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**RPPR Final Report**  
as of 27-Sep-2017

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**Title:** Detonation Synthesis of Nanomaterials

**Begin Performance Period:** 01-Nov-2016

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**Report Term:** 0-Other

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**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:** 0

**STEM Participants:** 1

**Major Goals:** The goal of the proposed effort was to synthesize nano-sized silicon carbide particles using detonation. The research objectives were to: 1) establish detonation synthesis capabilities at the Missouri University of Science and Technology (MS&T); and 2) initiate fundamental studies of formation mechanisms of nanosized SiC particles.

**Accomplishments:** Details described in uploaded PDF.

**Training Opportunities:** This project supported the training of one graduate student.

Martin Langenderfer, PhD student in Explosives Engineering was supported for 9 months as a 50% graduate research assistant (standard graduate appointment). As part of the project, he was mentored with regard to performing high quality research and preparation of technical presentations.

**Results Dissemination:** Two presentations were given at a technical conference during the performance of this project:

1. M. Langenderfer, C. Johnson, W. Fahrenholtz, and V. Mochalin, "Detonation Synthesis of Alpha-Variant Silicon Carbide," 20th Biennial Conference of the American Physical Society Topical Group on Shock Compression of Condensed Matter, St. Louis, MO, July 9-14, 2017.
2. V. Mochalin, "Detonation Nanodiamond: Synthesis, Deaggregation, Modification, Applications," 20th Biennial Conference of the American Physical Society Topical Group on Shock Compression of Condensed Matter, St. Louis, MO, July 9-14, 2017.

Two additional presentations that will discuss results from the project are planned for after the conclusion of the project.

1. W.G. Fahrenholtz, C. Johnson, V. Mochalin, M. Langenderfer, and S. Chertopalov, "Synthesis of Nanomaterials in Extreme Environments," Materials Science and Technology Annual Conference and Exhibition, Pittsburgh, PA, October 8-11, 2017.

M. Langenderfer, C. Johnson, W.G. Fahrenholtz, V. Mochalin, and S. Chertopalov, "Detonation Synthesis of Nanomaterials: Process Development and Testing," 44th Conference on Explosives and Blasting Techniques, International Society of Explosives Engineers, San Antonio, TX, January 28-31, 2018.

**Honors and Awards:** Nothing to Report

**RPPR Final Report**  
as of 27-Sep-2017

**Protocol Activity Status:**

**Technology Transfer:** A provisional patent application was filed based on the processes developed as part of the project:

“Detonation Synthesis of Nanomaterials” Filed August 8, 2017 by Missouri S&T. Inventors: W. Fahrenholtz, C. Johnson, and V. Mochalin. The patent application has been assigned Serial No. 62/542,365.

**PARTICIPANTS:**

**Participant Type:** PD/PI

**Participant:** William Gene Fahrenholtz

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Co PD/PI

**Participant:** Vadym Mochalin

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Co PD/PI

**Participant:** Catherine Johnson

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

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**Person Months Worked:** 9.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

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**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**RPPR Final Report**  
as of 27-Sep-2017

**Participant Type:** Technician  
**Participant:** Jeff Heniff  
**Person Months Worked:** 1.00  
Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

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**Paper Title:** Detonation Synthesis of Alpha-Variant Silicon Carbide  
**Authors:** Martin Langenderfer, Catherine Johnson, William Fahrenholtz, and Vadym Mochalin  
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**Final Progress Report**

# **Detonation Synthesis of Nanomaterials**

**W911NF-17-1-0001**

**Bill Fahrenholtz, Catherine Johnson, and Vadym Mochalin**  
**Missouri University of Science and Technology**

**August 14, 2017**

## 1. Foreword

This is the final technical report for the project “Detonation Synthesis of Nanomaterials”, which was funded at the Missouri University of Science and Technology by the Materials Synthesis and Processing program in the U.S. Army Research Office as grant W911NF-17-1-0001. This was funded as a Short Term Innovative Research (STIR) project. During its nine-month duration, the project has resulted in several positive outcomes. The most significant are:

- A facility for detonation synthesis was established that includes a dedicated detonation chamber, the ability to cast charges of different types of explosives, and the ability to incorporate additives into explosives;
- Nanodiamonds were produced by detonating mixtures of TNT and RDX in a blast chamber at Missouri S&T;
- The yield of nanodiamonds was improved by modifying the experimental conditions. The composition of the charge was modified to be 50 wt% TNT and 50 wt% RDX, the walls of the chamber were wet with water prior to detonation, and charges were encased in ice;
- Nanoparticles that possibly contain SiC were produced by adding silicon sources to the charges in the form of ground silicon powder or SiC precursor polycarbosilane;
- A provisional patent application was filed for the detonation synthesis of carbide ceramic nanoparticles.

The investigative team would like to acknowledge the contributions of several individuals to this project including:

- Martin Langenderfer, graduate student in Mining Engineering at Missouri S&T who coordinated the detonations and analyzed blast data;
- Sergii Chertopalov, post doctoral scholar in Chemistry at Missouri S&T who was responsible for purification and characterization of detonation soots;
- Jeff Heniff, Research Engineering Technician in the Rock Mechanics & Explosives Research Center who formulated charges and oversaw all detonations.

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### 3. Statement of Problem Studied

The goal of this project was to study detonation synthesis as a method to produce silicon carbide (SiC) nanoparticles. Oxygen-deficient explosive mixtures are used commercially to produce detonation nanodiamonds (DNDs), which typically have diameters in the range of 5 nm to 10 nm. The production of DNDs was optimized through experimental trials to maximize yield. Previous studies have reported detonation synthesis of alumina, titania, and nickel nanoparticles.<sup>1</sup> Our group aims to use detonation synthesis to produce SiC based nanoparticles. The pressures and temperatures achieved during detonation may promote formation of hexagonal  $\alpha$ -SiC nanoparticles whereas current methods produce cubic  $\beta$ -SiC nanoparticles. For nanoparticles synthesized by conventional methods, conversion of as-synthesized  $\beta$ -SiC nanoparticles to  $\alpha$ -SiC results in growth of the particles out of the nano-sized range.

