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Short Communication

Reactive hot pressing of Ti–B–C and Ti–C at 1200 °C

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Abstract

Stoichiometric and non-stoichiometric powder mixtures of Ti–B_4C and Ti–C with 1 wt% Ni were reactively hot pressed at 40 MPa, 1200 °C for 30 min. In both systems, the combined presence of Ni and non-stoichiometry enabled complete densification. While in Ti–C, non-stoichiometry by itself plays a significant role in promoting densification, the formation of intermediate borides in Ti–B_4C powder mixtures requires the additional presence of Ni which promotes full reaction through the formation of a transient liquid as established previously in Ti–BN powder mixtures.

Keywords: Borides; Carbides; Densification; Stoichiometry

1. Introduction

Titanium based—boride, carbide and nitride ceramics are of interest due to their high melting points (~3000 °C), high hardness (≥ 25 GPa) and good wear–erosion resistance. These materials have been considered for cutting tools, wear-resistant parts, high temperature melting crucibles under inert atmosphere. The processing of refractory hard materials based on carbides, borides and nitrides of transition metals have seen a progressive reduction in sintering temperature through the use of ultrafine grains, spark plasma sintering and reactive processing. Among these methods, some of the most dramatic reductions come from exploiting reactions with applied pressure. Thus, direct densification of TiB_2–TiN that requires temperatures in excess of 2000 °C [1–4]. Earlier reports of reaction sintering without pressure reported that 3Ti–B_4C powder compacts yielded 2TiB_2–TiC composites after treatment at 1000–1500 °C followed by sintering at 1800 °C to produce nearly fully dense material; however, density values were not reported [5]. Reactive hot pressing (RHP) of TiH_2–BN–B_4C (with 2 wt% nickel as an additive) at 1850 °C and 25 MPa were reported to yield TiB_2–Ti($C_{0.5}N_{0.5}$) and that of TiH_2–BN with 0–5 wt% nickel as an additive resulted in TiB_2–TiN composite [6,7]. In the latter case [7], the formation of TiN took place at 1000 °C, TiB_2 at 1200 °C, with the reaction completing at 1600 °C to yield a stoichiometric mixture of TiN–TiB_2. The composites made by reactive hot pressing at 1850 °C under 30 MPa for 30 min without Ni showed 98% relative density (RD), whereas the addition of 1 wt% Ni increased the RD to 99.9% and further addition of Ni (2 wt%) appeared to decrease the RD to 99.2%. The RHP of Ti–BN and Ti–B_4C mixtures with substantial Ni additions have been studied by several processes, including thermal explosion and high-pressure consolidation [8–10]. Large amounts of Ni (upto 25 at%) and high pressures (150 MPa) were used at 1200 °C. The final product contained Ni and Ni_3Ti in addition to TiB_2 and TiN/TiC. One of the possible mechanisms for densification at such lower temperatures has been attributed to the Ti–Ni eutectic [11] (~942 °C) leading to liquid phase sintering (Fig. 1).

Stoichiometric 3Ti–2BN with as little as 1 wt% Ni, reactively hot pressed at 1600 °C, showed the formation of transient liquid phase, which promotes densification [12]. By further exploiting the existence of non-stoichiometry, it was shown that the temperature may be further lowered to 1200 °C to yield a nitrogen deficient TiN_x–TiB_2 composite [13]. The same principle has been exploited in Zr–B_4C based systems in which reactive processing in combination with carbide

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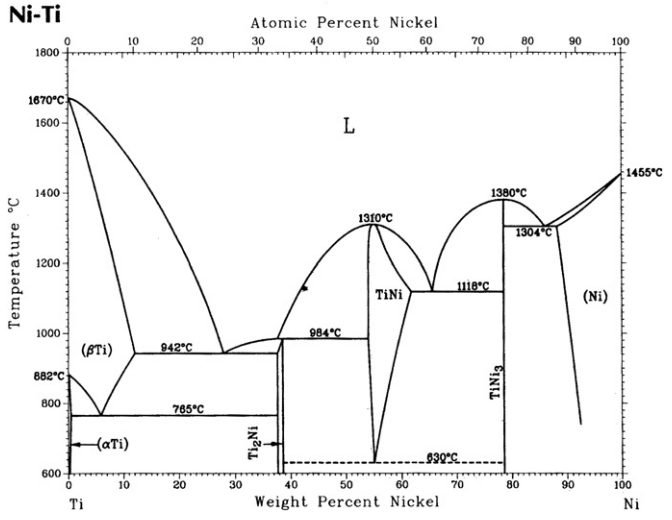

