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Abstract. A recent research study has been undertaken to develop facilities for conducting detonation synthesis of nanomaterials. This process involves a familiar technique that has been utilized for the industrial synthesis of nanodiamonds. Developments through this study have allowed for experimentation with the concept of modifying explosive compositions to induce synthesis of new nanomaterials. Initial experimentation has been conducted with the end goal being synthesis of alpha variant silicon carbide (α-SiC) in the nano-scale. The α-SiC that can be produced through detonation synthesis methods is critical to the ceramics industry because of a number of unique properties of the material. Conventional synthesis of α-SiC results in formation of crystals greater than 100 nm in diameter, outside nano-scale. It has been theorized that the high temperature and pressure of an explosive detonation can be used for the formation of α-SiC in the sub 100 nm range. This paper will discuss in detail the process development for detonation nanomaterial synthesis facilities, optimization of explosive charge parameters to maximize nanomaterial yield, and the introduction of silicon to the detonation reaction environment to achieve first synthesis of nano-sized alpha variant silicon carbide.

INTRODUCTION

The detonation synthesis process was invented in the 1960s by a group of Soviet scientists led by B.I. Zababakhin who found that shock compression of graphite could result in a phase transition of carbonaceous material to diamond [1]. The detonation of explosive compositions with a negative oxygen balance, such as Composition B, which is a mixture of RDX and TNT, resulted in the formation nanodiamonds from the free carbon in the detonation products when conducted in an inert atmosphere with adequate cooling. Since these discoveries, the phenomenon that has come to be known as detonation synthesis has been primarily used to produce detonation nanodiamonds (DNDs). The rapid reaction rates of an explosive detonation make detonation synthesis attractive for producing nanomaterials. Owing to their small size and unusual properties, DNDs have a range of applications from abrasives and surfactants to additives that improve thermal conductivity or wear resistance. The bioavailability also makes DNDs suitable for medical applications that have shown promise in clinical trials as a transport system for chemotherapeutics. DNDs are only one example of a desirable nanomaterial that can be produced by detonation synthesis. Modification of detonation conditions can be used to control the materials formed in the soot resulting from the detonation. With the rise of nanotechnologies comes the demand for new nanomaterials with specific, desirable properties. Novel production methods such as detonation synthesis are being researched to fill this need. [1]

Recently, a project was carried out to investigate the detonation synthesis of nanomaterials. The goals were twofold:

1. To develop the facilities to produce nanomaterials by replicating industrial DND production parameters that utilized only the explosive compositions themselves for material production;
2. To manipulate detonation conditions to produce a desired carbonaceous phase, α-SiC.

Alpha-variant silicon carbide (α-SiC) was selected as the target nanomaterial due to its desirable properties of high hardness, electrical conductivity, and thermal conductivity. These properties make α-SiC a key nanomaterial for strengthening metal alloys, nano-scale electronics, and lightweight, high strength ceramic composites [2]. The material was also selected because of the compatibility of several different types of silicon sources with suitable explosives for detonation synthesis.

BACKGROUND

For detonation synthesis to be successful, a number of factors must be considered. First, the constituents required to produce the desired material phases must be present. Cast compositions of RDX and TNT were selected as the base explosives for testing due to the successful use of these explosives for industrial DND production [1]. Mixtures containing TNT can have a negative oxygen balance that produces free carbon after detonation, shown in Equation 1). The negative oxygen balance present in RDX/TNT mixtures is a key parameter for the formation of ultra-nanocrystalline diamond, and other carbonaceous materials. The casting process used to make the RDX/TNT compositions is also amenable to produce new nanomaterials as it provides the opportunity for introduction and homogeneous mixing of additives into the explosive composition. For testing the production of silicon carbide, silicon-containing additives were introduced into charges during casting as crushed silicon powder or polycarbosilane, which is a silicon-containing organic compound. [3]

$$2 \, C_7H_5(NO_2)_3(s) \rightarrow 7 \, C(s) + 7 \, CO(g) + 3 \, N_2(g) + 5 \, H_2O(l) \tag{1}$$
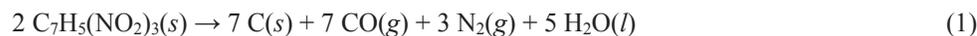
With the appropriate balance of constituents for production of the desired material in the detonation environment, temperature and pressure that promote the formation of the desired phases must be produced during detonation. These state variables are controlled not only by the type and quantity of energetic materials used in the detonation process, but also by the type and quantity of additives, which impact the ability of the explosives to achieve a steady state detonation. The reaction temperatures achieved from the detonation of RDX/TNT cast mixtures can range from 2000 to 3000 Kelvin with detonation pressures ranging from 24.3 to 28.7 GPa [4]. The ratio of explosives can be manipulated to keep the temperature within the range of 1800 to 2200 Kelvin, which is used in commercial production of α-SiC by the Acheson Method [5].