### 4. Summary of Most Important Results

During this project, four sets of detonations were conducted. The first set of detonations was used to evaluate the detonation chamber and produce initial soots for analysis. The second set of detonations focused on demonstrating that nanodiamonds could be produced in our chamber and modifying the detonation conditions to improve nanodiamond yield. The third set was the initial attempt for SiC formation while the final set focused on increasing the soot yield in SiC synthesis. The paragraphs that follow describe the results from each of the detonations.

#### 5.1 Round One

An initial round of detonations was used to evaluate the detonation chamber, which is shown in Figure 1. The chamber is made of steel and is set up so that it can be opened by sliding one of the halves horizontally away on two rails. The chamber was donated to the university by an alumnus. Although its original purpose is not known, we believe it was intended for explosive forming in the aerospace industry. When the project started the interior of the chamber was coated with aluminum-colored paint. In addition, the chamber was equipped with several ports that were open plus two chimneys that extended above the chamber. For the first set of detonations, the ports were covered with mild steel plates that were bolted into place, but the chimneys were left open. The chamber halves were then moved together and secured using twelve bolts that are evenly spaced around the circumference of the chamber. In preparation for this round of testing, a mold was produced by 3D printing for casting charges into a cylindrical shape (Figure 2). The threaded rod in the center of the mold was positioned to allow for detonating cord to be passed through the charge for initiation of the blast.

In the initial chamber testing, a series of increasingly larger Composition C-4 charges were detonated to test the integrity of the chamber and assess the use of a pressure sensor during detonation. In addition, some Composition B, which is a mixture of 2,4,6-trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX), charges were formulated and tested to determine if the planned initiation method was adequate. Charges of Composition B (or modified Composition B as described below) were prepared in a double boiler to ensure that the temperature remained below 100°C, which is far below the critical decomposition temperatures for both TNT and RDX. A copper bowl was used to contain the TNT, which was stirred during melting using a non-sparking whisk. The desired amount of RDX was added and stirred to promote dissolution. Prior to casting, the mold surfaces were covered with paraffin wax to enable removal of the

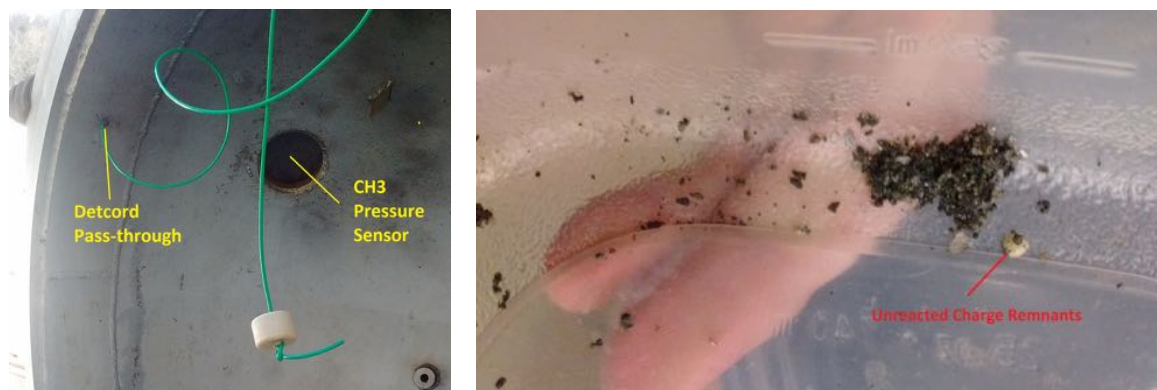
charge from the mold. When the consistency was suitable for casting, the melt was poured into the mold and allowed to cool to room temperature. Unfortunately, some unreacted charge remnants were found in the detonation soots produced from the Composition B charges (Figure 3). This round of tests led to several recommendations for future tests. First, the maximum size of the charges was set at about 240 g of Composition B based on the TNT equivalent of the charge. Second, the ports in the chamber were all secured using new plates and bolts plus the chimneys were sealed by welding steel plates into the openings inside the chamber. In addition, a new charge configuration was designed whereby a knot tied into the detonating cord was cast into the charge to ensure more intimate contact between the detonating cord and the charge. Finally, paint was removed from the interior of the chamber by sand blasting.



**Figure 1.** Pictures showing (left) the open detonation chamber, which is about 1.5 m in diameter, and (right) the initial 100 g Composition C-4 charge being loaded into the chamber.



**Figure 2.** Cylindrical mold produced by 3D printing and a Composition B charge cast in the mold. Note that the charge diameter is about 50 mm.



**Figure 3. Pictures showing (left) initial Composition B charge configuration and (right) some unreacted charge remnants in the detonation soot.**

## 5.2 Round Two

The goal of the second round of testing was to demonstrate that nanodiamonds could be formed using the available detonation chamber and to test different methods of detonation. Three charges were formulated, all with masses of 240 g, but the ratios of TNT to RDX varied as did the method of initiating detonation as summarized in Table 1. After each blast, the chamber walls were rinsed with water and the resulting slurries were collected for purification (Figure 4).

After collection, the soots required purification prior to analysis. The first step was to remove as much water as possible, which was done by centrifuging and decanting. Next, the remaining solids were dried overnight. The residual solids were mixed with a solution containing fuming nitric acid and concentrated sulfuric acid. This mixture was boiled and stirred to remove any metallic impurities such as iron from the blast chamber. The mixture was then diluted with water, cooled to room temperature, and centrifuged/decanted to collect the remaining solids. The solids were then washed in a mixture of nitric acid and hydrochloric acid followed by centrifuging and decanting. 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. The second set of conditions from Table 1 (50:50 weight ratio of RDX:TNT, initiated with detonating cord) produced soot that contained nanodiamonds based on x-ray diffraction analysis (Figure 5) of the purified soot. Hence, the project reached the first goal stated in the proposal, which was to determine conditions for production of nanodiamonds in the blast chamber.

