residual metal is similar in scale and volume fraction to that seen in TiN-TiB_2 (Fig. 6 (b)), which has been densified at 1600°C.[5] White spots are identified as Ni. The volume fraction of TiN estimated by image analysis in TiN-TiB_2 and TiN_x-TiB_2 is 60.02 ± 2.2 and 65.85 ± 7.68 respectively, which is in agreement with the values calculated using the reaction (1). The grains of TiN (1.14 ± 0.72 µm) and TiB_2 (0.64 ± 0.27 µm) observed in $TiN_{x\sim0.8}$-TiB_2 (Fig. 6 (a)) are finer than those in TiN-TiB_2 composite (TiN: 1.78 ± 0.87 µm and TiB_2 1.37 ± 0.79 µm) as shown in Fig. 6 (b).

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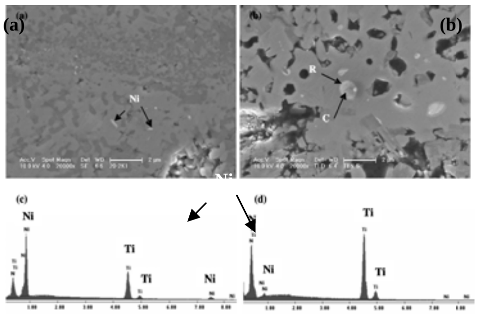

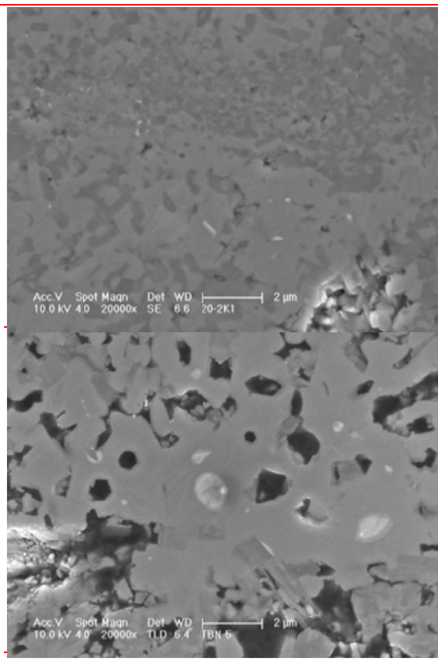

(c) (d)

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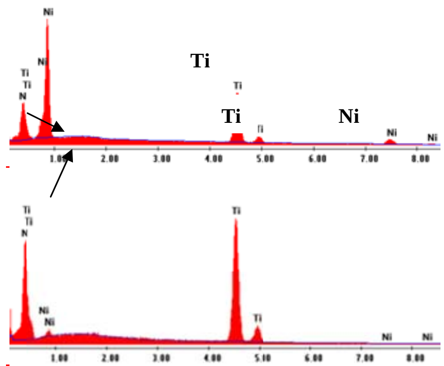
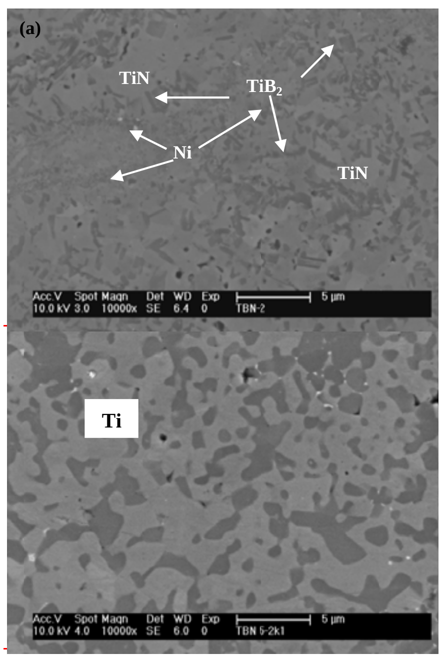


~~Figure~~Fig. 5: SEM Micrographs with EDAX Analysis of the Composite Produced with 1 wt% Ni at 40 MPa, 1200°C for 1 min. (a) TiN-TiB_2, White Regions are Ni, (b) TiN_x-TiB_2 Showed the Ni-rich Region, (c) EDAX of Ni Rich Core
(C) and (d) Ti-rich Rim (R).