In open air, carbonaceous detonation products oxidize to carbon monoxide and/or carbon dioxide. Hence, detonation synthesis must take place in a controlled environment so that elemental carbon can form as a reaction product. Precipitation of solid carbon also enables its reaction with additives present in the explosives to form other phases, such as adding silicon to form silicon carbide. During this project, argon was used to displace oxygen in the detonation environment due to its high density; however, other inert gasses or vacuum could be used to remove oxygen from the detonation environment. Any contaminants present during detonation can also impact on the purity of the detonation products. To produce the desired materials, the detonation environment should be free of other contaminants [3].

After detonation, the cooling rate of the reaction products plays a key role in the phases produced. For example, the introduction of additives that absorb thermal energy can produce metastable materials by promoting rapid quenching from the detonation conditions [1]. The reversion of nanodiamond to graphite and other non-diamond carbon is one example of an undesirable, post detonation phase change. Rapid cooling the detonation products can be achieved by adding water, ice, or inert gas to the detonation environment. The resulting absorption of thermal energy promotes rapid reduction of temperature in the presence of the high pressures produced by detonation, which can promote the formation of detonation products [3].

METHODOLOGY

Detonation Synthesis Vessel Preparation

The first objective of the detonation synthesis project involved replicating process parameters for detonation synthesis. Producing DNDs as well as studying detonation synthesis of other nanomaterials, namely silicon carbide, required producing the necessary compositions, temperatures, and pressures in the detonation environment. The 1.8 m^3 pressure vessel, shown in Figure 1a, was donated to the university, and though its original purpose is not known, it is believed that it was intended for use in explosive forming metal in the aerospace industry. Background research in the field of detonation synthesis indicated that by sealing the vessel and blocking of the vent stacks with steel plates, the pressure vessel could be made suitable for the production of nanomaterials such as α-SiC.

Testing Procedure

During detonation synthesis testing, 240-gram cast charges composed of RDX and TNT were hung roughly at the center of the test vessel. The charges were suspended by 8 gram/meter HMX detonating cord used to initiate the charges from a hook welded at the top of the pressure vessel. The detonating cord was then fed through a purging pass-through in the upper part of the vessel for external initiation using an electric detonator to remove contaminants produced by the detonator from the detonation environment. With a charge hung in place, the test vessel was closed and sealed. Each of the 12 pins that lock the hemispherical vessel shells together were tightened to 10 kg-m of torque ensuring that a balanced pressure distribution sealed the two shells. Once the vessel was sealed, argon gas was flowed into the chamber at, 11 m^3/ hr. through the valve at the bottom of the vessel. The feed rate was selected to minimize mixing of the argon with the air in the vessel during purging so that the heavier argon would displace the air through a vent at the top of the vessel. An oxygen monitor at the ventilation port indicated that the majority of air had been removed from the detonation environment, then this port was sealed with putty, and the valve at the bottom of the vessel closed. An electric detonator was then connected to the tail of detonating cord outside the chamber, and the test charge was fired. The vessel was then opened so that the detonation soot could be collected.

