

In-situ Densification of Combustion Synthesized Nickel Aluminide-Carbon Nanotube Composites from Nanoreactants

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Abstract

In-situ densification and combustion synthesis was investigated as a unique processing technique for the formation of carbon nanotube reinforced nickel aluminides. Nano-sized reactants were utilized to form NiAl-CNT composites with densities up to 96% of the theoretical and nanosized grains were observed. For composites synthesized with 1-wt% single-walled carbon nanotubes a 30 % improvement in Vickers microhardness was observed over the monolithic material. The same improvement was not observed for multi-walled carbon nanotubes. It is demonstrated that with increased carbon nanotube loading the reaction is critically impacted leading to pre-melting and hence low product density, and a reduction in Vickers microhardness.

Introduction

Carbon nanotube (CNT) reinforced composites have been the focus of much research during the past few years. They are considered the ultimate reinforcement material with a Young's modulus of 1.2 TPa [1] for single-walled carbon nanotubes (SWCNTs) and 950 GPa [2] for multi-walled carbon nanotubes (MWCNTs). While the majority of research in this area has been focused on polymers; ceramics, metals and alloys have also been investigated. For ceramic, metal and alloys the processing methodologies have been those primarily used in traditional powder technology [3-5]. The most significant issue with these processing methods is a long term exposure to high temperatures which results in partial damage of the CNTs and also increases the vulnerability of the CNTs to interfacial reactions with the matrix material. Therefore, in order to retain the desired reinforcement properties the exposure to high temperatures must be minimized [6].

In-situ densification and combustion synthesis offers a route for the formation of dense composites reinforced with CNTs that may be completed within seconds compared to hours in conventional processing, therefore minimizing the long exposure time to high temperatures. This processing technique utilizes the exothermic heat of reaction to spontaneously transform reactants, when ignited, to desired products. With this synthesis technique a variety of reactant powder sizes can be utilized to yield products with nano to micron sized grains. While very high temperatures (>3000K) can be reaching during the combustion reaction, those temperatures are maintained for only a fraction of second [7]. By utilizing this method it is possible to synthesize a variety of ceramic and intermetallic materials that are reinforced with CNTs.

Experimental

The objective of this experimental study was to extend our previous research work [8] on combustion synthesis of CNT-reinforced materials by further investigating the high

temperature reaction of Ni and Al with nano-sized reactants and varying additions of CNTs. For this work the mixing solvent, dispersant, and methodology are varied and we address what effect varying CNT addition has on the product morphology, the phase composition, and the Vickers microhardness of the composites.

The following raw materials were utilized: SWCNTs (Helix Materials, $d=1.4$ nm), MWCNTs (Cheap Tubes, $d=8-15$ nm), Ni powder (Argonide, $d=100$ nm), and Al powder (Novacentrix, $d=80$ nm). The stoichiometric reaction between nickel and aluminum was investigated. In the case of nano-sized aluminum there is a considerable aluminum oxide layer present (23% for 80 nm) and must be accounted for. The resulting material is a nickel mono-aluminide alumina composite.

Prior to varying the addition of CNTs into the reactive mixture several different solvents, dispersants, and mixing techniques were investigated. The following solvents were used: phenyl ethyl alcohol, ethanol, and isopropyl alcohol. Two different dispersants were tested: sodium dioctyl sulfosuccinate and 1C Coulter. Sonication with and without additional mechanical mixing was used. Mechanical mixing was achieved using a SPEX 8000 shaker with 3 mm stainless steel grinding media. The results and most effective methodology are discussed below.

Simultaneous combustion synthesis and densification experiments of these composites were conducted in a uniaxial press at a preheating temperature of 520 °C and a densification pressure of 200 MPa as shown in Fig 1a.