**Table 1. Summary of conditions used for second round of testing.**

| Test | RDX:TNT mass ratio | Initiator          | Nanodiamonds? | Image in Figure 4 |
|------|--------------------|--------------------|---------------|-------------------|
| 1    | 60:40              | Detonating cord    | No            | a                 |
| 2    | 50:50              | Detonating cord    | Yes           | b                 |
| 3    | 50:50              | Electric detonator | No            | c                 |



Figure 4. Pictures of chamber after detonation and soot collected from the second round of detonation tests. Note that chamber diameter is about 1.5 meters.

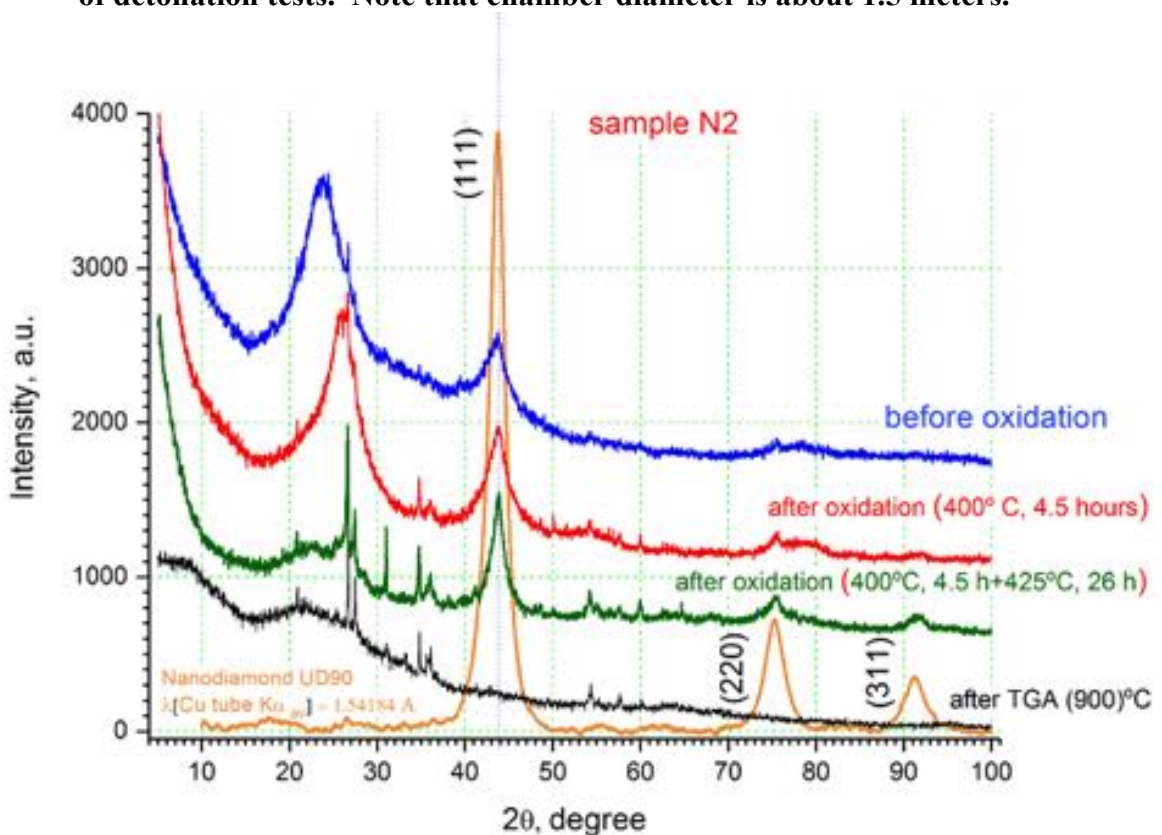


Figure 5. X-ray diffraction patterns of powder from Test 2 in the second round of detonations: before oxidation (blue), after oxidation at 400°C (red) and 450°C (green). For color and after oxidation – red color and green), after TGA (black), and from a commercial nanodiamond powder (orange).

Several conclusions were reached based on the second round of testing. First, the presence of water inside of the detonation environment had a profound impact on the quantity of soot recovered from the detonations. The presence of water increases the cooling capacity of the detonation environment due to its high heat capacity.<sup>2</sup> The presence of water on the surface of the vessel may also promote soot adherence to the chamber walls, which also makes the soot easier to collect. With the presence of nanodiamonds in the second test sample, increasing the cooling capacity within the vessel appears to be a key in increasing the yield of soot and ultimately the yield of nanomaterials within the soot.

### 5.3. Round Three

After XRD confirmation of the presence of nanodiamonds in the detonation soots produced in the second round of testing, the project focus shifted to producing SiC nanoparticles and increasing the soot yield in detonations. A series of six detonations were conducted in this round. The compositions of the explosives and other conditions are summarized in Table 2.