The first production tests led to several discoveries that impacted the test protocol going forward. First, soot from the detonation deposited on the vessel walls as a thin layer as shown in Figure 1b. This soot needed to be collected as an aqueous suspension produced by rinsing the soot from the vessel walls into collection bins. Second, the presence of water on the walls of the vessel before detonation visibly increased the soot yield, as indicated in Figure 1c. For all future tests, the vessel walls would be wet with water before testing, and the chamber kept sealed for 10 minutes after detonation to allow soot to deposit on the vessel walls prior to collection. In light of the results of these first production tests, a modified testing procedure accounting for these factors was developed that would increase soot yield for future tests.
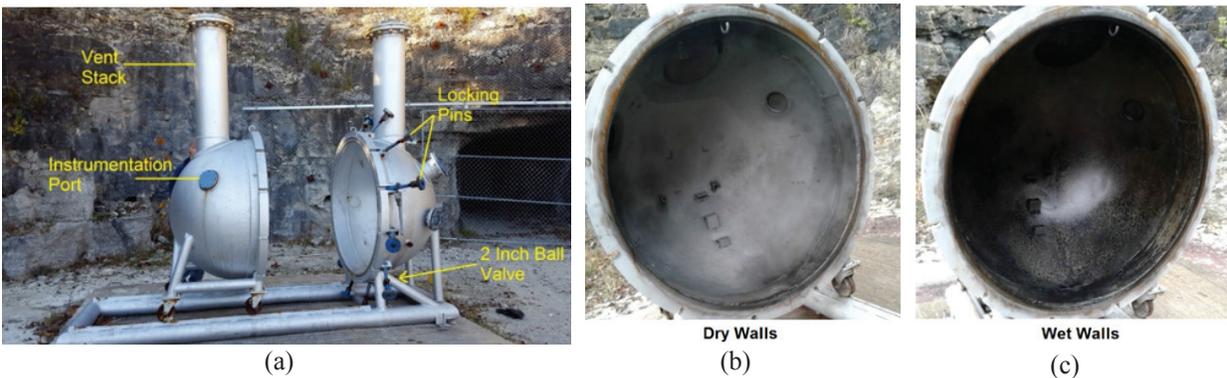

| (a) | (b) | (c) |

FIGURE 1. Test vessel used for detonation synthesis (a), detonation soot deposition with the presence of water (b) and without the presence of water (b)

RESULTS AND ANALYSIS

Following the procedure developed for testing, eight sequential tests were conducted to evaluate the production of nanomaterials. The test parameters outlined in Table 1 were selected to evaluate various factors that affect soot production including explosive composition, environmental cooling, and the effect of siliceous additives. The goal of tests one through four was to demonstrate that nanodiamonds could be formed using the available pressure vessel. The charges were formulated, all with masses of 240 g, but the ratios of TNT to RDX varied as did the detonation conditions for the charges as summarized in Table 1. After each blast, the chamber walls were rinsed with water and the resulting slurries were collected for purification. The test vessel was thoroughly cleaned in between each test to prevent cross-contamination between experiments. The test vessel was thoroughly cleaned in between each test to prevent cross-contamination between experiments.

For tests one and two, the 50:50 mass ratio of RDX to TNT produced more than double the soot and ultimately nanodiamonds of the 60:40 charge These results agreed with the background literature that greater concentrations of carbon are produced from the more negatively oxygen balanced TNT and would yield more carbonaceous products [1]. Tests three and four indicated that encasing the charges in ice greatly increased the material production which agrees with the theory that increasing the environmental cooling of the detonation environment enhances the thermodynamic stability of the detonation products. [3]. Tests five through eight incorporated a silicon source into the charge and exhibited similar results to tests one through four regarding material production with the greatest soot yield from charges encased in ice.

TABLE 1. Results of Detonation Test Series

Test	RDX:TNT mass ratio	Detonation Conditions	Explosive mass (g)	Soot mass (g)	Soot Yield (%)	Yield After Purification (%)
1	50:50	Wet chamber	239	15.1	6.3	1.5
2	60:40	Wet chamber	243	7.4	3.1	0.4
3	50:50	Wet chamber and encased in ice	245	60.8	24.8	4.3
4	50:50	Wet chamber and encased in dry ice	239	30.3	12.6	4.1
5	50:50	Wet chamber and 10 g ground Si	247	14.1	5.7	3.6
6	50:50	Wet chamber and 10 g PCS	238	20.2	8.4	6.1

After collection, the soots required purification prior to analysis. The first step was to remove as much water as possible. This was accomplished by centrifuging and decanting. Next, the remaining solids were dried overnight. For Tests 1-4, without added silicon, the residual solids were mixed with a solution containing fuming nitric acid and concentrated sulfuric acid. This mixture was boiled and stirred with a reflux condenser installed for 24 hours. Next, all samples were stirred into a solution of nitric and hydrochloric acids for 24 hours to remove any metallic impurities such as iron from the test vessel. The mixture was then diluted with water, cooled to room temperature, centrifuged, and decanted to collect and dry the remaining solids. After drying, samples that appeared to contain oxide impurities such as sand were washed with hydrofluoric acid by stirring for 24 hours. The remaining solids were then washed with deionized water until the pH of the supernatant was 5 or greater. The final purification step was furnace oxidation to remove residual carbon. Soots were heated to 400°C for 4.5 hours and then 425°C for 26 hours. The purified soot was then characterized using x-ray diffraction analysis.

