

Pressure un-assisted reactive powder processing of high-density aluminide composites

K. Morsi*, N. Wang

Department of Mechanical Engineering, San Diego State University, 5500 Campanile Drive, San Diego, CA 92182, USA

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Abstract

The combustion synthesis of aluminide intermetallic composites has been extensively studied during the past three decades. A major problem in the combustion synthesis of intermetallic composites has been poor density and poor homogeneity of the final product. This has resulted in the need for the application of pressure to densify the product in addition to high temperature heat treatments to homogenize it. This paper discusses a new strategy for elemental green compact design that promotes considerably improved densities of combustion synthesized nickel aluminide–titanium carbide composites (at 20 vol.% TiC loading) without the application of external pressures. The paper covers ball milling studies, compaction behavior and the effect of elemental powder/green compact microstructural design on the porosity, phase content, microstructure and hardness of the combustion synthesized product. Product porosities as low as 1.4% have been produced using this new design compared to 25% using conventional means of powder processing prior to combustion synthesis, this has also contributed to a greater than five times improvement in hardness of the resulting product.

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1. Introduction

Combustion synthesis is a low-energy process that has been used to produce intermetallics, ceramics and composites from powder compacts at relatively low processing temperatures and in very short processing times [1,2]. In the combustion synthesis of nickel aluminides under the thermal explosion mode of ignition, the powder compact is uniformly heated to a temperature above the ignition temperature (~640 °C). Following ignition, the compact reacts throughout its volume converting the nickel (Ni) and aluminum (Al) into the desired nickel aluminide intermetallic depending on initial composition. The reaction is exothermic so the compact is raised to very high temperatures that can sometimes equal/exceed the melting point of the intermetallic being formed. Products are usually porous, this has lead one of the authors to apply bulk deformation processes (extrusion/forging) simultaneously while the specimen is hot to generate consolidated materials [3,4]. One of the pre-

requisites for successful reactive processing using combustion synthesis is that molten aluminum (the low melting point phase) should be able to efficiently spread throughout the compact, and effectively surround the nickel particles. The process has also been termed reactive transient liquid phase sintering [5]. The addition of ceramic reinforcements (e.g. titanium carbide (TiC)) to the 3Ni+Al mixture has a number of detrimental effects [6]. First, the spreading of Al will be restricted by the presence of TiC. Second, TiC will act as a heat sink and thus the maximum attainable temperature achieved during the reaction (i.e. the combustion temperature) will be reduced. Both of these effects will lead to an increase in product porosity and in-homogeneity with an increase in volume fraction of TiC reinforcement. Recently, Yeh et al. reported a decrease in product density with increase in TiC content for combustion synthesized NiAl–TiC composites [7]. The detrimental effect that ceramic reinforcements have on the product porosity and homogeneity has lead a number of researchers to simply apply pressure during or immediately after the reaction, in order to generate high-density products and also use high temperatures to homogenizes the microstructure when reinforcing the intermetallic with a ceramic phase [8–11]. In this paper we introduce

* Corresponding author. Tel.: +1 619 594 2903; fax: +1 619 594 3599.
E-mail address: kmorsi@mail.sdsu.edu (K. Morsi).

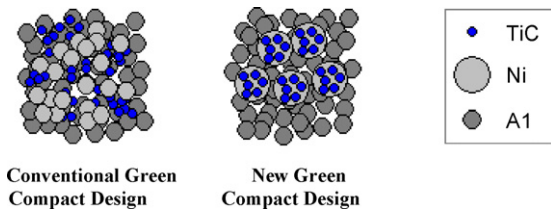


Fig. 1. Conventional and proposed microstructural designs of composite green compact prior to combustion synthesis.

a new microstructural design of the green compact that basically removes the ceramic reinforcement from the path of molten Al to allow more efficient spreading, resulting in high product densities without the need for an externally applied pressure. Fig. 1 is a schematic of the new and conventional compact design. The TiC is embedded in the high temperature phase (Ni) through the process of ball milling, which can also have the effect of introducing lattice defects that can improve diffusion characteristics during the reaction. The effect of this new design on the Vickers hardness of the final product is also discussed.