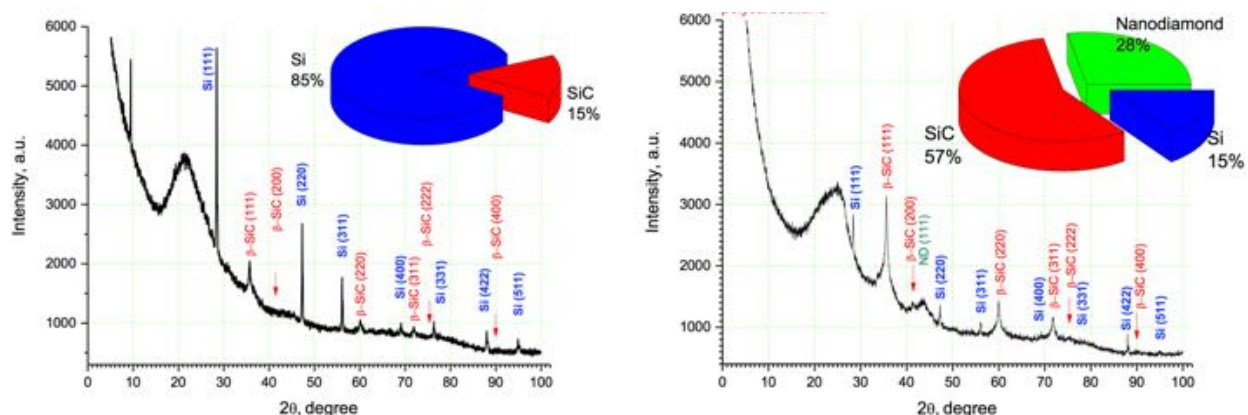
The first test (Test 4) was designed to repeat conditions from Round 2 as a baseline for comparison of other tests. The charge mass was 50% RDX and 50% TNT. The walls of the chamber were sprayed with water prior to detonation, which yielded 15.1 g of soot, or 6.3 wt% yield based on charge mass. Test 5 examined a change in the RDX:TNT ratio. In this case, the ratio was changed to the standard Composition B ratio of 60 wt% RDX and 40 wt% TNT. The detonation was again conducted after wetting the chamber walls, but the soot yield decreased to 7.4 g or 3.1% of the original charge mass. Test 6 was designed based on a finding reported in Russian literature that claimed that encasing the charge in ice increased the soot yield. In this case, the results were dramatic, increasing the soot yield to 60.8 g (24.8% by mass), which is more than double the yield of any other condition. Test 7 examined a similar mechanism to Test 6, but the charge was encased solid CO<sub>2</sub> (dry ice) prior to detonation. Although the soot mass was double of the baseline condition examined as Test 4, dry ice was not nearly as effective as water ice based on soot yield with dry ice that was only half that of the ice test. Tests 8 and 9 were the first attempts to produce materials other than nanodiamonds. For Test 8, crushed silicon powder was added to the charge while for Test 9, polycarbosilane (PCS) was added. Compared to the baseline, the addition of Si decreased the mass yield while adding PCS increased it.

**Table 2. Summary of explosive compositions and other conditions used for the six detonations accomplished in the third round of testing.**

| Test | RDX:TNT mass ratio | Other Conditions                 | Explosive mass (g) | Soot mass (g) | Soot Yield (%) |
|------|--------------------|----------------------------------|--------------------|---------------|----------------|
| 4    | 50:50              | Wet chamber                      | 239.5              | 15.1          | 6.3            |
| 5    | 60:40              | Wet chamber                      | 243.3              | 7.4           | 3.1            |
| 6    | 50:50              | Wet chamber + encased in ice     | 245.5              | 60.8          | 24.8           |
| 7    | 50:50              | Wet chamber + encased in dry ice | 239.5              | 30.3          | 12.6           |
| 8    | 50:50              | Wet chamber + 10 g ground Si     | 278.3              | 14.1          | 5.1            |
| 9    | 50:50              | Wet chamber + 10 g PCS           | 269.7              | 20.2          | 7.5            |

After purification, soots from Tests 8 and 9 were characterized using x-ray diffraction analysis to determine the crystalline phases that were present. The diffraction patterns

underwent further analysis using Rietveld refinement to quantify the amounts of the crystalline phases. When silicon powder was added (Figure 6, left), the crystalline phases detected in the purified soot contained about 85 wt% silicon and about 15 wt% SiC. Of particular note, the three most intense peaks for Si, which were the (111) at about 28.6°, the (220) at ~47.6°, and the (311) at ~56.5° were strong. In addition, comparing to the XRD pattern in Figure 5, the XRD pattern for Test 2 did not have peaks at any of the angles of the three most intense Si peaks. Note that no peaks related to nanodiamonds were found in the soot for Test 8. The addition of PCS to the explosive mixture (Figure 6, right) resulted in the formation of crystalline phases that were estimated to be ~57 wt% silicon carbide, ~28 wt% nanodiamonds, and about 15 wt% silicon. While the peaks labeled as SiC in the XRD patterns in Figure 6 are consistent with the formation of  $\beta$ -SiC, the XRD patterns in Figure 5 have small peaks at the same angles as the most intense peaks from the SiC test, which are SiC (111), SiC 220, and SiC (311). Hence, the XRD results are not conclusive proof of the formation of crystalline SiC due to the overlap from the other test. The results from Tests 8 and 9 are summarized in Table 3. Further analysis is needed to confirm the presence of crystalline SiC in the detonation soots of Tests 8 and 9.



**Figure 6.** X-ray diffraction patterns and the corresponding results from Rietveld analysis for detonation soots collected for charges containing silicon powder (left) and polycarbosilane (right).