Fig. 1. Binary Ti–Ni phase diagram [11].

non-stoichiometry has brought the densification temperature down from 2000 °C to 1200 °C [14]. To the best of our knowledge, these represent the lowest temperatures at which ZrC [15] and TiB_2–TiN [12,13] have been densified. The importance of such processes is not confined to these materials but extends to composites such as ZrB_2–SiC [16] and ZrB_2–ZrC–SiC [17] in which non-stoichiometric ZrC can play a role as part of the final product or as part of an initial reaction product that eventually disappears. Previous reports on RHP of Zr–B_4C–Si powder mixtures showed the formation of ZrB_2-SiC and ZrB_2-SiC–ZrC composites at 2000 °C [18] and 1600 °C [19] respectively. In the latter study [19], ZrB_2–SiC–ZrC composite achieved a final density of 97.3% using planetary ball milled Zr–Si–B_4C powders that were held at 1450 °C for 3 h followed by RHP at 1600 °C. The ability to densify in this case was attributed to the defects created during ball milling and the removal of oxide impurities. A similar effect may be expected in TiC and TiB_2–TiC (and possibly other transition metal and nonmetal compounds) but is yet to be established, though densification of TiC from Ti–C powder mixtures at 1600 °C was ascribed to transient plasticity of a non-stoichiometric carbide [20–23]. The present paper seeks to demonstrate that exceptionally low temperatures may be sufficient for densification of TiC and TiB_2–TiC by suitably exploiting the twin roles of Ni and carbide non-stoichiometry.

2. Experimental procedure

Powder mixtures of Ti with the appropriate reactants (B_4C, C) used are given in reactions (1),(2):

$$Ti + xC \rightarrow TiC_x \text{ where } x = 1,\ 0.67 \quad (1)$$

$$(3+x)Ti + B_4C \rightarrow 2TiB_2 + (1+x)TiC_y \text{ where } y = 1/(1+x) = 1,\ 0.67 \quad (2)$$

Powders of Ti: ~99.5% pure and particle size ~44 μm (M/s Alfa-Aesar, MA), B_4C: ~99% pure and particle size 10–20 μm (M/s Boron Carbide India Ltd., Mumbai); carbon: 99% pure and particle size 1–7 μm (M/s Alfa-Aesar, MA) and Ni: ~99.5 pure and particle size ~4 μm (M/s Inco, London, UK) have been used in the present study.

Table 1
Starting mixtures, phases, density and lattice parameter of the monolithic and composites reactive hot pressed at 40 MPa, 1200 °C for 30 min.

Sl. no.	Starting mixture	Phases	Density,g/cm^3 (% RD)	[a]Lattice parameter (Å) of TiC
1	Ti–C	TiC, C	4.12 (88)	4.321
2	Ti–C (1 wt% Ni)	TiC, C	4.17 (89)	4.323
3	1.5Ti–C	$TiC_{x\sim0.67}$	4.26 (94)	4.311
4	1.5Ti–C (1 wt% Ni)	$TiC_{x\sim0.67}$	4.55 (99)	4.313
5	3Ti–B_4C	TiB_2, TiC, Ti_3B_4, TiB	3.75 (75)	4.321
6	3Ti–B_4C (1 wt% Ni)	TiB_2, TiC, Ti_3B_4	4.35 (87)	4.328
7	3.5Ti–B_4C	TiB_2, TiC, Ti_3B_4, TiB	3.84 (78)	4.312
8	3.5Ti–B_4C (1 wt% Ni)	TiB_2, TiC, Ti_3B_4	4.53 (99.9)	4.314

[a]Lattice parameters are averages from a broad peak.