(b)



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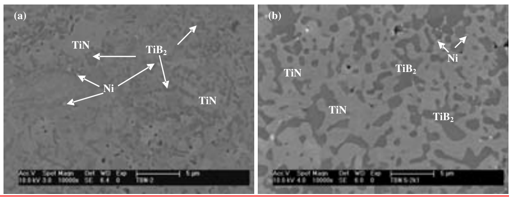
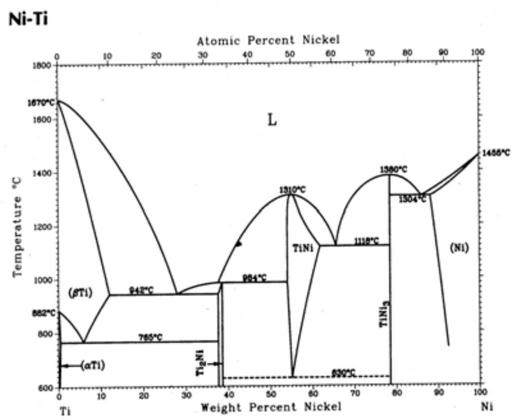


FigureFig.– 6: SEM Micrographs of the Composites Produced with 1 wt% Ni at 40 MPa, 30 min: (a) $TiN_{x0.8}$-TiB_2 at 1200 °C and (b) TiN-TiB_2 at 1600 °C.

4.1.3 *Role of Ni in Densification of the Composites*

It was reported in the earlier work [4] on RHP of stoichiometric 3Ti-2BN powder mixture with 1 wt% Ni required at least 1850°C to attain 99.9% RD. The densification temperature was reduced to 1600°C [5] by the application of pressure at 950°C due to presence of transient Ni-Ti liquid phase. Starting with the non-stoichiometric Ti-BN powder mixture with 1 wt% Ni resulted in completion of reaction and densification of $TiN_{x\sim0.8}$-TiB_2 composites at temperature as low as 1200°C. Referring to the Ni-Ti phase diagram (FigureFig.– 7) suggests a mechanism for excess Ti in promoting densification. In order to obtain liquid phases under equilibrium conditions in the powder mixture, the Ti and Ni content should be 90 wt% and 10 wt%. But in the present case the amount of Ni is 1 wt% for the total mixture and for the Ti alone it is only 1.33 wt% (TiN-TiB_2) and 1.28 wt% (TiN_x-TiB_2). Thus, for the formation of liquid phase under equilibrium conditions more than 90% of Ti should have first reacted with BN in the solid state. In the present study, reaction and densification proceed in parallel. The conversion of a reactant mixture to product phases (TiN and TiB_2) at around ~942°C leads to a local increase of Ni: Ti ratio in the vicinity of Ni particle. In this liquid phase unreacted BN dissolves much faster than in the solid-state, which aids in the completion of the reaction. It was also noticed in an earlier study [5], that the application of pressure at 950°C during heating (Ni-Ti eutectic at 942°C) promotes a uniform distribution of liquid phase and the formation of inter-particulate contacts, thereby accelerating the reaction and densification. Addition of excess Ti in the present study, maintains the liquid phase compositional trajectory at 1200°C (Fig. 7) and application of pressure at 950°C leads to higher densification.



FigureFig.- 7: The Ti-Ni Binary Phase Diagram [36]

study, maintains the liquid phase compositional trajectory at 1200°C (Fig. 7) and application of pressure at 950°C leads to higher densification.

4.2 ZrB_2–-ZrC Composites

4.2.1 *Reaction of Zr-B_4C Powder Mixtures:*

The XRD patterns of ZrB_2-ZrC composites produced starting with stoichiometric and non-stoichiometric mixture of Zr and B_4C powder (with 1 wt% Ni and without Ni) at 40 MPa, 1200°C for 30 min show peaks corresponding to ZrB_2 and ZrC (FigureFig.– 8) with tiny peaks of ZrO_2. The shift of ZrC peaks towards higher angle as the composition deviates from stiochiometry is seen in (Fig. 8-(d) and (e)).