**Table 3.** Summary of Process Parameters and SiC Production in Detonations 8 and 9.

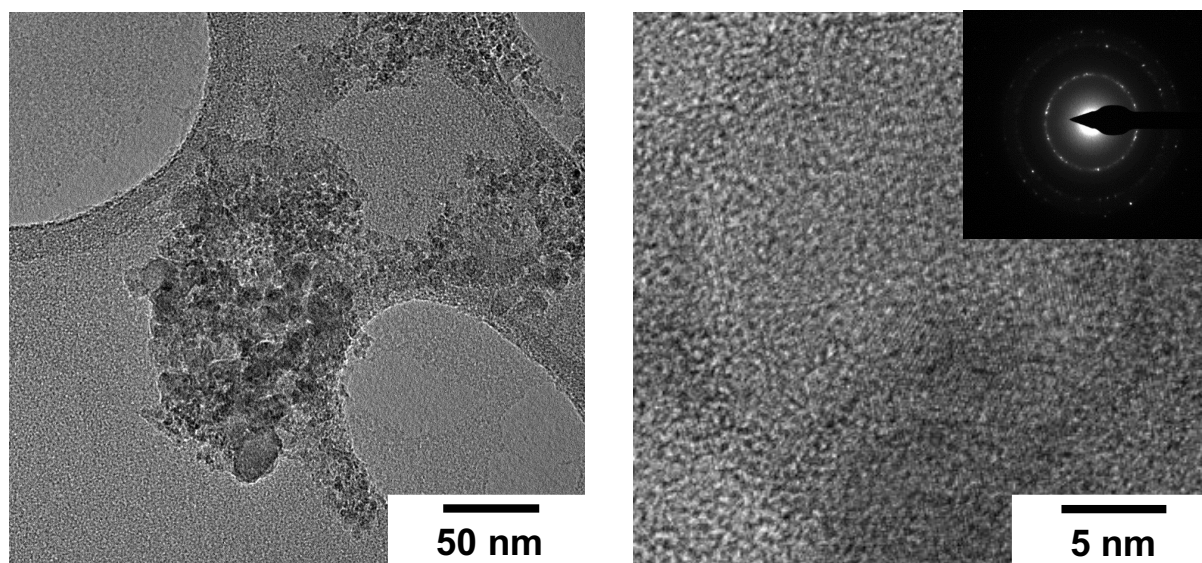
| Detonation Number | RDX:TNT mass ratio | Charge Mass (g) | Si Source       | SiC in soot (wt%) | ND in soot (wt%) | SiC Size (nm) |
|-------------------|--------------------|-----------------|-----------------|-------------------|------------------|---------------|
| 8                 | 50:50              | 278             | Silicon         | 15                | 28               | 32            |
| 9                 | 50:50              | 270             | Polycarbosilane | 57                | 0                | 43            |

Detonation soots were further characterized in an attempt to unambiguously confirm the presence of nanodiamonds or SiC nanoparticles. Transmission electron microscopy (TEM) was used to image nanoparticles, while complementary selected area electron diffraction (SAED) was used to characterize the crystallinity of different nanoparticles. The soot from Test 4 contained clusters of crystalline solids (Figure 7). At low magnification, clusters of particles were observed on the TEM grid. Closer examination of the soot particles revealed that some were crystalline particles about 10 nm in diameter based on lattice imaging. Analysis of the SAED patterns indicated were consistent with the presence of diamonds (Table 4). Hence, TEM/SAED confirmed the presence of nanodiamonds, which is consistent with XRD analysis of this soot.

Although not shown here, soots containing nanodiamonds also contained carbon nano-onions, which can be produced when nanodiamonds are thermally decomposed.

**Table 4. Indexing of electron diffraction pattern shown in Figure 7 (right) indicating Miller indices of peaks that match diamond structure shown in column ND.**

| Ring | D (1/nm) | R (1/nm) | d (Å) | ND  |
|------|----------|----------|-------|-----|
| 1    | 9.23     | 4.61     | 2.168 | 111 |
| 2    | 15.01    | 7.50     | 1.333 | 220 |
| 3    | 17.62    | 8.81     | 1.135 | 311 |
| 4    | 18.27    | 9.13     | 1.095 |     |
| 5    | 20.88    | 10.44    | 0.958 | 400 |
| 6    | 22.93    | 11.46    | 0.872 |     |
| 7    | 25.70    | 12.85    | 0.778 | 331 |



**Figure 7. TEM images of soot from Test 4 showing (left) a cluster of particles and (right) a high resolution image of a crystalline particle with inset SAED pattern.**

The detonation soot produced when polycarbosilane was added (Test 9) was more complex. After purification by acid treatment followed by oxidation, clusters contained particles with different morphologies and sizes (Figure 8). Clusters appeared to contain different types of particles that produced different contrasts when viewed at lower magnification. At higher magnification, agglomerated crystallites that ranged from about 5 nm to about 30 nm in diameter were observed. At higher magnification, lattice fringes were apparent, indicating that the particles were crystalline. Due to the number of particles in each cluster, typical SAED patterns contained rings or spots from multiple particles and were difficult to interpret as they appeared to contain rings from multiple phases. In this case, the TEM/SAED analysis does not provide unambiguous confirmation of the presence of crystalline SiC in the detonation soot. However, the possible presence of SiC nanoparticles is also supported by energy dispersive x-ray analysis (Figure 9), which indicated that Si and C were present in some nanoparticles. Other elements that were detected included Cu, Fe, C, Cl, and O. A 400 mesh Cu grid was used for TEM

analysis, which presumably led to the detection of Cu. A large fraction of Fe is present in the raw soot from the chamber while Cl was a residue from hydrochloric acid used in purification. Carbon is present in the soot and also as a thin layer on the TEM grid. The acid treatments remove most of the Fe, but some remains in the soot. Oxygen is also present as an impurity, presumably as a surface oxide on Si-containing nanoparticles and on the Cu TEM grid.