Ti and C/B_4C powder mixtures were prepared by using TiO_2 milling media and hexane for 24 h. The powder mixtures were dried at ~100 °C for 5 h to evaporate the hexane. One weight percent Ni was added to the starting total mixture and a few selected powder mixtures were also prepared without Ni. While a small amount of weight loss of ~0.5 wt% was noticed in the TiO_2 milling media, no peaks of oxide were detected in the X-ray diffraction pattern of the starting milled powders. The powder mixtures were heated in vacuum to 1200 °C at 5–8 °C/min and pressed for 30 min at 40 MPa. The details of RHP experiments may be found in our earlier papers [12–15].

The composites were characterized by density measurement (water displacement method), identification of phase formation and lattice parameter measurement by X-ray diffraction (XRD) and microstructural observation by optical microscopy (Model EPIPHOT 200, Nikon, Japan) and field emission scanning electron microscopy (FESEM, Carl Zeiss, Germany) with energy dispersive X-ray microanalysis (EDAX-Oxford Instruments, UK).

The temperature chosen for densification is based on the trends in earlier experiments on Zr–B_4C [14] and Ti–BN [13] systems where it was shown that 1200 °C served as a defining temperature that could enable differentiation of systems according to how readily they could be densified. Table 1 summarizes the details of reactive powder mixtures, experimental conditions, phases present, lattice parameter and densities achieved.

3. Results and discussion

The results on phase analysis, lattice parameter measurements followed by microstructure and densification of reactive hot pressed (RHPed) samples are presented.

3.1. Phase identification

The X-ray diffraction study results of RHPed Ti–C (Fig. 2) show that the product phase (TiC) with stoichiometric powder mixtures contained residual carbon phase (Fig. 2(b) and (c)) while non-stoichiometric powder mixtures do not show carbon, whereas a small peak of Ti is seen (Fig. 2(d) and (e)). The addition of Ni reduces the residual carbon

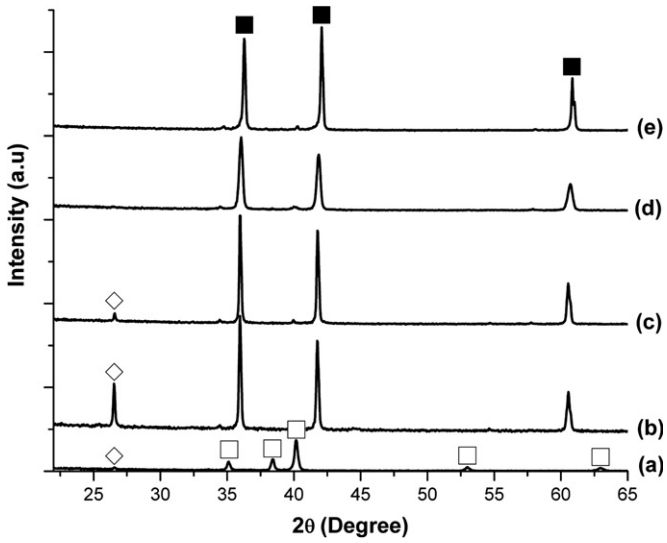

Fig. 2. XRD patterns of the (a) starting powder mixture, (b) Ti–C, (c) Ti–C (1wt% Ni), (d) 1.5Ti–C and (e) 1.5Ti–C (1 wt% Ni). □: Ti, ▲: carbon and ■: TiC.