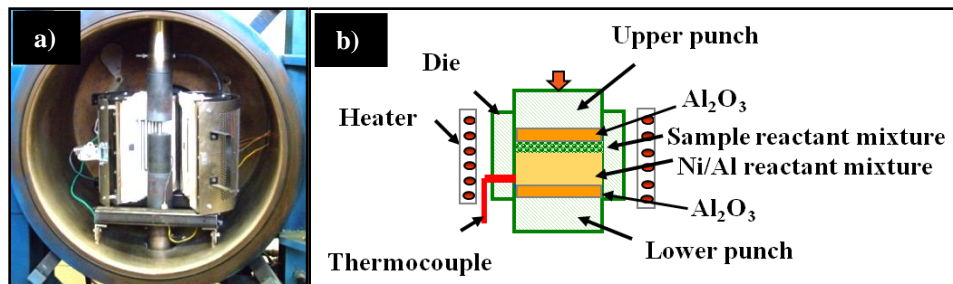


Fig. 1. a) *Experimental equipment and, b) die setup for the in situ combustion synthesis and densification of carbon nanotube loaded reactant mixtures to produce nanocomposites.*

For these experiments a 0.5" inconel graphite foil lined die and vacuum atmosphere were utilized. In these experiments a small amount (approx. 2 g) of reactant mixture containing CNTs was used. Due to a high level of heat losses, an additional chemical energy source had to be added in order to simulate the combustion process on a larger scale. This was accomplished by placing the reactant mixture under study above 10 grams of micron Ni/Al reactant mixture and placing 1 g Al₂O₃ on top and bottom as a non-conducting medium as shown in Fig 1b.

Vickers microhardness was measured with a Buehler Micromet 4 Hardness Tester using a 500 g load, with a 10 s dwell time. Samples were mounted and polished with SiC paper from 240-1200 grit, then followed with 1 μ m and 0.5 μ m Al₂O₃ suspensions prior to microhardness measurement. Density measurements were made using Archimedes principle.

Results

Mixing Methodology

In this work several different solvents, dispersants, and mixing methodologies were evaluated. These experiments were conducted for 1-wt % SWCNT addition. The effectiveness was based on the resulting Vickers microhardness as shown in Table 1. Initial synthesis for this system was conducted using phenyl ethyl alcohol (PEA) as the mixing solvent [8], as indicated by the low microhardness value this method led to low density samples and insufficient dispersion of the CNTs. The use of SDS as pre-dispersant also yielded poor results due to interaction of the dispersant with the Al nanopowder during the combustion process.

Table 1. Vickers microhardness (GPa) values for composites synthesized with 1-wt% SWCNT addition.

MIXING METHOD	SOLVENT	Ethanol	PEA	IPA
	DISPERSANT			
Sonication	none	2.92±0.51	2.74±0.40	
Sonication	SDS	2.34±0.27		
Sonication + 30min SPEX shaker w/media	none			3.48±0.17
Sonication + 30min SPEX shaker w/media	1C Coulter			4.62±0.13

It was found that the most effective mixing technique utilizes pre-dispersion of the SWCNTs with 1C Coulter as the dispersant, followed by mechanical mixing via the SPEX shaker. The dispersant is removed with vacuum treatment at 130°C. All subsequent experiments were conducted using 1C Coulter as the dispersant with 20 minutes of sonication followed by 30 minutes of SPEX shaker mixing.

Product Morphology and Phase Composition

SEM was used to compare the product morphologies for composites synthesized with 0, 1, 2.5, and 5-wt% addition of SWCNTs. Samples were fractured and the interior morphology imaged. As shown in Fig 2 when 1-wt% to 5 wt% SWCNT addition is compared a significant difference is observed. For the 1-wt% material nearly full density (96 % TMD) was achieved and there are regions of melt as well as nano-sized grains observed.

