Research Proposal

“Combustion Synthesis of Carbon Nanotube Reinforced Materials”

Nanoscience & Nanoengineering

PhD candidate

Lori J. Groven

Summary

The main objective of this research is to explore the following hypothesis: Combustion synthesis is an attractive method for the synthesis of carbon nanotube reinforced materials, with controlled porosity, and improved and/or desired mechanical and electrical properties. With the use of nanoreactants and electroless metal coated carbon nanotubes one can achieve nanostructured materials with improved interfacial adhesion between matrix and the carbon nanotubes.

The initial study will be focused on the electroless nickel coating of single and multi-walled carbon nanotubes. Effective dispersions of nickel coated nanotubes in reactant mixtures using both dry and wet methods will be evaluated using TEM/SEM. Simultaneous combustion synthesis and densification experiments and microwave sintering studies will be conducted using the optimal dispersion of reactants and coated CNTs.

In these experiments, several parameters will be varied including: concentration of metal coated CNTs and reactants, reaction stoichiometry, and degree of dilution to adjust the maximum adiabatic reaction temperature and to control the resulting structure of products. Synthesized composites will be characterized using a variety of analytical tools including: XRD, SEM, TEM, BET, AFM, and nano-indentor.

The significance of the proposed research is the fundamental advancement of knowledge in the area of combustion synthesis of intermetallic and ceramic–CNT reinforced composites. Experimental research studies will contribute to a better understanding of the simultaneous combustion synthesis and densification of materials using nanoreactants with the addition of coated CNTs. Findings from this research should be beneficial to material science and reaction engineering communities.

The proposed work was developed by me and a colleague from the Los Alamos National Lab during the summer of 2005 with preliminary work being done fall 2005 at the South Dakota School of Mines and Technology in the laboratory of my Ph.D. advisor, Dr. Jan Puszynski. To my knowledge the utilization of coated carbon nanotubes in the combustion synthesis of intermetallics and ceramics is an original concept and has not been reported in the literature.

Literature Survey

Carbon nanotubes are of significant scientific interest due to their remarkable electronic and mechanical properties. With a Young's modulus reported at 1.2 TPa for single-walled carbon nanotubes (SWCNTs) and 950 GPa for multi-walled carbon nanotubes (MWCNTs) they are considered the ultimate replacement for carbon fibers as reinforcement material.[1, 2] However, it has also been reported that nanotubes may only be wetted by liquids, or by molten metals with surface tension in the range of 100-200 mN/m.[3]

The majority of the reported research on the addition of CNTs to composites has been polymer based, followed by ceramics, and some work reported on metal matrix composites (MMCs) composed of either single metals or intermetallics such as Fe_3Al.[4-11] For both ceramic and metal matrix composites processing is generally accomplished by ball milling of the CNTs with the matrix material in powder form followed by spark plasma sintering or hot isostatic pressing in nitrogen.

A comprehensive survey of the literature for research pertaining to the combustion synthesis or reactive processing of carbon nanotube loaded composite materials resulted in a single report from Thostenson et al.[12] They reported the fabrication of reaction bonded silicon carbide carbon nanotube composites. In their work they first dispersed MWCNTs in a polymer resin with SiC loading and then carbonized. Following this the carbonized perform was then placed in contact with molten Si in a vacuum atmosphere above 1400 °C in order for reactive infiltration to occur. Their work definitively demonstrated that carbon nanotubes can withstand reactive processing to form carbon nanotube reinforced ceramic composites. In addition, they demonstrated that even a very small addition of CNTs resulted in a significant decrease in electrical resistivity without significantly changing the mechanical properties of the SiC.