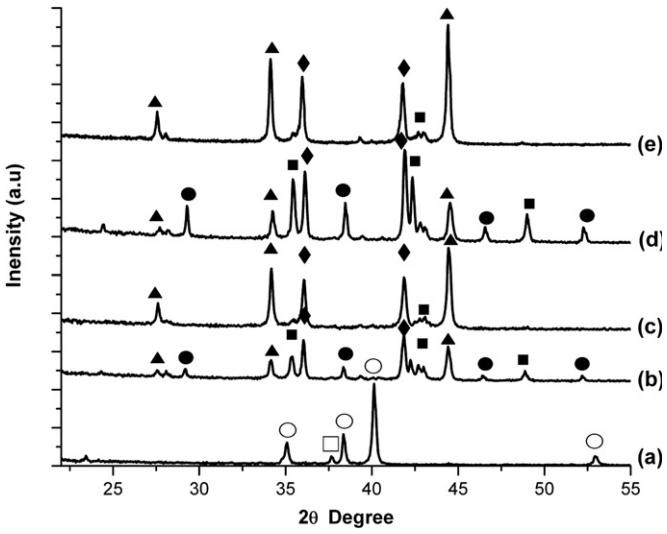

Fig. 3. XRD patterns of the (a) starting powder mixture, (b) 3Ti–B_4C, (c) 3Ti–B_4C (1 wt% Ni), (d) 3.5Ti–B_4C and (e) 3.5Ti–B_4C (1 wt% Ni). ○: Ti, □–B_4C, ▲ -TiB_2, ♦ -TiC, ■: Ti_3B_4, ●: TiB.

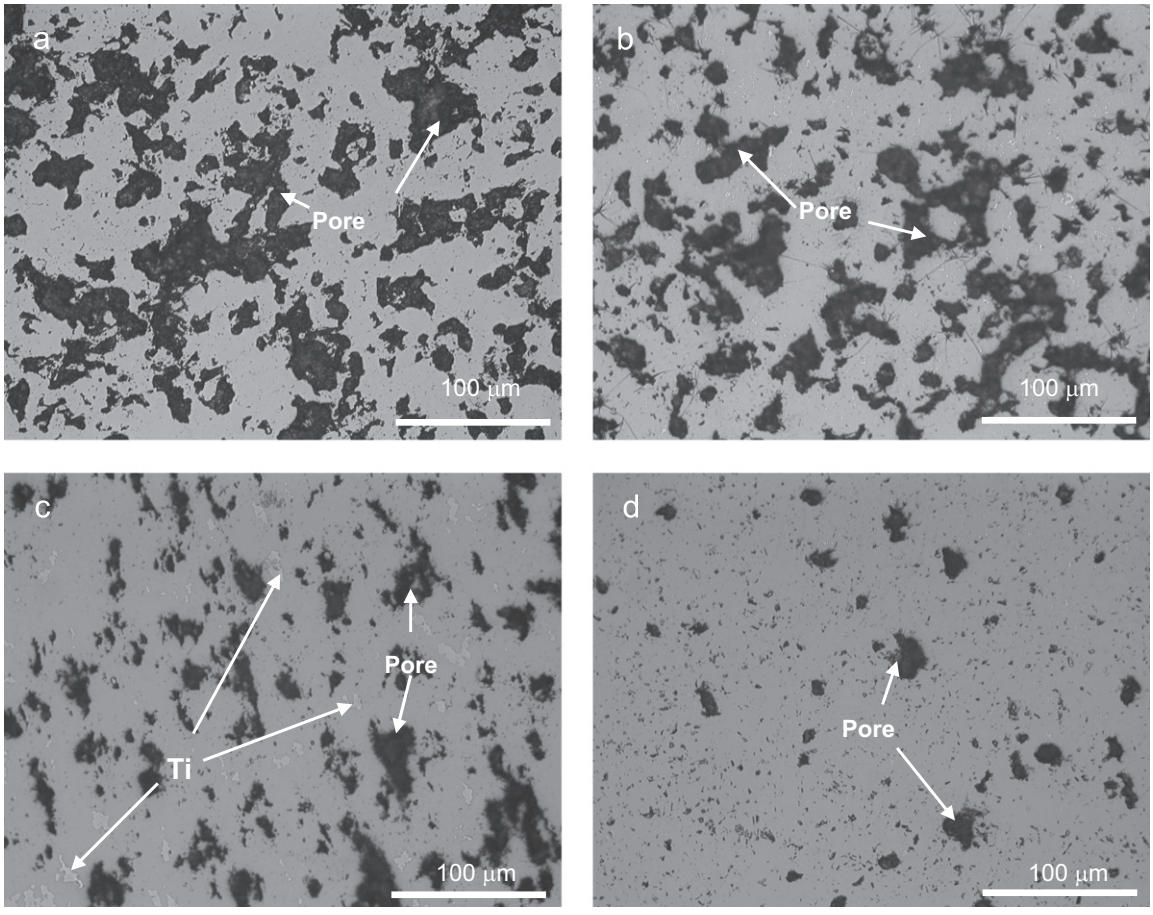

Fig. 4. Optical micrographs of TiC monoliths produced at 40 MPa, 1200 °C for 30 min: (a) Ti–C, (b) Ti–C with 1 wt% Ni, (c) 1.5Ti–C and (d) 1.5Ti–C with 1 wt% Ni.