2. Experimental procedures

Commercially pure Ni (5–10 μm), Al (8–11 μm), and TiC (2 μm) powders (Atlantic Equipment Engineers, NJ, USA), were used as the starting materials (all particle sizes are manufacturer quoted values). Micrographs of the powders are shown in Fig. 2.

The composition of the powder mixture was chosen to give a final product of Ni_3Al with 20 vol.% TiC after complete conversion.

The Ni and TiC powders were first rotator mixed for 1.5 h then ball-milled for 10 h (interrupted runs) in a SPEX 8000 mixer under an argon atmosphere. WC-Co balls were used as the milling media. The ball-to-powder weight ratio used was 4:1. This process was conducted to embed/disperse the TiC into the nickel powders. The milled Ni–TiC composite powders were then gently rotator mixed for 1.5 h with the remaining Al making up the balance. The elemental powders at this stage are referred to as composition A. Prior to ball milling, all powders were vacuum degassed at 120 $^\circ\text{C}$ for 10 h. This is important so as not to trap/embed any moisture or low-boiling point impurities with the TiC or Ni into the new composite particles, which would evaporate and expand during the reaction and cause unwanted porosity. Green specimens used or the combustion synthesis experiments were produced by pressing the powders in a die with diameter of 8 mm, and height ~ 3 mm (to a relative density of 70–75%). The specimens were then combustion synthesized in a tube furnace under argon atmosphere by heating at 10 $^\circ\text{C}/\text{min}$ to a temperature of 700 $^\circ\text{C}$ and dwelling for 15 min followed by cooling. For comparison Ni, Al and TiC were rotator-mixed for 1.5 h compacted and combustion synthesized under exactly the same