For general processing of carbon nanotube loaded metal composites recent research shows that there is significant issue with dispersion and adhesion of the carbon nanotubes to the matrix material resulting in poorer than expected results.[7,8] Based on these results researchers have moved to precoating of the CNTs to enhance matrix to tube adhesion. To date several methods have been explored for coating

of CNTs. These include e-beam evaporation, electrochemical reduction, and nanoparticle dispersing methods. Of these, the most scalable is by far the electroless bath method (chemical reduction method) which is a simple procedure that is suited well to mass production. In fact this is the only method that has been explored in terms of inclusion into MMCs.[13] To date it has been reported that CNTs have been coated with Cu, Co, Ni, Ag, Mg, and Ti using the electroless bath method (chemical reduction).[13-17] This method employs the following three steps:

1) **Oxidation:** The CNTs are introduced into a strong acid bath such as HNO_3:H_2SO_4 and generally refluxed for several hours.
2) **Sensitization/Activation:** Following oxidation the CNTs are introduced into either separate baths of $SnCl_2$-HCl and $PdCl_2$-HCl for 30 minutes or into a single bath composed of both tin and palladium chloride. However, better coating results have occurred when separate baths are utilized.
3) **Coating:** After activation the CNTs are introduced into a bath that follows the general composition shown below, where M represents the desired metal.

Table 1. *General composition of electroless baths.*

Chemical	Concentration (g/L)
MSO_4·hydrate	20-25
$Na_3C_6H_5O_7·2H_2O$	5-30
$NaH_2PO_2·H_2O$	15-25
NH_4Cl	60
$Pb(NO_3)_2$	$4.5x10^{-2}$-2.5
Bath temperature	20-40 ° C
pH (adjusted w/ NH_4OH)	~8.0-9.0

The deposition rate of metal ion is primarily controlled by the pH and temperature of the electroless bath. Typically if the temperature is above 40ºC then the minimum deposition rate is ~2.5

μm/hr.[18] Therefore for coating of CNTs the temperature is reduced and adjustments to the traditional bath composition are made in order to reduce the deposition rate to nm/hr.

At this time, there are no reported research results on either microwave sintering or reactive microwave synthesis of ceramic or intermetallic-CNT reinforced composites. The unique union of microwave processing and combustion synthesis allows for better quality products due to enhanced control of the process when compared to conventional sintering. One of the key advantages of utilizing microwave sintering of CNT-reinforced materials is a significant time reduction of that over conventional sintering. For example, the traditional ceramic Al_2O_3 can be sintered to nearly full density at 1400 ºC in a few minutes where as it would take nearly 2 hrs at 1600 ºC to achieve the same results.[22] Ahmad et al has demonstrated very successful microwave assisted synthesis with the classic Ti + C system and shown that control of these types of reactions is easily achieved by adjusting power level, susceptor quantity, and initial density of the compact. [23]

Proposed Research

It is proposed to explore combustion synthesis of carbon nanotube reinforced composites by utilization of metal coated single and multi-walled carbon nanotubes (CNTs). These results will be compared to the same composites synthesized with uncoated CNTs. It is believed that the metal coating will provide for improved interfacial bonding.

Based on the preliminary results demonstrating the successful synthesis of CNT reinforced composites via combustion synthesis technique, it is proposed to further investigate the topic with metal coated single and multi-walled carbon nanotubes.

Specific research objectives include:

- comprehensive study on metal coating of both multi and single –walled carbon nanotubes via electroless coating and chemical reduction processes;
- investigation of simultaneous combustion synthesis and uniaxial densification of systems consisting of uncoated or coated CNTs and Ni-Al, Ti-B, T-B_4C;

- fundamental reactive microwave sintering studies of systems of uncoated and coated CNTs (Ni-Al, Ti-B, T-B_4C, Al-N) to form dense and porous composites;
- kinetics study of reactive systems composed of nanoreactants with and without addition of CNTs;
- development of mathematical model that predicts combustion characteristics of reactive systems with addition of CNTs.

Expected Significance

Scientific significance of the proposed research will be in fundamental understanding of the synthesis of carbon nanotube reinforced composites; both intermetallic and ceramic using combustion synthesis technique. The research will contribute to a better understanding of carbon nanotube reinforcement composites formed in a one-step processing technique; in particular which systems are carbon nanotubes compatible with, what interaction do they have with the matrix when they are uncoated or coated, what reinforcement do they provide to the synthesized composites, and what effect the addition of such reinforcement has on the product morphology of the synthesized product. The anticipated technological achievements of the proposed research will result in development and optimization of synthesis and processing parameters for CNT reinforced composites using the combustion synthesis route.