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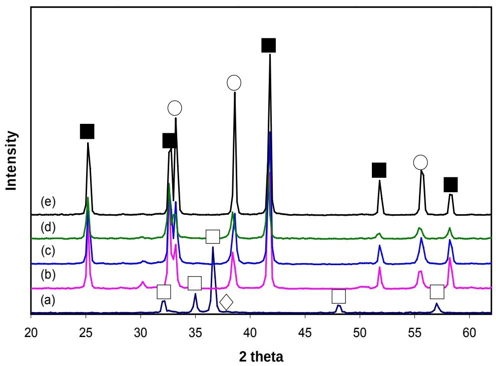

Fig. 8: The XRD Patterns of the ZrB_2-ZrC Composites 40 MPa, 1200°C for 30 min: (a) Starting Powder Mixture, (b) Stoichiometric with wt% Ni, (c) Non-Stoichiometric Without Ni, (d) Non-Stoichiometric with wt% Ni and (e) Non-Stoichiometric Without Ni (■-ZrB_2, ○-ZrC, □-Zr, ◇-B_4C and Δ-ZrO_2)

The lattice parameter of ZrC in the composite produced with Ni at 1200°C is 4.686 Å and without Ni at 1200°C is 4.674 Å. The lattice parameter of ZrC_x in the non-stoichiometric composite is 4.661 Å (1000ºC for 5 min) and increases to 4.667 Å (40 MPa, 1000ºC for 30 min). After the reaction is complete at 1200°C, the lattice parameter of $ZrC_{x\sim0.67}$ in the composite is 4.682 Å. The lattice parameter of ZrC_x in the composites produced without Ni at 1000°C, 1200°C and 1400°C are 4.667, 4.676 and 4.682 Å respectively. The differences in the measured lattice parameters of ZrC and $ZrC_{x\sim0.67}$ in the composites (4.686 and 4.682 Å) are consistent with the reducing trend as reported in the literature ($ZrC_{0.97}$ – 4.698 Å and $ZrC_{0.58}$ - 4.691 Å) [37]. The lattice parameters of ZrB_2 are 3.167 Å and 3.53 Å respectively, which are in good agreement with those reported in JCPDS (34–0423).

4.2.2 *Microstructural Observations*

The typical optical micrographs of the composites produced with and without Ni at 1200°C clearly showed completion (Fig. 9 (a)) and incompletion of the reaction with 3 vol% of B_4C (Fig. 9(b)). However, the reaction was found to be complete when the temperature was increased to 1400/1600°C. The composites produced with 1 wt% Ni at 1400°C and 1600°C for 30 min indicate a small reduction in porosity (5 to 3.5%).

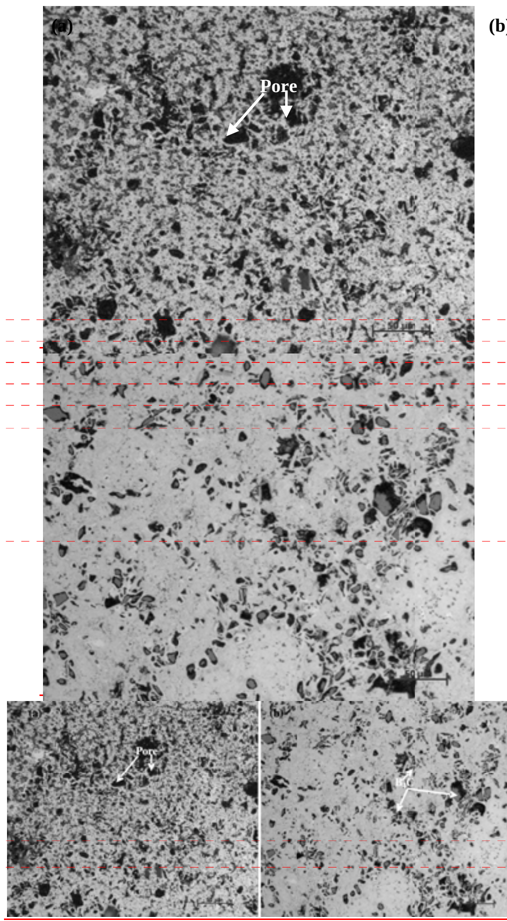

Fig. 9: Optical Micrographs of the Stoichiometric Composites Produced at 40 MPa, 1200°C for 30 min: (a) with 1 wt% Ni and (b) Without Ni. The Dark Regions are Pores and Gray Regions in (b) are Partially Reacted B_4C (3 vol%) Particles

The typical optical micrographs of the non-stoichiometric composites produced at 1200°C for 30 min with 1 wt%

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Ni and without Ni showed fully dense (Fig. 10 (a)) with small amount (0.3 vol%) of unreacted B_4C (Fig. 10 (b)).