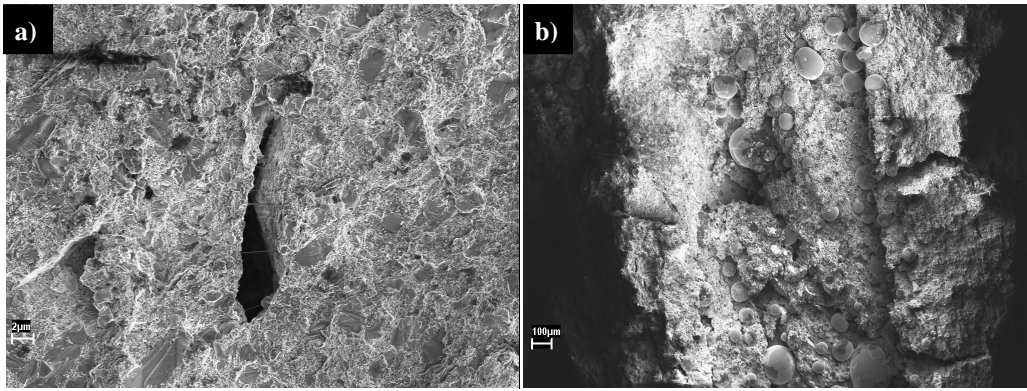


Fig.2. Fractured surfaces of *in-situ* densification and combustion synthesized nickel aluminide composites; a) 1-wt% and b) 5-wt% SWCNT addition.

The SWCNT addition can clearly be seen as the CNTs clearly bridge any residual porosity within the sample. For both the 2.5 and the 5-wt % SWCNT additions the product is very porous due to the pre-mature formation of product as indicated by the spherical particles. EDS of these spheres confirm that they are not an individual reactant melted but rather the desired product NiAl.

XRD patterns of the composites revealed that for all compositions that full conversion to the desired product, NiAl, is achieved as shown in Fig 3. In addition, no carbide peaks are detected.

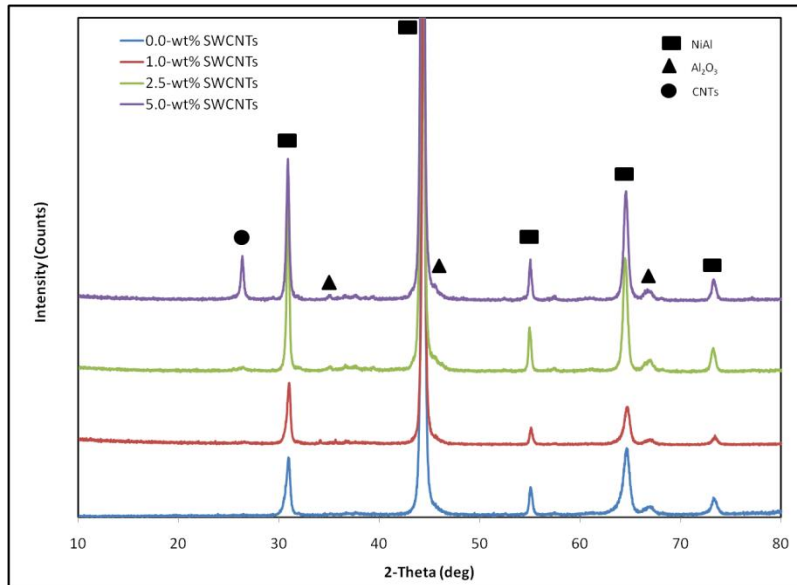


Fig 3. XRD patterns for *in-situ* densification and combustion synthesized nickel aluminide composites.

Microhardness

Vickers microhardness was measured for 0, 1, 2.5, and 5-wt% SWCNT additions and for 1-wt% MWCNT addition. Due to the pre-mature formation of product within higher CNT addition the resulting products exhibited low densities and therefore low microhardness values

with increased CNT addition. As shown in Fig. 4 there is a 30 % improvement in the Vickers microhardness for composites synthesized with nano-sized reactants and 1-wt% SWCNT addition over that of monolithic.