which can be seen as reduction in the peak height of carbon phase. It may be noted that the non-stoichiometric powder mixture with Ni addition yields sharper peaks indicating a more homogeneous composition. The XRD patterns of the RHPed Ti–B_4C powder mixtures display more complex behavior (Fig. 3). The reaction does not proceed to completion (in both stoichiometric and non-stoichiometric starting powder mixtures) and significant amounts of sub-borides such as Ti_3B_4 and TiB are present (Fig. 3(b) and (d)). As an illustration, an example of the intermediate state in such a reaction might be

$$3.5Ti + B_4C \rightarrow 0.3TiB + 0.35Ti_3B_4 + 1.15TiB_2 + TiC \quad (3)$$

The equilibrium phase diagram of the Ti–B–C system displays binary phases, TiB, Ti_3B_4, TiB_2 and TiC [24–26]. At the temperature of interest (~1200 °C) it is observed that the non-stoichiometric 3.5Ti–B_4C powder mixture lies close to the $TiC_{0.65}$–TiB_2 tie line. However, because of incomplete reaction, the products formed are TiB, Ti_3B_4, TiB_2 (Fig. 3(b), and (d) Table 1). Such an intermediate state is readily understandable, given that the reaction is known to proceed by the dissolution of B_4C into Ti [20], thereby leading to the initial formation of Ti-rich borides which are highly stable and whose conversion to TiB_2 is slow in the solid state. This sluggishness of reaction is borne out by earlier studies which indicated that 4Ti:B_4C powder mixtures yielded the final products of TiC_x and TiB_2 phases at ~1750 °C [22,23], whereas composites produced up to 1600 °C through two-step process retained Ti_3B_4 as a minor additional phase, with TiC_x and TiB_2 [20,25]. In the present study the addition of 1 wt% Ni to both stoichiometric and non-stoichiometric Ti–B_4C powder mixtures is found to suppress the formation of TiB, leaving only a small amount of Ti_3B_4 phase (Fig. 3(c) and (e)), due to the enhanced rate of reaction assisted by diffusion in a liquid phase. The expected reaction may be written as (for purposes of illustration and comparison with Eq. (3)):

$$3.5Ti + B_4C \rightarrow 1.8TiB_2 + 1.4TiC_{0.71} + 0.1Ti_3B_4 \quad (4)$$

The expected volume fractions of TiB_2, $TiC_{0.71}$ and Ti_3B_4 are ~57, ~35 and ~8% respectively. Reactions (3) and (4) are meant for illustrative purposes to show how the formation of TiB and Ti_3B_4 can lead to intermediate carbon stoichiometries in the TiC phase that are higher than expected. Since plasticity increases with deviation from stoichiometry, the persistence of sub-borides can therefore retard sintering.