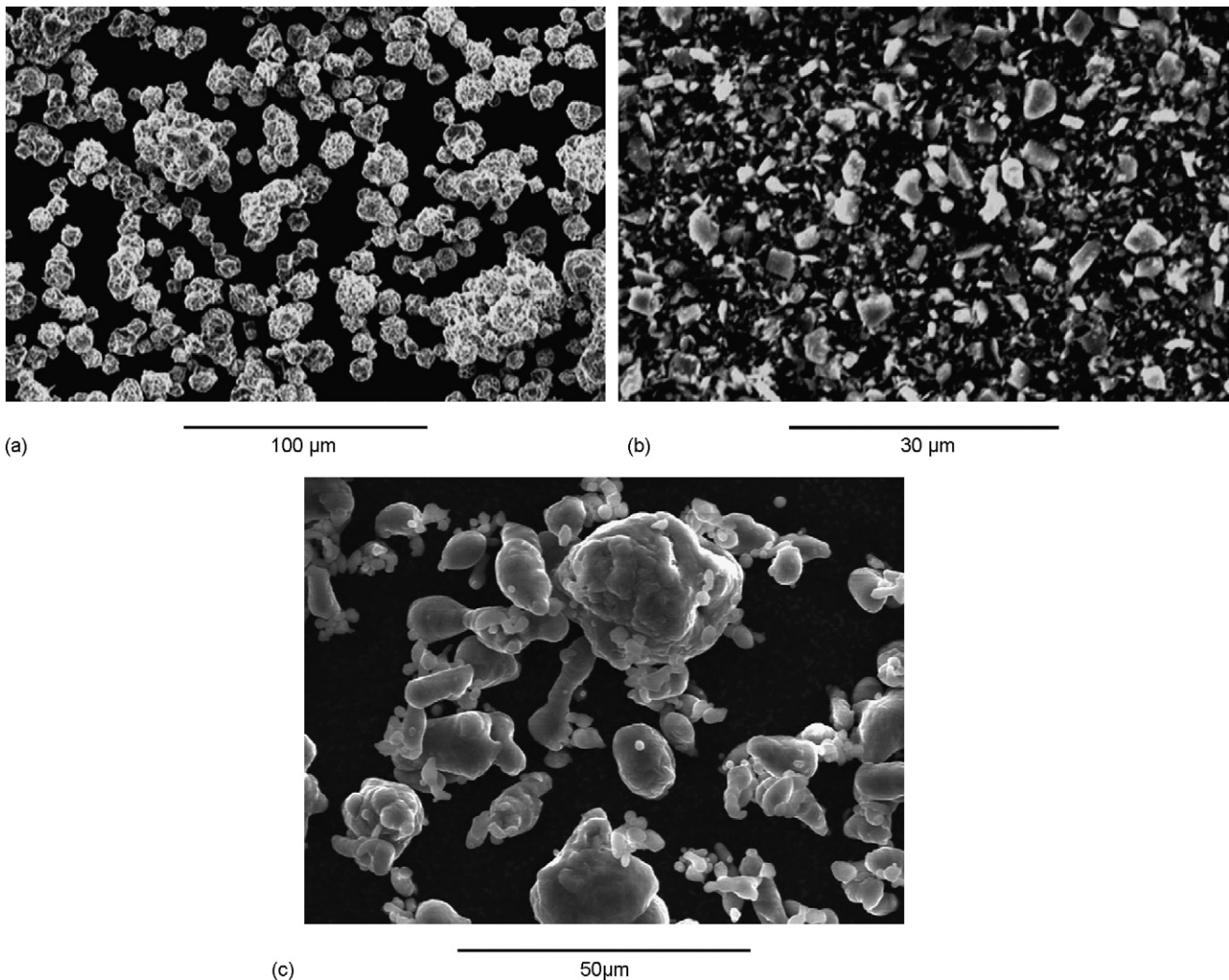


Fig. 2. (a) SEM image of initial Ni powders. (b) SEM image of initial TiC powders. (c) SEM image of initial Al powders.

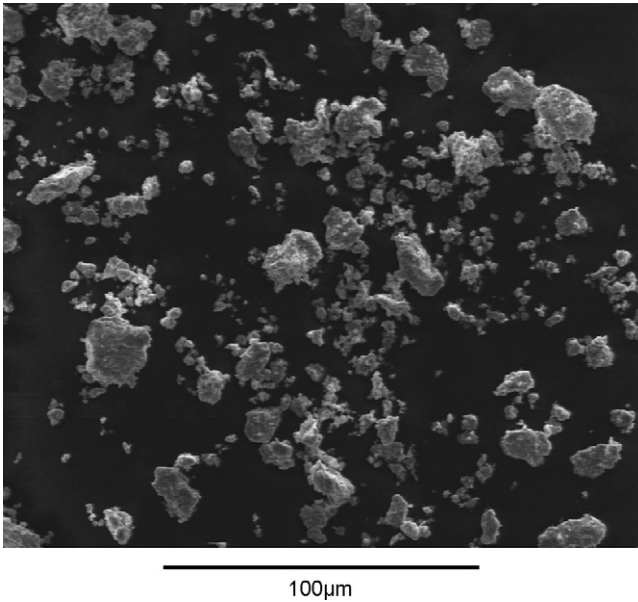


Fig. 3. Ni–TiC powder after 1 h of ball milling.

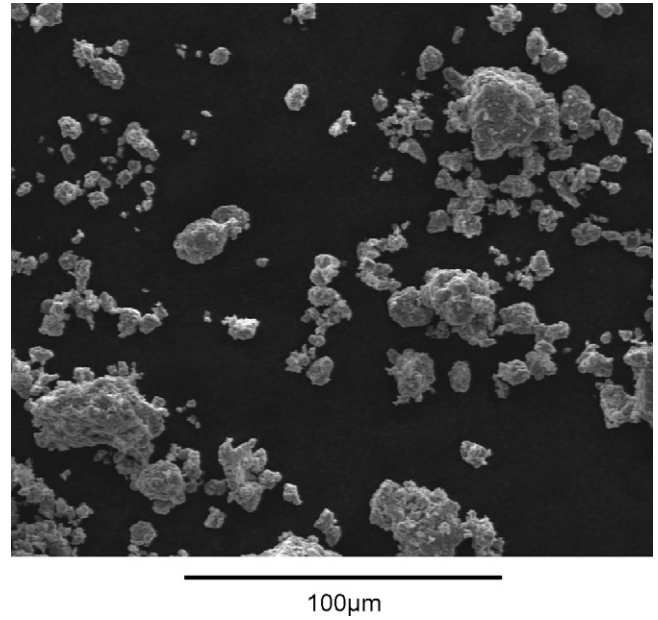


Fig. 5. Ni–TiC powder after 5 h of ball milling.