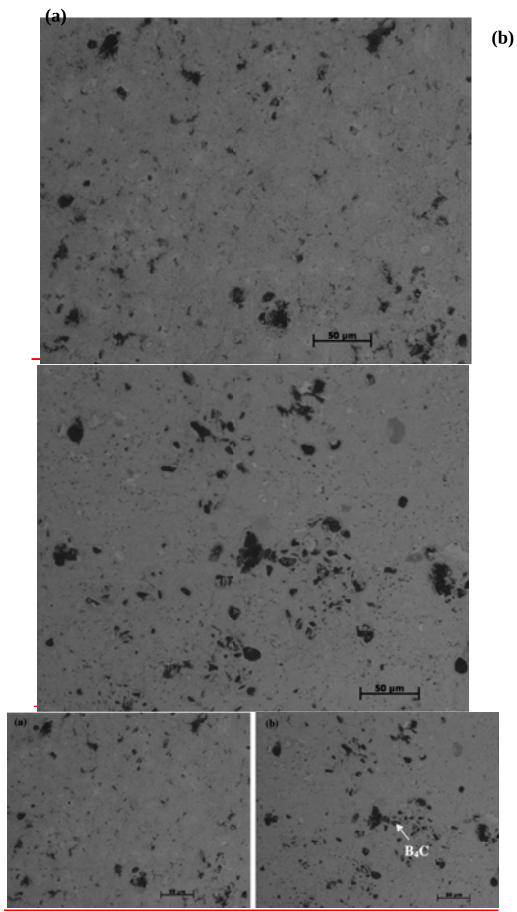


Fig. 10: Optical Micrographs of the Non-Stoichiometric Composites Produced at 40 MPa, 1200°C for 30 min: (a) with 1 wt% Ni and (b) without Ni

The typical SEM micrographs of the etched stoichiometric composite produced with 1 wt% Ni at 1200°C (Fig. 11 (a)) showed the fine grain microstructure (0.4 ± 0.2 µm for ZrB_2 and 0.3 ± 0.1 µm for ZrC) and composite produced at 1600°C showed coarse grain structure (1.6 ± 0.4 µm for ZrB_2 and 1.2 ± 0.3 µm for ZrC), however the grain sizes achieved are much finer than those reported earlier.[38, 39] The typical SEM micrographs of the etched non-stoichiometric composite produced with 1 wt% Ni at 1200°C (Fig. 11 (b)) showed the grain sizes of ZrB_2 and ZrC are 0.6 ± 0.2 µm and 0.4 ± 0.1 µm respectively.

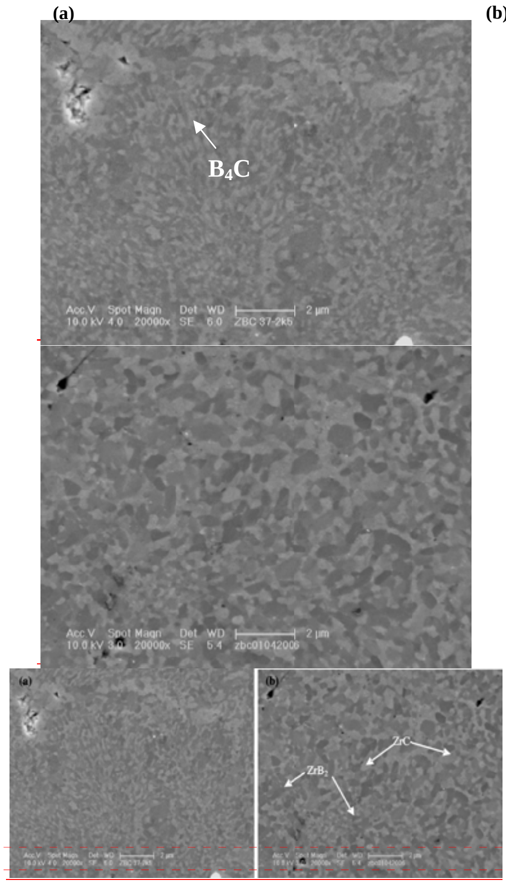


Fig. 11: SEM Micrographs of the Composites Produced with 1 wt% Ni at 40 MPa, 1200°C for 30 min: (a) Stoichiometric and (b) Non-stoichiometric. The Dark Gray Particles are ZrB_2 and Light Gray Particles are ZrC Grains