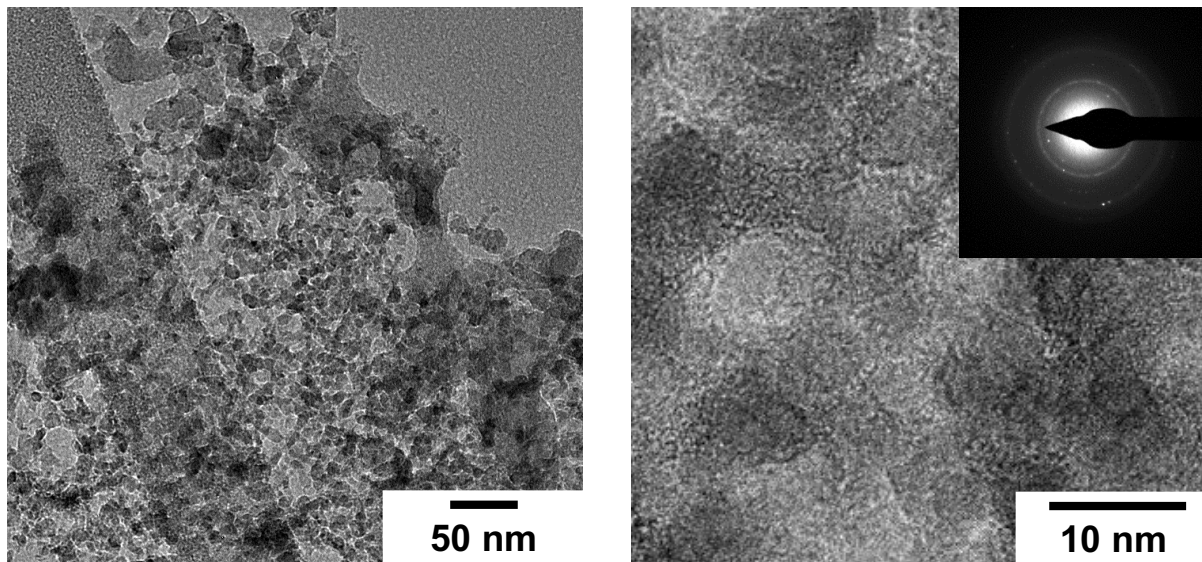
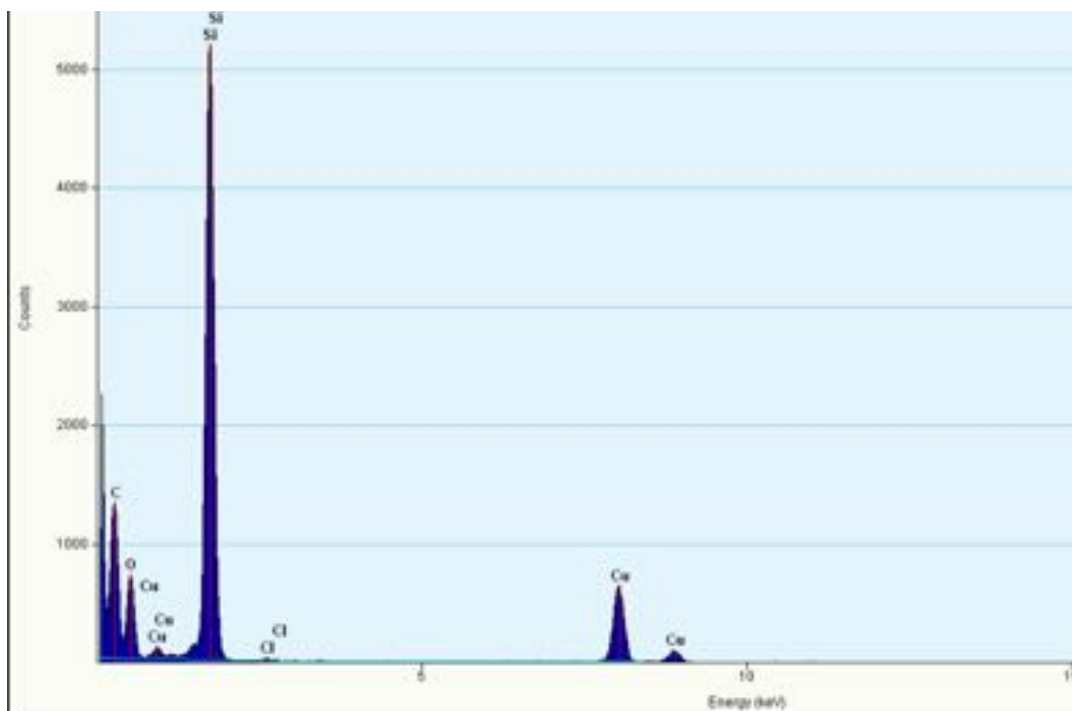


Figure 8. TEM images of detonations soot from Test 9.

Table 5. Indexing of electron diffraction pattern from crystallites shown in Figure 8 (right) indicating Miller indices of peaks that match different crystal structures including silicon (Si), hexagonal SiC ( $\alpha$ -SiC), cubic SiC ( $\beta$ -SiC) and nanodiamond (ND).

|   | D (1/nm) | R (1/nm) | d (Å)  | Si | $\alpha$ -SiC | $\beta$ -SiC | ND |
|---|----------|----------|--------|----|---------------|--------------|----|
| 1 | 8.0      | 3.99     | 2.5034 |    | 103           | 111          |    |
| 2 | 9.7      | 4.86     | 2.0561 |    | 106           |              |    |
| 3 | 13.0     | 6.50     | 1.5393 |    | 110           | 220          |    |
| 4 | 15.8     | 7.88     | 1.2689 |    | 205           | 222          |    |
| 5 | 18.5     | 9.23     | 1.0834 |    |               |              |    |



**Figure 9.** Energy dispersive x-ray analysis of soot from Test 9 showing that Si and C were present. Note that Cu is from the TEM grid and Fe, Cl, and O are impurities in the soot.