conditions (this will be referred to in the paper as composition B) (in this case all powders were also vacuum degassed prior to compaction). The green compacts were also pressed to similar green densities to composition A. Also compaction curves for both powder compositions were generated by pressing each powder at six different compaction pressures (two specimens were used for each pressure and the average relative density plotted). Microstructural examination of the cross-section was done after the specimens were cut, ground and polished to 1 μm finish. Scanning electron microscopy and X-ray diffraction (XRD) were used for microstructural examination and phase analysis. Product porosity was measured using image analysis. Hardness testing was conducted using a Vickers macro hardness tester using a load of 10 kg.

3. Results and discussion

Figs. 3–6 are low magnification electron micrographs depicting the general evolution of Ni–TiC powders with ball milling

time. With increase in milling time from 1 to 10 h, the powder evolved from a flaky external texture into a smoother and more coherent surface. The ball milling process involves deformation, cold working, fracturing and re-welding of Ni powder. TiC particles have also been seen to fracture during the process. These TiC particles become trapped in between the fractured and re-welded Ni particles during ball milling. A continuation of this process results in a homogeneous distribution and dispersion of fractured and refined TiC in Ni particles. The Ni–TiC composite particle size also is found to change with milling time.

Fig. 7 is a higher magnification micrograph of a typical Ni–TiC composite powder particle after ball milling for 10 h, showing the morphology. The particle consists of nickel with

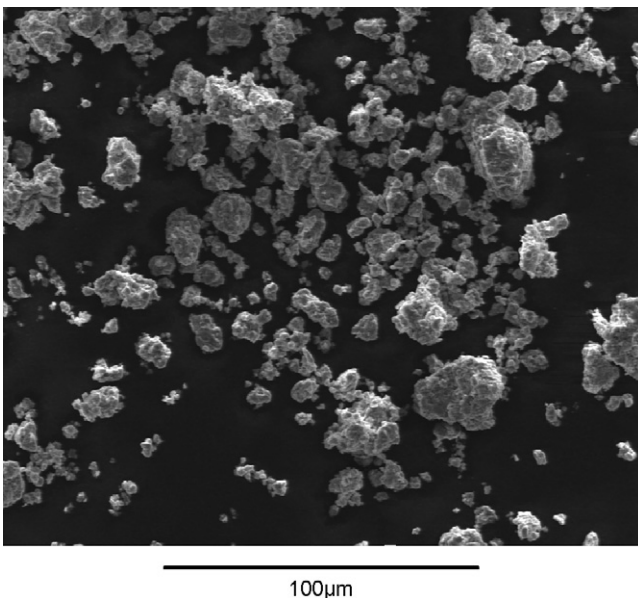


Fig. 4. Ni–TiC powder after 3 h of ball milling.

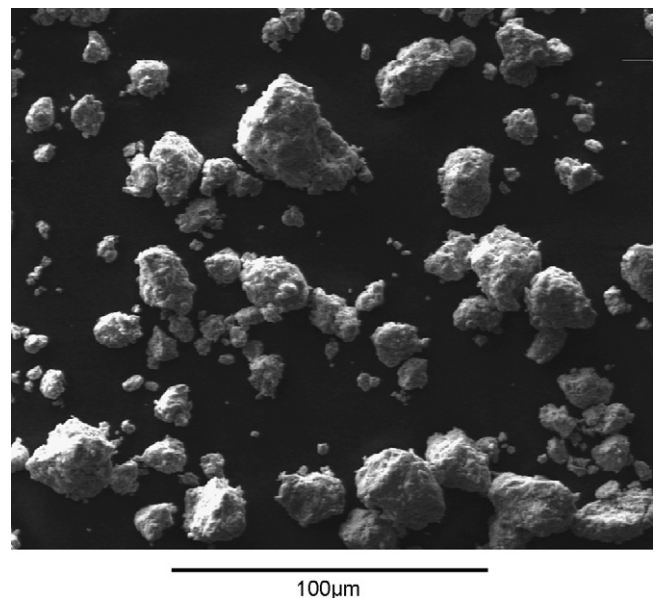


Fig. 6. Ni–TiC powder after 10 h of ball milling.