4.2.3 *Densification of ZrB_2-ZrC_x composites*

The density of the stoichiometric composites increases from 5.43 g/cm^3 (86% RD) at 1200°C to 6.13 g/cm^3 (97.3% RD) at 1600°C. The density of the non-stoichiometric composites increases from 5.72 g/cm^3 (90% RD) at 1000°C to 6.20 g/cm^3 (99% RD) at 1200ºC. The composites produced without Ni also showed similar densities and it appears that there is no effect of Ni addition on densification. The hardness and fracture toughness of the composites are 19–22 GPa and 5.5 MPa.m$^{1/2}$ respectively. The most remarkable finding in the present study is the role played by excess Zr in reducing the process temperature to as low as 1200°C for ZrB_2-ZrC_x composites and to achieve full density of ~99% RD. In the stoichiometric composite, the lattice parameter of ZrC (4.674 Å) is low compared to the Ni containing composite (4.686 Å), where the reaction is complete. However, the final densities of the composites are similar. This suggests the formation of non-stoichiometric ZrC_x aids in densification even in stoichiometric composites.

The key issue in the present study is the how fine microstructure as described above can promote densification at low temperature with specific reference to yielding and creep of transition metal carbides. The flow stress will be lower and diffusion rate will be faster as the transition metal carbides deviates from stoichiometry. The transition metal carbides (TiC, ZrC) are known to exist over a range of compositions, e.g., Ti and Zr carbides have C/metal ratio ranging from 0.65 to 0.98.[31, 32] These carbides are extremely hard and their yield strength at room temperature approaches the ideal strength. At high homologous temperatures these are very soft and creep rapidly. For example, the yield strength of $TiC_{0.66}$ is about 63 MPa as compared to 400 MPa for $TiC_{0.93}$ at 1200°C.[40] Also at temperatures around 1000°C, the carbides of Ti and Zr undergo brittle to ductile transition and deform readily - (111)[110] - addition to the room temperature slip system [41] of (110)[110]. In reactive densification of the Ti/B_4C system, it has been reported that the formation of TiC_x helps in the densification of TiB_2–TiC composites at 1600–1800°C.[2, 23]

Also, in the case of $TiC_{0.95}$, the critical resolved shear stress (CRSS) is reported to decrease from ~141 MPa at 1000°C to ~72 MPa at 1200°C, while that of $TiC_{0.79}$ the CRSS decreased from ~91 MPa (1000°C) to ~44 MPa (1200°C).[42] The ZrC, like its group IV counterpart TiC, shows falling yield strength with deviations from ideal stoichiometry. For $ZrC_{0.875}$, the CRSS reduces from ~163 MPa at 1000°C to ~87 MPa at 1200°C.[40] In the non-stoichiometric composite the C/Zr ratio is proposed to be ~0.67 ($ZrC_{x\sim0.67}$) and hence its CRSS is expected to be even lower. Thus, during hot pressing, it is likely that the local stresses around particle contacts are considerably higher than the nominal applied stress (40 MPa applied at 1000°C) and can exceed the flow stress, thereby leading to plastic flow, which can aid densification at 1200°C. As already discussed, the formation of non-stoichiometric ZrC_x at the early stage enhances the densification by deformation even in stoichiometric composites.

The observation that the amount of partially reacted B_4C (0.3 vol%) in the non-stoichiometric composite produced without Ni at 1200°C is very much lower than (3 vol%) stoichiometric composite. Thus the addition of excess Zr accelerates the reaction due to the mobility of the point defects in non-stoichiometric ZrC_x.

An additional mechanism for densification comes from vacancy creation through non-stoichiometry, which is known to enhance the mass transport through solid-state diffusion during sintering in ceramics. Non-stoichiometric carbides are characterized by a large effective diffusion coefficient (D_{eff}) as a result of which they sinter more easily than stoichiometric carbides. The D_{eff} for ZrC_x phases was found to grow appreciably with increase in carbon-vacancy concentration at all temperatures, from 5.1×10^{-15} m^{2}s^{-1} for $ZrC_{0.95}$ to 1×10^{-10} m^{2}s^{-1} for $ZrC_{0.68}$ at 1800°C.[37] It has also been reported that the activation energy for collective recrystallization of ZrC_x decreases from 53.4 kcal/mol at x = 0.97 to 42.8 kcal/mol at x = 0.65.[43]

4.3 ZrB_2 –ZrC_x–SiC Composites

The XRD patterns of the ZrB_2-ZrC_x-SiC (ZBCSC) composites produced according to reaction (3) at 1400°C and 1600°C for 30 min (Fig. 12) showed the presence of ZrB_2, ZrC_x and SiC with tiny peaks of m-ZrO_2 can be seen in both the composites.