The third round of detonations led to several advances. First, the presence of materials that absorb energy during detonation, such as ice and dry ice, increase the mass yield of detonation soot. Encasing the charge in ice prior to detonation was particularly effective, leading to the collection of soot that had a mass that was about 25% of the charge mass, which was about eight times the soot yield for the baseline conditions (Detonation 4). Dry ice also increased the soot yield, but was not as effective as ice. This is likely due to the lower mass of dry ice and also the lower energy absorbed per unit mass to vaporize dry ice. Incorporating silicon powder or polycarbosilane into the explosives led to the formation of Si-containing particles in detonation soots. Although XRD and TEM analysis were consistent with the presence of SiC as crystalline nanoparticles, these tests were not conclusive and further support is needed to unambiguously confirm the presence of SiC nanoparticles.

#### 5.4. Round Four

A fourth round of detonations was conducted to further examine the formation of SiC. Tests 10 and 11 were conducted in an effort to increase the yield of Si-containing particles in the soot by encasing the charges in ice. Using Tests 8 (silicon powder) and 9 (polycarbosilane) from Table 2 for comparison, encasing charges in ice led to an increase in soot yield when Si or polycarbosilane were added. Test 10 used nominally the same conditions as Test 8, except that the charge was encased in ice. Likewise, Test 11 was nominally the same as Test 9, except that the charge was encased in ice. With Si powder present, soot yield increased from 14.1 g to 61.6 g when ice was used. For polycarbosilane, the soot yield increased from 20.2 g to 49.6 g. At the conclusion of the project, these soots have not been purified or analyzed, but these tests confirmed that the presence of ice, presumably as a cooling agent during detonation, more than

doubled the soot yield for Si-containing detonation synthesis. Soots will be further analyzed in the future to determine the effect of ice on the morphology and composition of the soots.

**Table 6. Summary of conditions used for fourth round of testing.**

| Test | RDX:TNT mass ratio | Other Conditions         | Explosive mass (g) | Soot mass (g) | Soot Yield (%) |
|------|--------------------|--------------------------|--------------------|---------------|----------------|
| 10   | 50:50              | 10 g Si, encased in ice  | 272.5              | 61.6          | 22.6           |
| 11   | 50:50              | 10 g PCS, encased in ice | 267.9              | 49.6          | 18.5           |

## 5. Significant Contributions and Future Opportunities.

This STIR project had several important outcomes including:

1. The project enabled establishment of a new facility for detonation synthesis, which we believe is unique among U.S. universities. The facility includes a dedicated detonation chamber with technical support and expertise for casting charges of different compositions, sizes, and shapes.
2. Round two of testing demonstrated that our group has the ability to produce detonation nanodiamonds. Even though nanodiamonds are produced commercially by detonation in other countries, we believe that we are the only university in the U.S with the demonstrated capability for producing detonation nanodiamonds at this time.
3. The production of soot was increased substantially by adding an ice shell around charges. The third round of testing demonstrated that the soot mass increased by a factor of four when the charge was encased in a shell of ice compared to otherwise identical conditions without ice.
4. The detonation synthesis process was demonstrated for additional materials. Charges were formulated that contained silicon powder or polycarbosilane as silicon sources. Even though the formation of crystalline SiC has not been unambiguously confirmed at this time, analysis indicated that SiC may be present. Further purification of the soot will hopefully enable confirmation of SiC formation in the near future.

The project has also pointed to several intriguing opportunities for future investigations including:

1. Confirmation of SiC formation: The highest priority is to confirm the formation of SiC nanoparticles and identify the phase of SiC that has formed. Identification would be aided by further purification of the detonation soot to removed more of the extraneous phases. Additional characterization methods such as Raman spectroscopy and nuclear magnetic resonance spectroscopy will also be employed in the investigation. Once SiC formation is confirmed, the results will be published in a high impact journal based on the novelty and potential broad applicability of this method.
2. Demonstrating detonation synthesis: Confirming the formation of SiC by detonation synthesis would confirm that detonation synthesis is capable of forming a broad variety of nanomaterials. Specifically, if SiC was formed by detonation of the charge containing Si powder, the results would indicate that carbon from the explosives can be harnessed to react with other species in the detonation environment. Based on the temperatures and pressures inside the detonation wave, we believe that the increased activity of carbon

could be used to produce unique nanomaterials in a variety of systems including those containing boron, most metals, and metalloids.

3. The availability of a detonation chamber at a research university provides for intriguing possibilities to gain further insight into several fundamental research areas. By instrumenting the chamber with sensors and other diagnostics, fundamental questions about the formation mechanism of nanodiamonds, the role of ice, and the effects of size/shape/composition of the charge could be examined.
4. Nanomaterials produced by detonation synthesis will provide additional avenues for fundamental studies. Some of the potential areas of interest are explosive compaction and sintering of nanoparticles and conventional densification of nanoparticles to produce bulk nanograined ceramics.
5. The availability of the detonation chamber combined with the ability to formulate charges with additives provides the opportunity to produce nanodiamonds doped with a variety of additives or with controlled surface chemistry. For example, nanodiamond surfaces could be doped with metals to induce fluorescence or to increase electrical conductivity.
6. A new chamber designed specifically for detonation synthesis would significantly enhance the ability to control the detonation synthesis process, collect soot after detonation, and to add instrumentation to collect data on formation mechanisms during detonation. Our experience with the current chamber combined with expertise of team members in blast wave modeling and synthesis of nanodiamonds provides clear guidance with regard to desired features for a new detonation chamber that would enhance our research capabilities.

## **6. Bibliography**

1. Ultrananocrystalline diamond: synthesis, properties, and applications. Ed. by O.A. Shenderova, D. M. Gruen, and W. Andrew, Elsevier, 2012.
2. A. Vul', and O. Shenderova. Detonation Nanodiamonds, edited by Alexander Vul', and Olga Shenderova, Pan Stanford Publishing, 2014.