Experimental Plan (Broad Description)

The experimental plan for this research is broken into four distinct branches. These are as follows:

1. Metal coating of carbon nanotubes
2. Combustion synthesis and in-situ densification of carbon nanotube reinforced intermetallics and ceramics with coated and uncoated CNTs (solid-solid systems)
3. Microwave sintering and reactive synthesis of CNT reinforced composites (solid-solid, gas-solid systems)
4. Characterization of nanoreactants and coated CNTs and their densified products

5. FEA modeling of condensed phase reactions to predict combustion characteristics for reactant mixtures with addition of CNTs.

Metal Coating of CNTs

For this research the primary coating method that will be investigated will be electroless (essentially chemical reduction). With this method it is possible to coat nanotubes with Cu, Ag, Co, Mg and Ni, as well as other metals. For this specific work the most useful coating is Ni due to the wide variety of Ni based systems that may be investigated via combustion synthesis; such as nickel aluminides. The steps that will be conducted in order to perform this coating method are:

1) **Oxidation:** HNO_3: H_2SO_4 (3:1) reflux at 110 °C for 6 hrs
2) **Sensitization and Activation:** Immersion in 0.1 M $SnCl_2$-0.1 M HCl for 30 min, immersion in 0.0014 M $PdCl_2$-0.25 M HCl for 30 min
3) **Electroless Plating:** Introduction into electroless bath for 20-40 min

The initial bath composition that will be investigated is listed in Table 2. Subsequent baths will be investigated to minimize the phosphorous and lead content. The general composition of these baths is listed in Table 2, where the amount of sodium citrate and sodium hypophosphite may be adjusted to drive the rate of deposition and overall coating quality.

Table 2. *Electroless bath conditions, initial and alternative bath compositions.*

Chemical	Concentration (g/L)		Chemical	Concentration (g/L)
$NiSO_4 \cdot 6H_2O$	25		$NiCl_2 \cdot 6H_2O$	30
$Na_3C_6H_5O_7 \cdot 2H_2O$	5		$Na_3C_6H_5O_7 \cdot 2H_2O$	10
$NaH_2PO_2 \cdot H_2O$	15		$NaH_2PO_2 \cdot H_2O$	10
NH_4Cl	60		Bath temperature	20 ° C
$Pb(NO_3)_2$	2.5			
Bath temperature	20 ° C			
pH (adjusted w/ NH_4OH)	~8.0			

In addition to exploring Ni as a coating, Ti will also be investigated using the reduction of $TiCl_3$ with $NaBH_4$. In this method the CNTs are first dispersed in a solution of $TiCl_3$ and then a 1M $NaBH_4$ solution is added dropwise as a reducing agent while under constant sonication. Reported results on the use of this coating method show a very uniform coating of Ti. [21] Following coating with Ti these CNTs will be utilized for the synthesis of Ti based composites such as TiB_2, TiC-TiB_2, and TiNi. In the case of TiNi it will be possible to include both Ni coated and Ti coated CNTs.

In-situ Combustion Synthesis and Densification of CNT Reinforced Composites

In-situ combustion synthesis and densification will be conducted on the following systems:

$Ni + Al + x\ CNTs \rightarrow NiAl + x\ CNTs$ $\quad T_{ad} = 1911\ K$

$Ti + 2B + x\ CNTs \rightarrow TiB_2 + x\ CNTs$ $\quad T_{ad} = 3200\ K$

$Ti + B_4C + x\ CNTs \rightarrow 2\ TiB_2 + TiC + x\ CNTs$ $\quad T_{ad} = 2800\ K$

These condensed phase reactions allow for the use of Ni coated and Ti coated CNTs and will allow for verification of the survivability of the CNTs in combustion synthesis reactions for various combustion temperatures as indicated by the adiabatic combustion temperatures listed above.