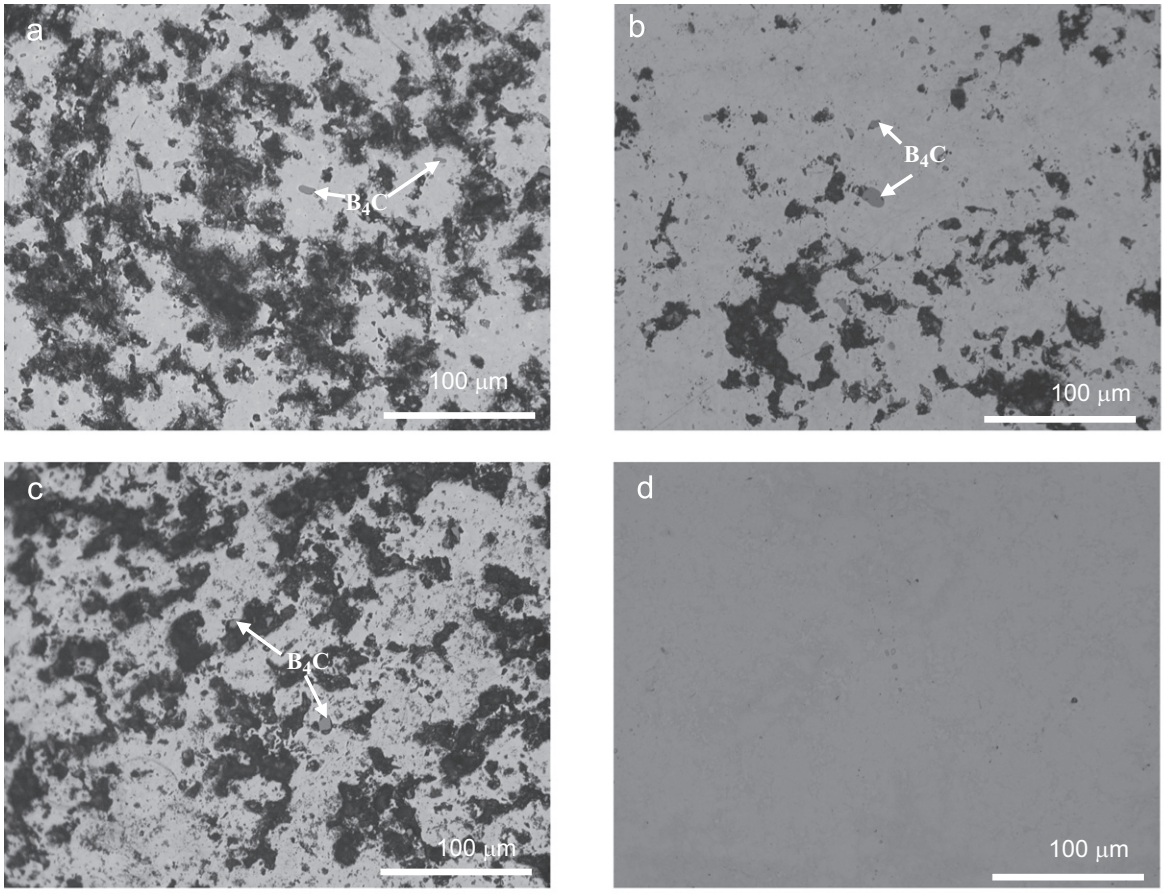

Fig. 5. Optical micrographs of TiB_2–TiC composites produced at 40 MPa, 1200 °C for 30 min: (a) 3Ti–B_4C, (b) 3Ti–B_4C with 1 wt% Ni, (c) 3.5Ti–B_4C and (d) 3.5Ti–B_4C with 1 wt% Ni.

3.2. Lattice parameter of TiC

In support of the above observations on the extent of reaction in TiC forming systems, it is seen that the lattice parameters of TiC produced with stoichiometric (4.321 Å without Ni and 4.323 Å with Ni) and non-stoichiometric (4.311 Å without Ni and 4.313 Å with Ni) reactant powder mixtures are different. The differences in the measured lattice parameter for TiC and $TiC_{x\sim0.67}$ in the composites (4.323 Å and 4.313 Å) are consistent with the trends reported in the literature (TiC—4.3265 Å and $TiC_{x\sim0.67}$—4.3222 Å) [27]. Broad reflections (400, 311, 420, 422 and 511) from the stoichiometric Ti–C powder mixture clearly indicate that the samples have a wide range of compositions. An addition of 1 wt% Ni to the 1.5Ti–C powder mixture produces sharp peaks indicates a uniformity composition (Fig. 2, curve-e). This observation is similar to that seen in Zr–C mixture RHPed at 1200 °C [15] which displayed variable carbon content while additional heat treatment at 1800 °C led to homogeneous composition and grain growth. In case of Ti–B_4C powder mixtures, the XRD peaks for TiC also showed similar broadening, indicative of a wide composition range, but more complex behavior than the binary powder mixtures, owing to the formation of intermediate borides.