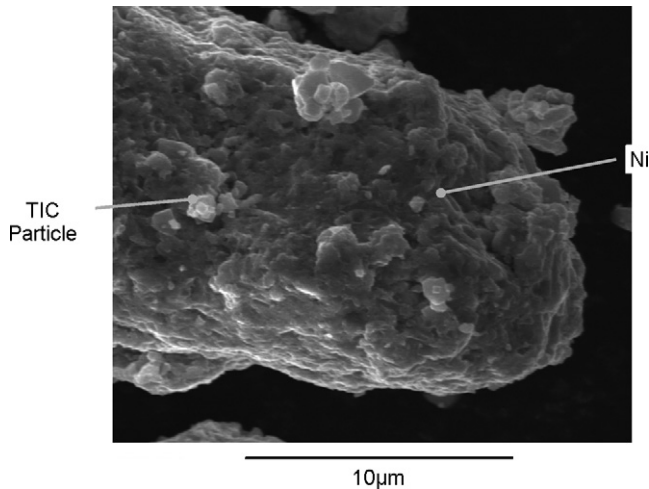


Fig. 7. Ni–TiC powder particle after 10 h of ball milling.

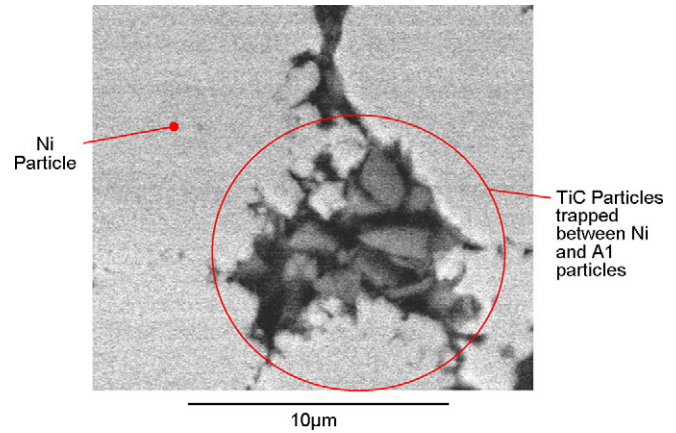


Fig. 9. SEM of cross-section of compacted composition B specimen prior to combustion synthesis.

well-dispersed TiC particles. As mentioned, TiC was also generally observed to decrease in size with ball milling time. As mentioned, for composition A, the 10 h ball-milled Ni and TiC composite powders were further rotator mixed with Al powder followed by combustion synthesis.

Figs. 8 and 9 show the polished cross-sections of the Ni + TiC + Al green compact microstructure of the new green compact design (Fig. 8) and conventional design (Fig. 9). It is clear that TiC is well dispersed in the nickel powders for the new design, and would therefore be subsequently removed from the path of the molten Al during the reaction. The TiC also appears to have been fragmented into smaller submicron particles. On the other hand, in the conventional powder mixed green compact; a large fraction of TiC particles are seen to be agglomerated into distinct regions and not well distributed throughout the microstructure prior to the reaction.

As seen from Fig. 10, composition A powders exhibit lower compactability than composition B (i.e. at any given pressure the rotator mixed powders are pressed to higher densities). This result is expected since the ball-milled Ni within the Ni + TiC

composite powders in composition A would have experienced some cold working. Also the decrease in TiC average particle size and the improved distribution of TiC within Ni during ball milling increases the overall TiC/Ni contact area resulting in an increased yield/flow stress of the powders which leads to poor compactability. This effect appears to be dominant despite the generally larger particle size for the composition A powders.