One of the critical issues in this research is effective mixing of the initial reactants with the CNTs. It has been previously determined that mixing of reactants and CNTs is at an optimum when all materials fall in the same size domain therefore in the case of the synthesis of Ni/Al nanoreactants provide the best mixing conditions. However, utilizing nanosized Ti is problematic and other mixing strategies must be explored. These include the possible use of small quantities of dispersant, as well as wet mixing in a solvent that CNTs are highly dispersable in. Therefore for this research a variety of reactant sizes, dispersants, and mixing solvents will be investigated in order to achieve the most effective initial mixing.

In-situ combustion synthesis and densification will be conducted in the already constructed experimental setup shown in Figure 1. This equipment is capable of a preheating temperature of 1500 K and densification pressures up to 200MPa for a 0.5" die. Vacuum or inert atmosphere may be utilized.

Following combustion synthesis the resulting materials will be characterized using TEM/SEM, XRD, and Vickers microhardness.

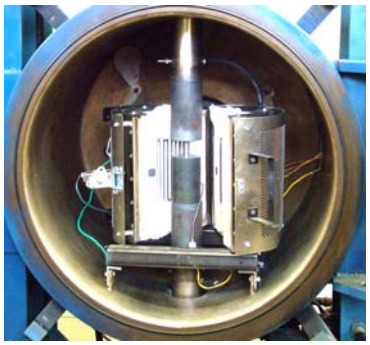

Figure 1. *Equipment for in-situ densification and combustion synthesis of CNT loaded composite materials.*

Figure 2. *Microwave furnace for sintering and reactive sintering of CNT loaded composite materials.*

Microwave sintering and reactive synthesis of CNT reinforced composites

Microwave sintering and reactive synthesis will be conducted on the above systems in addition to the gas/solid system (Al/N_2) using the equipment shown in Figure 2. This equipment is a 2.45 Ghz, 6 kW, microwave sintering furnace equipped with a dual color pyrometer where air or inert atmosphere, He, N_2, or Ar may be utilized.

In this research first sintering of initial materials with CNT addition (e.g. NiAl + CNTs) will be explored. This will be followed by the reactive synthesis of the same systems explored with in-situ densification and combustion synthesis. There has been no previous work published on microwave sintering or reactive synthesis of composites with the addition of CNTs to this date. These materials will then be characterized using TEM/SEM, XRD, and Vickers microhardness.

Mathematical modeling

Mathematical modeling of condensed phase reactions in millimeter and sub-millimeter geometries will be conducted using two commercial software packages: FlexPDE and COMSOL. Both FlexPDE and

COMSOL are capable of utilizing a self adjusting mesh size which allows the transient analysis of these types of reactions with very high reaction rates. It is desired to model the reactions listed above and predict the combustion characteristics for various system configuration. In the case of absence of gas formation during the combustion synthesis the governing equations in a cylindrical coordinate system that will be implemented into the model are listed below:

$$[(1-\varepsilon)C_{pm}\rho_m + \varepsilon\rho_g C_{pg}]\frac{\partial T}{\partial t} = \frac{\partial(k\partial T/\partial r)}{\partial x} + \frac{1}{r}\frac{\partial(kr\partial T/\partial r)}{\partial r} + \frac{(1-\varepsilon)(-\Delta H_r)W\rho_m}{M_A}\frac{\partial \eta}{\partial t} \qquad (1)$$

$$\frac{\partial \eta}{\partial t} = K_o \exp[-E/RT](1-\eta)^n \qquad (2)$$

Initial and boundary conditions will be dependent on system configuration and the type of heating mode being investigated.

Relation of the proposed program to goals of the research cited in the literature survey

The relation of the proposed program to the goals of the research cited in the literature survey is to extend the knowledge in the area of synthesis and fabrication of CNT loaded composites via combustion synthesis and microwave sintering. In addition by utilizing coated CNTs in the synthesis of these materials one of the main objectives of materials scientists of obtaining mechanically enhanced composites with the use of CNTs may be realized.

Extension of Research to Future Work

The extension of this research to future work is apparent as very few of the known combustion synthesis reactions will be explored during the course of this research program. Therefore it is expected that this work may be extended to include a number of condensed phase reactions, gas-solid reactions, as well as the utilization of not only metal coated CNTs but oxide coated CNTs. In addition the interfacial reactions between the CNTs and matrix remain to be explored as well as dispersion at high CNT concentration.