3.3. Microstructural observations and densification of samples:

Optical micrographs of RHPed Ti–C monoliths produced with stoichiometric (Ti–C) and non-stoichiometric (1.5Ti–C) powder mixtures without and with 1 wt% Ni (Fig. 4), shows the effect of Ni on reaction and densification. The block regions are pores in all the samples, differentiating the pores and carbon (Fig. 4(a) and (b)) as indicated in XRD (Fig. 3(b) and (c) is difficult optically. The presence of excess Ti can be seen from shining particles in Fig. 4(c) and is supported by XRD patterns, which show a small peak of Ti at $2\theta\sim40$. The decrease in porosity can be seen in Fig. 4(d). Optical micrographs of RHPed composites starting with 3Ti–B_4C and 3.5Ti–B_4C powder mixtures with 1 wt% Ni (Fig. 5), illustrate the effect of Ni and excess Ti on reaction and densification. Partially reacted B_4C is seen in the stoichiometric mixture with Ni (Fig. 5(a)), similar to that seen in composites produced with stoichiometric and non-stoichiometric powder mixtures without Ni, whereas non-stoichiometric (3.5Ti–B_4C) composite with Ni (Fig. 5(b)) showed virtually complete reaction and densification. This observation is similar to that reported earlier on non-stoichimetric mixtures of Ti–BN [13], in which the formation of transient Ti–Ni liquid at 942 °C (Fig. 1) enables concurrent