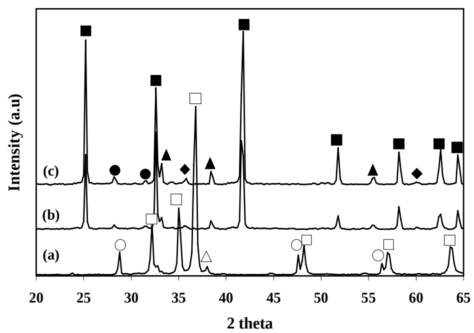
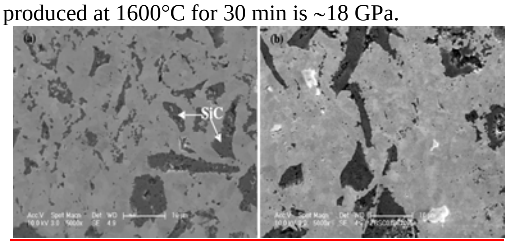


Fig. 12: The XRD Patterns of the ZBCSC Composites Produced with 1 wt% Ni at 40 MPa for 30 min: (a) Starting Powder Mixture, (b) 1400°C and (c) 1600°C (■-ZrB_2, ▲-ZrC, ◆-SiC, □-Zr, ○-Si, △-B_4C and ●- mZrO_2)

The densities of the composites increase from 4.67 g/cm^3 (~82% RD) at 1400°C to 5.55 g/cm^3 (~97% RD) at 1600°C. The composite produced without Ni at 1600°C is 5.61 g/cm^3 (~98% RD). These results may be compared with the earlier reports on densification of ZrB_2-ZrC-SiC composites by RHP [29] and SPS [44], which required temperature greater than 1800°C. Typical back-scattered electron (BSE) images of the composite with 1 wt% Ni and without Ni at 1600°C for 30 min (Fig. 13) showed the distribution of ZrB_2, ZrC_x and SiC. The volume fraction of SiC estimated in the composite from image analysis is 16 ± 4. The hardness of the composite produced at 1600°C for 30 min is ~18 GPa.



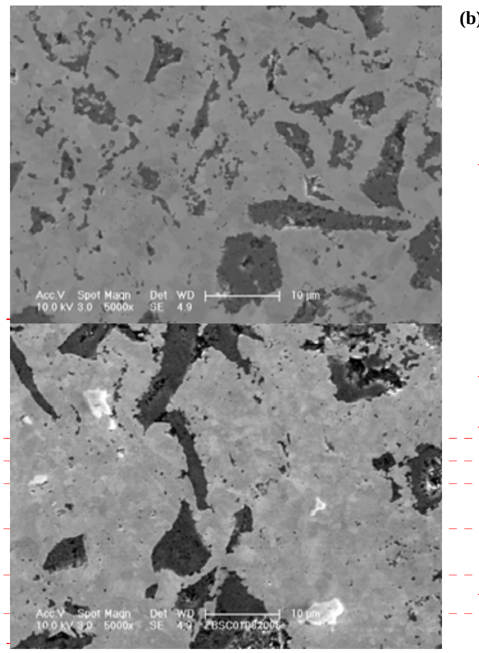


Fig. 13: Back Scattered Electron Images of the ZrB_2-ZrC_x-SiC Composites Produced at 40 MPa, 1600°C for 30 min: (a) with 1 wt% Ni and (b) without Ni

5. CONCLUSIONS

Reactive processing method has been successfully used to densifiy TiN-TiB_2, ZrB_2-ZrC and ZrB_2-ZrC-SiC composites under moderate pressure and temperature. Addition of excess Ti to the starting Ti-BN compositions with the presence of Ni plays a crucial role in bringing down the densification temperature to 1200ºC, which is lower by 300 to 400°C than the reported value in literature. The densification was attributed to the maintaining the Ti-Ni transient liquid phase for longer time. Presence of excess Zr with Zr-B_4C leading to yield 98% RD composites at 1200°C owing to the formation of deformable transient non-stoichiometric ZrC_x grains during RHP. The densification in ZrB_2-ZrC-SiC composites was also similar to the ZrB_2-ZrC_x composites. The relative density, hardness and fracture

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toughness of the composites are comparable with those reported in literature.

ACKNOWLEDGEMENT

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