Student's Original Contributions

In addition to this proposal being the original research idea of the student, the contributions of the student are listed below:

Equipment:

- Development of experimental setup for accomplishing successful in-situ combustion synthesis and densification;
- Microwave system for sintering studies.

Technical:

- Development of CNT coating techniques;
- Development of effective reactant-CNT mixing techniques;
- Mathematical modeling software investigation, followed by recommendation for purchase of FlexPDE and COMSOL.

The general schedule for the completion of this research is as shown in Table 4:

Table 4: *Estimated completion of research schedule.*

TASK	Sept-Dec 06	Jan-May 07	June-Sept 07	Sept-Dec 07	Jan-May 08	June-July 08	July 08-May 09	June-Aug 09
Initial coating investigation	x							
Mixing analysis	x							
Initial synthesis of reinforced NiAl w/ coated & uncoated CNTs	x							
Equipment ordered/obtained	x							
Initial synthesis of reinforced TiB_2-TiC, TiB_2, AlN		x						
Initial mathematical modeling in FORTRAN and FlexPDE completed		x						
Development of microwave system with Research Experience for Teachers project (Al_2O_3)- 6 weeks			x					
International presentation of results (France)			x					
Collaborative work development with Sandia National Laboratory			x					
Collaborative work with SDSM&T – Applied Physics publication			x					
Completion of full study of NiAl with uncoated CNTs				x				
Collaborative work with coated CNTs				x				
Coating methodology perfected for electroless Ni				x				
Ti coating of CNTS					x			
Completion of full study of in-situ densification and combustion synthesis of Ti/B_4C, and Ti/B with uncoated and coated CNTs					x			
Completion of mathematical modeling in small geometries					x			
Collaborative partnership formation with (3 weeks research experience in Poland)						x		
Completion of full study of microwave sintering of NiAl, TiB_2, TiB_2-TiC and reactive sintering of Ni-Al, Ti-B_4C, Ti-B, and Al-N_2.							x	
Dissertation Completion								x

Nomenclature

ε - porosity	unitless
C_{pm} – Heat capacity of the reactive mixture	J/kg K
C_{pg} – Heat capacity of the gas	J/kg K
k – Thermal conductivity	W/m K
ρ_m – Bulk density of the reactive mixture	g/cc
ρ_g – Bulk density of the gas	g/cc
M_A – Molecular weight	kg/mol
W – Weight fraction of species	kg i/kg mixture
$-\Delta H$ – Heat of reaction	J/mol i
K_o – Pre-exponential factor	1/s
E – Activation energy	J/mol
R – Universal gas constant	J/mol K
T – Temperature	K
t – Time	s
η – Degree of completion	-
n- Order of reaction	-
r – Radial direction	m
x – Horizontal direction	m

Acronyms

CNT – Carbon nanotubes

MWNTs – Multi-walled carbon nanotubes

SCNTs – Single-walled carbon nanotubes

SHS – Self-propagating high temperature synthesis

CS – Combustion synthesis

Appendices

A – Original NSF Graduate Research Fellowship application with reviewer comments

B – Preliminary publication of results

L.J. Groven, J.A. Puszynski, "Effect of Carbon Nanotube Addition on Morphology of SHS Synthesized Materials", Int J. of Self Propagating High Temperature Synthesis, vol. 16 (4), 2007, pp. 189-198

C – Coating methodologies

X. Chen, J. Xia , J. Peng, W. Li, S. Xie, "Carbon nanotube metal matrix composites prepared by electroless plating". Composites & Sci Tech 2000; 60: 301-6.

Y. Cho, C. Kim, H. Moon, Y Choi, S. Park, et al., "Electronic Structure Tailoring and Selective Adsorption Mechanism of Metal-coated Nanotubes", Nano Letters, vol. 8 (1), 2008, pp. 81-6.

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. T. W. Ebbesen, "Wetting, filling and decoration carbon nanotubes", J. Phys. Chem Solids, vol. 57, 1996, pp.951-955.

4. A. Peigney, Ch. Laurent, E. Flahaut, and A. Rousset, "Carbon nanotubes in novel ceramic matrix composites". Ceram Int, vol 26, 2000, pp. 677-83.