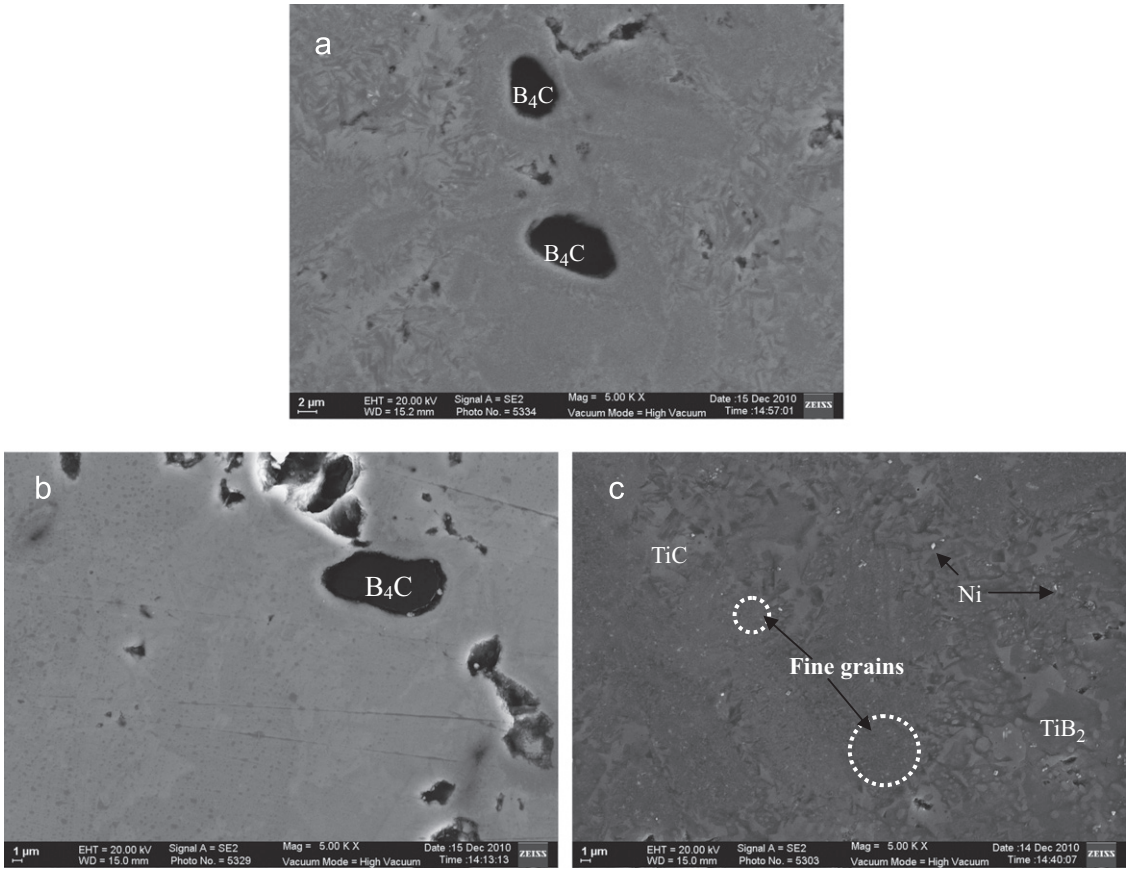

Fig. 6. SEM micrographs of composites produced at 40 MPa, 1200 °C for 30 min: (a) 3Ti–B_4C (1 wt% Ni), (b) 3.5Ti–B_4C and (c) 3.5Ti–B_4C (with 1 wt% Ni). Black particles in (a) and (b) are partially reacted B_4C particles, dark gray are TiB_2, light gray are TiC and white are Ni.

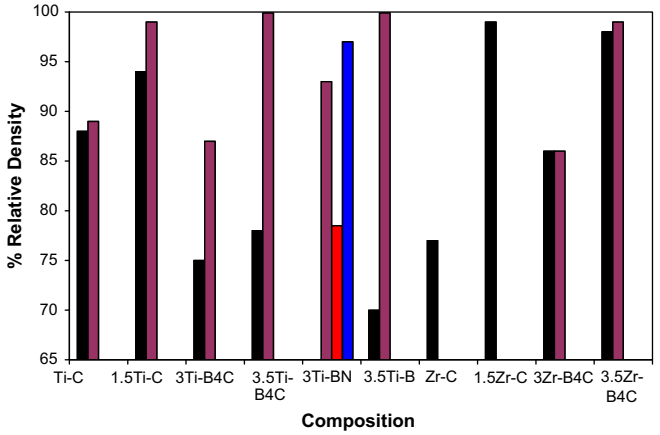

Fig. 7. Histogram of composites with different starting mixtures versus % relative density achieved at 40 MPa for 30 min: effect of Ni on densification (1200 °C: : without Ni, : with 1 wt% Ni) and 1400 °C: : without Ni and : with 1 wt% Ni).

reaction and densification. Stoichiometric Ti–B_4C composite (with Ni) showed partially reacted B_4C particles, with TiB_2 and TiC (Fig. 6(a)). In the non-stoichiometric composite (with Ni), the dark, gray and platelet regions are corresponding to TiB_2, TiC_x and Ti_3B_4, while white regions are identified as Ni in Fig. 6(b). A finer grained microstructure has been observed in many clusters, and has similar appearance to those reported in earlier studies [20,22].

The above results show that TiC and TiB_2–TiC may be produced to near theoretical density at 1200 °C with additions of ~1 wt% Ni. A comparison (Fig. 7) with earlier work on Ti–B–N [12,13], Zr–C [15] and Zr–B–C [14] suggests that non-stoichiometry directly enables densification in both the pure carbides and also in Zr–B_4C mixtures with Ni only promoting a more rapid completion of the reaction. Mixtures of Ti–B_4C, on the other hand are unable to exploit plasticity in the non-stoichiometric carbide because of the intermediate formation of Ti-rich borides which effectively reduce the carbide non-stoichiometry and its potential beneficial role. Such an effect is absent in Zr–B_4C powder mixtures owing to the absence of intermediate borides in the Zr–B system.

While we have not shown the role of transient liquid phase explicitly in the present work, it appears likely that the principle of using transient liquid phases through minor additions of an element, such as Ni, can help in promoting reaction, such as already demonstrated in the Ti–B–N system [12,13].

4. Conclusions

Theoretical density can be achieved at 1200 °C during reactive hot pressing to produce TiC and TiB_2–TiC composites by exploiting carbide non-stoichiometry in the presence of trace amounts of nickel.

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