Fig. 11 shows an XRD plot of the precursor powders used for both compositions prior to combustion synthesis. The figure shows that for both compositions the peaks belong to Al, Ni and TiC. This means two things. First, for composition A, no new phases are clearly generated after ball milling and therefore no obvious interfacial reaction between the Ni and TiC during ball milling is evident. Also there is no significant peak broadening in composition A compared to composition B, for the nickel peaks. Hence nanostructured Ni has not been formed.

Fig. 12 is a scanning electron micrograph of the reacted compact of composition B. As mentioned earlier the melting and spreading of Al is an integral part of the combustion synthesis process. The Al spreads through capillary forces and surrounds the Ni particles. Moreover, Ni/Al reaction further occurs through diffusion. It is evident from the micrograph that the reaction did not go to completion. Nickel particles are seen with outer

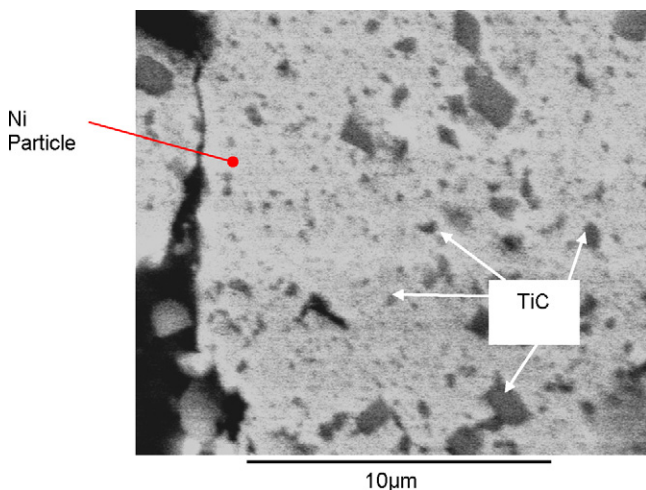


Fig. 8. SEM of cross-section of compacted composition A specimen prior to combustion synthesis.

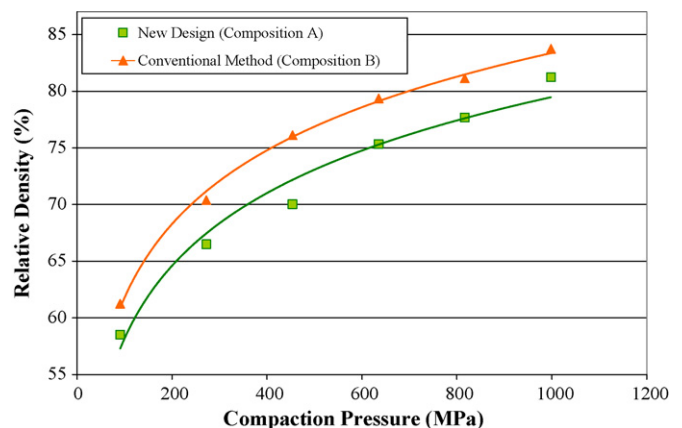


Fig. 10. Compaction pressure vs. relative density for composition A and B powders.

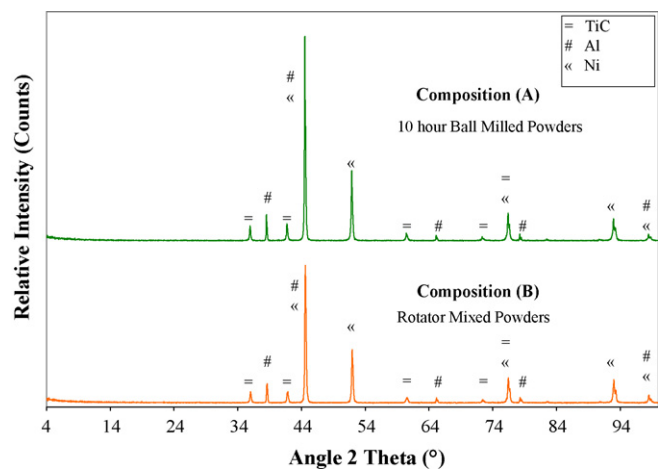


Fig. 11. X-ray diffraction scans of elemental powders for composition A and B, respectively.

concentric rings of intermetallic phases, but with a clear nickel un-reacted core (confirmed by energy dispersive spectroscopy (EDS)).