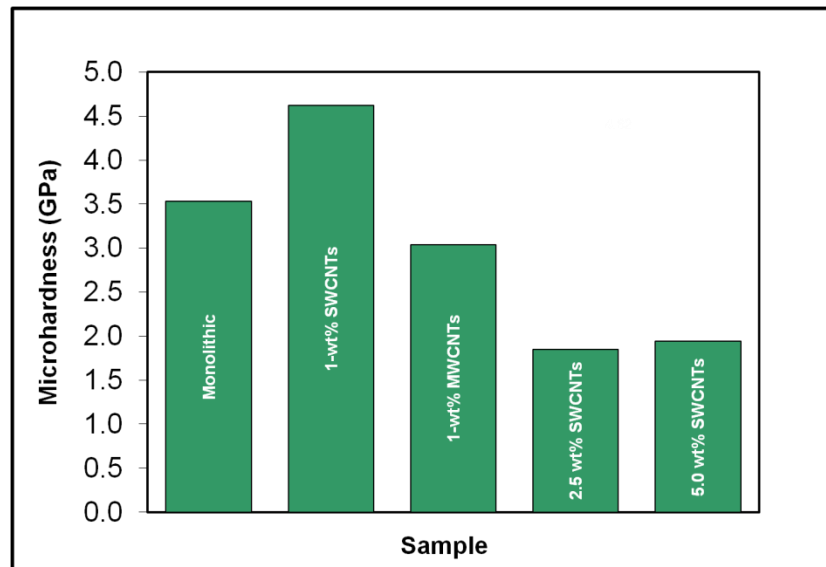


Fig. 4. Vickers microhardness for in-situ densification and combustion synthesized nickel aluminide composites with varying CNT additions.

This was not the case for composites synthesized with 1-wt% MWCNTs. For 1-wt% MWCNT addition there was a reduction rather than an improvement in the microhardness. This is due to the low product density achieved in this system. Representative product densities are listed in Table 2 for the different composites synthesized with this technique.

Table 2. Representative product densities for CNT-reinforced NiAl composites.

Sample	0 wt% CNTs	1 wt% SWCNT	1 wt% MWCNT	2.5 wt% SWCNT	5 wt% SWCNT
Density, g/cc	4.74	5.30	4.84	4.39	3.47

Summary

In summary this work has clearly demonstrated that in-situ densification and combustion synthesis coupled with CNTs offers a processing route to CNT-reinforced composites. The role of appropriate mixing methodologies in achieving composites with improved properties has been shown. In addition, the critical effect increased CNT addition has on the reactive processing of these types of materials was discovered and is presently being further examined from the perspective of increased thermal conductivity of the reactive mixtures.

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References

- [1] J.P. Salvetat, G.A. Briggs, J.M. Bonard, R.R. Bacsa, A.J. Kulik, T. Stöckli, et al., "Elastic and shear moduli of single-walled carbon nanotube ropes," *Phys Rev Lett*, vol. 82(5), 1999, pp. 944-7.
- [2] F. Lupo, R. Kamalakaran, C. Scheu, N. Grobert, and M. Rühle, "Microstructural investigations on zirconium oxide-carbon nanotube composites synthesized by hydrothermal crystallization," *Carbon*, vol. 42, 2004, pp.1995-99.
- [3] A. Peigney, Ch. Laurent, E. Flahaut, and A. Rousset, "Carbon nanotubes in novel ceramic matrix composites". *Ceram Int*, vol 26, 2000, pp. 677-83.
- [4] T. Kuzumaki, O. Ujije, H. Ichinose, and K. Ito, "Mechanical characteristics and preparation of carbon nanotube fiber-reinforced Ti composite," *Adv Eng Mater*, vol. 2(7) 2000, pp. 416-8.
- [5] Tiny Tubes Boost for Metal Matrix Composites. *Met Powd Rep*, 2004, pp.40-3.
- [6] K. Metenier, S. Bonnamy, F. Beguin, C. Journet, P. Bernier, et al., "Coalescence of single-walled carbon nanotubes and formation of multi-walled carbon nanotubes under high pressure treatments," *Carbon*, vol. 40, 2002, pp. 1765-73.
- [7] A. Varma, A. S. Rogachev, A. S. Mukasyn, and S. Hwang, "Combustion Synthesis of Advanced Materials: Principles and Applications", *Adv. in Chem. Eng.*, vol. 24, pp. 79-225, 1998.
- [8] L.J. Groven and J.A. Puszynski, "Effect of Carbon Nanotube Addition on SHS Materials", *International Journal of Self-Propagating High Temperature Synthesis*, Vol. 16, No. 4, pp. 189-198, 2007.