Tests 1-4, and 6 resulted in unambiguous confirmation of the production of DND through material characterization via X-ray diffraction (XRD). Test 5 however, did not result in the production of DND likely due to an excess amount of silicon in the composition. Characterization of the detonation products from the silicon doped charges have indicated the presence of silicon as well as beta-silicon carbide in size ranges of 32 and 43 nanometers for test charges five and six based on peak broadening. Rietveld analysis was used to determine the amount of each material present in the soots for the doped charges. The results of this analysis indicated 15 wt.% SiC for the silicon doped charge, Figure 2a, and 57 wt.% SiC for the PCS doped charge, Figure 2b. These results, however, could not be treated as definitive proof of the production of SiC due to the most prominent SiC (111), SiC (220), and SiC (311) indicating peaks also occurring, though less prominently, in the characterization of soots without added silicon. At present, definitive characterization of soots from the silicon doped charges is pending further analysis.
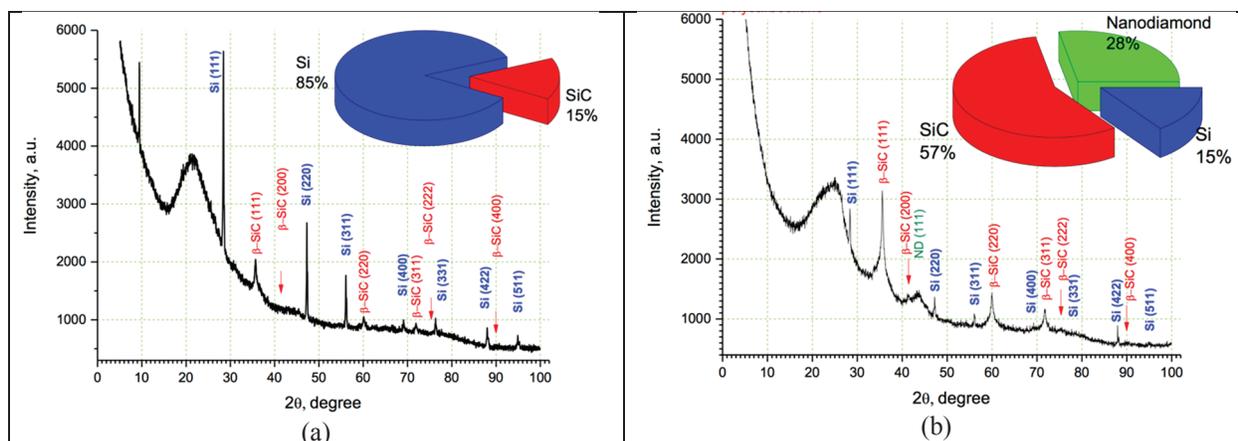
FIGURE 2. X-ray diffraction patterns and the corresponding results from Rietveld analysis for detonation soots collected for charges containing silicon powder (a) and polycarbosilane (b).

CONCLUSION

The detonation synthesis project has resulted in the confirmed production of nanodiamonds from the detonation of RDX/TNT compositions. This achievement meets the goal of developing the facilities to produce nanomaterials by replicating industrial DND production parameters that utilized only the explosive compositions themselves for material production. Highest yields were seen from RDX/TNT charges with a 50/50 mass ratio encased in ice with environmental cooling by an inert gas. These results agree with the background literature about the effects of charge composition and environment on the production of detonation nanodiamonds. Testing involving manipulation of detonation conditions to produce a desired carbonaceous phase, α-SiC is currently underway. Successful production of beta-silicon carbide is suspected via XRD and Rietveld analysis, with unambiguous confirmation of the production of this phase pending further analysis. Future tests will continue to seek the production of alpha variant silicon carbide through modifications of the variables that impact detonation synthesis. These studies will broaden the understanding of the process of detonation synthesis, and enable higher levels of control over the materials that can be produced through this method.

ACKNOWLEDGEMENTS

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