Again, it is important that the Al spreads efficiently and quickly during the process since following ignition, and due to the exothermic nature of the reactions, the compact temperature is raised to high values that are maintained only for very short periods of time (seconds). The presence of TiC in the path of Al will certainly restrict its movement (in addition to acting as a heat sink that absorbs the energy of the reaction and reduce the overall maximum temperature achieved).

In Fig. 12, TiC particles can also be seen agglomerated and segregated in regions between the particles (resembling the green microstructure). The presence of these groups of particles will also add another negative effect (excess porosity). TiC is a high melting point material (melting point in excess of 3000 °C) and the temperatures experienced during the reaction, in addition to the short duration of reaction will not be enough to sinter these particles together. This will therefore leave inter-particle porosity between these TiC particles. Hence the porosity observed for composition B after reaction consists of small and large pores belonging to the microstructural porosity in addition to these

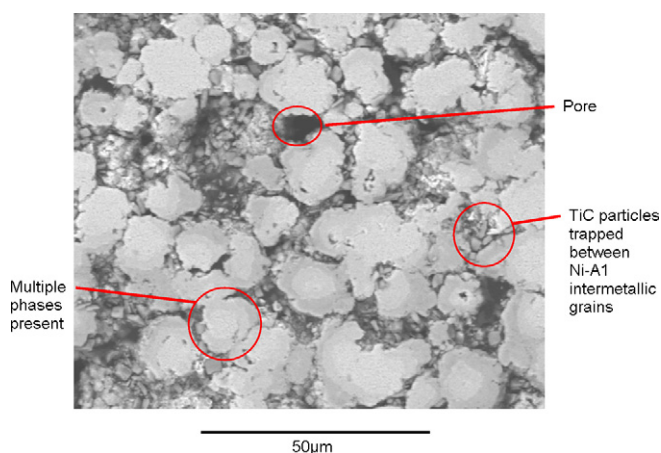


Fig. 12. SEM image of composition B reacted at 700 °C.

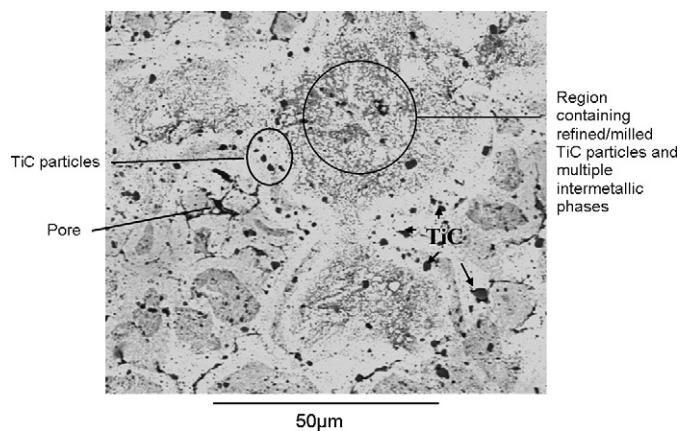


Fig. 13. SEM image of composition A reacted at 700 °C (different size TiC are seen).

small inter-TiC-pores. Detailed image analysis has revealed that the total porosity for this composition and its standard deviation is $24.7 \pm 4.2\%$. This is in large contrast to the porosity content of reacted composition A ($1.4 \pm 0.6\%$). The microstructure was almost fully dense; this is seen in Fig. 13. The dark grey regions are TiC particles. Also note that the microstructure contains regions with similar but very fine features. These contain TiC particles that have been milled down during the ball milling process to submicron sizes. The same type of features were also seen when the green compact was sectioned and polished prior to the reaction (Fig. 8). It is clear that in Composition B the TiC particle size has not been reduced in size. For composition A, although TiC particles exist that have not been reduced in size, a considerable amount of TiC has been refined as mentioned.