5. T. Kuzumaki, O. Ujiie, 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.

6. T. Kuzumaki, K. Miyazawa, H. Ichinose, K. Ito, "Processing of carbon nanotube reinforced aluminum composite". J Mater Res 1998; 13:2445–9.

7. R. Zhong, H.T. Cong, P.X. Hou, "Fabrication of nano-Al based composites reinforced by single-walled carbon nanotubes". Carbon 2003; 41(4):848–51.

8. K.T. Kim, K.H. Lee, S. Cha, C. Mo, S.H. Hong, "Characterization of Carbon Nanotubes/Cu Composites Processed by Using Nano-sized Cu Powders". Mat Res Soc Symp Proc 2004; 821: 3.25.1-6.

9. "Tiny Tubes Boost for Metal Matrix Composites", Met Powd Rep 2004; 40-3.

10. T. Laha, A. Agarwal, T. McKechnie, S. Seal, "Synthesis and characterization of plasma spray formed carbon nanotube reinforced aluminum composite". Mat Sci & Eng A 2004; 381: 249-58.

11. L.X. Pange, K.N. Suna, S. Rena, et al.,"Fabrication and microstructure of Fe_3Al matrix composite reinforced by carbon nanotube," *Mat. Sci & Eng A*, vol. 447, 2007, pp. 146-9.

12. E.T. Thostenson, P.G. Karandikar, T.W. Chou, "Fabrication and characterization of reaction bonded silicon carbide/carbon nanotube composites", J. Phys D, vol. 38, 2005, pp. 3962-65.

13. E. Carreno-Morelli, J. Yang, K. Hernadi, J.W. Seo, C. Bonjour, et al., "Carbon nanotube/magnesium composites", Physica Status Solidi (a), vol. 201 (8), 2004, pp. R53-55.

14. J.P. Tu, Y.Z. Yang, L.Y. Wang, X.C. Ma, X.B. Zhang, "Tribological properties of carbon-nanotube-reinforced copper Composites". Tribology Letters 2001; 10(4):225-8.

15. C.M. Probst, C. Goujon, R. Gauvin, R.L. Drew, "Enhanced Wettability by Copper Electroless Coating of Carbon Nanotubes". Ceramic Eng & Sci Proc 2005; 26(3): 263-70.

16. Y. Feng, H. Yuan, "Electroless plating of carbon nanotubes with silver". J Mat Sci 2004; 39: 3241-3.

17. X. Chen, J. Xia, J. Peng, W. Li, S. Xie, "Carbon nanotube metal matrix composites prepared by electroless plating". Composites & Sci Tech 2000; 60: 301-6.

18. R.C. Agarwala, V. Agarwala, "Electroless alloy/composite coatings: a review", Sadhana, vol 28, parts 3 &4, June/Aug 2003, pp. 475-493.

19. L.J. Groven, Simultaneous Combustion Synthesis and Densification of Nickel Aluminide/Alumina Nanocomposites. Rapid City SD, USA, South Dakota School of Mines and Technology, *MS Thesis*, 2007.

20. L.J. Groven, J.A. Puszynski, "Effect of Carbon Nanotube Addition on Morphology of SHS Synthesized Materials", Int J. Self Prop High Temp Synth, vol. 16 (4), 2007, pp. 189-198.

21. Y. Cho, C. Kim, H. Moon, Y Choi, S. Park, et al., "Electronic Structure Tailoring and Selective Adsorption Mechanism of Metal-coated Nanotubes", Nano Letters, vol. 8 (1), 2008, pp. 81-6.

22. K.H. Brosnan, G.L. Messing, and D.K. Agrawal, "Microwave Sintering of Alumina at 2.45 GHz", J. Am. Ceram. Soc., vol 86 (8), 2003, pp. 1307-12.

23. D. Agrawal, J. Cheng, Y. Fang, and R. Roy, "Microwave Processing of Ceramics, Composites and Metallic Materials", Microwave Solutions for Ceramic Engineers, American Ceramic Society, 2004, pp. 206-228.