What is truly significant is that the porosity content of reacted composition A is extremely low, showing the effectiveness of the new green compact microstructural design. The TiC is however not distributed evenly in the microstructure, resembling more a dual matrix, i.e. regions of reinforced material (where the Ni–TiC composite particles have been reacted) surrounded by un-reinforced regions (EDS analysis revealed these surrounding regions to be inhomogeneous in nature but also predominantly Ni_3Al). It should be mentioned that the median particle size of the ball-milled Ni–TiC powders was determined through sieve analysis and found to be $\sim 23 \mu\text{m}$ which is larger than the nickel particle size. This favors a more interconnected Al powder network within the green compact which would also help in the densification and reactivity. The porosity levels obtained at this TiC content is unprecedented to the best of the authors' knowledge for combustion synthesized nickel aluminide composites (without the application of an external pressure).

XRD scans on both reacted compositions are shown in Fig. 14.

The XRD scans show that TiC is still present following the reaction for both compositions. Moreover, the microstructure is multi-phased in both cases signifying the reaction did not go to completion (i.e. did not form 80 vol.% Ni_3Al and 20 vol.% TiC). Instead, a number of phases have been formed including Al_3Ni , Al_3Ni_2 , Ni_3Al , NiAl in addition to un-reacted Ni and Al for composition B and solid solutions of Ni/Al for compo-

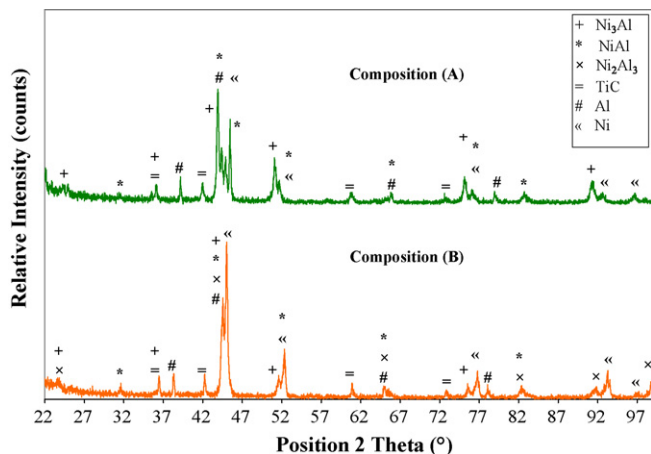


Fig. 14. X-ray diffraction scans of reacted compacts for compositions A and B, respectively.

sition A. What is evident is that a larger amount of Ni_3Al is present in composition A (the new microstructure design), i.e. the reaction was more complete, compared to that for composition B. High temperature heat treatments or optimizing the ball milling parameters to control the Ni–TiC composite particle defect structure may be needed to fully homogenize these microstructures. This is the subject of future work.

The Vickers hardness number for the reacted specimens with the new microstructural design was 220 ± 8 VH10 compared to 39 ± 3 VH10 for the conventional case. The drastic difference between the hardness values of these two materials is primarily due to the difference in porosity levels, phase content and the ineffectiveness of TiC at reinforcing the material in the conventional design, where they are seen to form agglomerates with inter-particle porosities. Moreover the TiC in the new design has been refined and better distributed through the ball milling process making them more effective at reinforcing and strengthening the material.

4. Conclusions

A number of conclusions from the present study can be drawn:

(1) Conventional mixing of Ni + Al + TiC powder followed by compaction and combustion synthesis results in mul-

tiphase intermetallic microstructures with porosity content $\sim 25\%$.

- (2) A highly dense compact ($\sim 1.4\%$ porosity) was produced following combustion synthesis using a new green compact microstructural design that involves embedding TiC into the nickel particles and removing them to a large extent from the path of the molten aluminum during the combustion synthesis of nickel and aluminum. This porosity level is unprecedented at this TiC loading without the application of external pressure.
- (3) The Vickers hardness of the reacted material using the new green compact design was over five times that of the conventionally processed material.
- (4) The new microstructural design resulted also in a multi-intermetallic phase microstructure; however Ni_3Al yield was greater than that for conventionally mixed material.
- (5) Future work will examine different reaction processing parameters and heat treatment procedures to fully homogenize the resulting microstructure.

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