## 7. Appendices

### 7.1 Detonation Methodology

- 1) Casting of charges
  - a) Materials
    - i) 120 grams desensitized RDX
    - ii) 120 grams TNT
    - iii) Additives (silicon powder, polycarbosilane)
    - iv) 1.8 meters (6 feet) of 8.5 g/m (40 grain/ft) HMX based Detonating Cord
    - v) Paraffin wax
  - b) Equipment
    - i) Double boiler apparatus
    - ii) Hot plate
    - iii) Copper mixing kettle
    - iv) Non sparking stirrer
    - v) Casting mold
    - vi) Heat gun
  - c) Procedure
    - i) Heat water in double boiler apparatus to boiling temperature
    - ii) Tie an 8 wrap Uli knot in Detonating Cord as shown in Figure A-1
    - iii) Heat casting mold walls using heat gun and apply a thin film of paraffin wax to promote release of charge after casting and cooling
    - iv) Secure Uli knot at center of charge volume using pass through in mold as shown in Figure A-2
    - v) Once water has reached 90°C, add TNT to copper kettle and heat kettle in water while stirring continuously until TNT has melted
    - vi) With TNT melted add powdered RDX and stir until uniformly mixed and liquidized
    - vii) Add dopant material and stir until uniformly mixed
    - viii) Pour sufficiently mixed composition into prepped mold.
    - ix) Allow charge to cool and solidify approximately 20 minutes
    - x) Remove charge from mold while still slightly warm for release purposes, ensuring that composition has cooled sufficiently for outside surface to solidify
    - xi) Charges can be encased in ice or otherwise modified as required prior to testing
- 2) Detonation synthesis
  - a) Materials
    - i) (2) 200-250 gram Composition B or other explosive clearing charges
    - ii) 250 gram doped RDX/TNT test charge with 1.2 m (4 ft) detonating cord tail
    - iii) Argon gas
    - iv) (3) Electric detonator
    - v) 20 grams duct sealant putty
    - vi) Electrical tape
  - b) Equipment
    - i) 1.8 m<sup>3</sup> ellipsoidal pressure vessel with bare untreated steel walls and top and bottom purge ports

- ii) Torque wrench
- iii) 2-1/4" socket
- iv) High flow argon regulator
- v) Capacitive discharge blasting machine
- vi) Misting water sprayer
- vii) 20 liter collection bin for soot collection
- viii) Synthetic wire brush
- ix) Oxygen monitor
- x) 4 liter sample storage reservoirs (at least two per test)

c) Procedure

i) Before first test of series:

- (1) Hang clearing charge from top interior hook in center of test vessel using electric initiator as shown in Figure A-3 with initiator leads passing through the top purge port
- (2) Close test vessel and tighten all 12 locking pins to 10.4 m-kg (75 ft-lb) using torque wrench and 2-1/4" socket to ensure even pressure distribution across flange seal
- (3) After securing test site, fire clearing charge in sealed test vessel with capacitive discharge blasting machine
- (4) Rinse interior vessel walls with water and thoroughly scrub with synthetic wire brush to remove contaminants from detonation environment
- (5) Repeat Steps 1-4 for second clearing charge

ii) After vessel cleaning:

- (1) Hang test charge from top interior hook in center of test vessel using detonating cord tail as shown in Figure A-4 with detonating cord tail passing through top purge port
- (2) Wet vessel walls with water to increase environmental cooling and provide deposition site for airborne post detonation soot
- (3) Close test vessel and tighten all 12 locking pins to 10.4 m-kg (75 ft-lb) using torque wrench and 2-1/4" socket to ensure even pressure distribution across flange seal
- (4) Attach regulated argon source to bottom purge port on vessel, and fix oxygen monitor to top purge port
- (5) Purge sealed pressure vessel with argon at a rate of 11 m<sup>3</sup>/hr (6.5 ft<sup>3</sup>/min) verifying purge using an oxygen monitor. Approximately 8-10 minutes.
- (6) Close bottom purge valve, and disconnect argon source
- (7) Seal top purge port using sealant putty around detonating cord
- (8) Secure electric detonator to exterior detonating cord tail using electrical tape.
- (9) After securing test site fire test charge
- (10) Allow 10 minutes to elapse for airborne detonation soot to deposit on vessel walls
- (11) Open test vessel
- (12) Using misting sprayer rinse detonation soot from top to bottom of test vessel in sweeping motions and collect as aqueous solution at bottom of vessel using 20

liter collection bin, and distribute solution to sample reservoirs for material characterization

(13) Rinse vessel walls with water and thoroughly scrub with synthetic wire brush

(14) Repeat steps 1-13 for each test in series



Figure A-1. 40 grain detonating cord with Uli knot



Figure A-2. Prepmed cylindrical Composition B mold with centered Uli knot



Figure A-3. 200 gram C4 clearing charge



Figure A-4. 250 gram test charge of RDX/TNT with polycarbosilane added.

## 7.2 Purification of Detonation Soots

Three purification steps were used for detonation soots that contain the nanodiamonds: 1) treatment in a solution of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ; 2) treatment in a solution of  $\text{HCl}$  and  $\text{HNO}_3$ ; and 3) furnace oxidation in air. A two step purification process was used for detonation soots that possibly contained  $\text{SiC}$ : 1) treatment in a solution  $\text{HCl}$  and  $\text{HNO}_3$ ; and 2) oxidation in furnace in air. In both cases, furnace oxidation can be performed before or after treatment in acid solutions with the same effect.

Before the acid treatment or oxidation, water had to be removed from the initial slurries that were collected by washing the walls of the detonation chamber. The slurries were first allowed to sit undisturbed overnight to allow the solids to settle out of suspension. After settling, the clear liquid above the sedimented solids was decanted using water jet vacuum pump (Figure A-5) and sediment was then dried in beaker on hot plate at  $90^\circ\text{C}$  or using a rotary evaporator (Figure A-6).

- 1) Treatment in a solution of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ 
  - a) Reagents
    - i) 75 mL of nitric acid ( $\text{HNO}_3$ ), ACS, 68.0-70.0%, liquid, Alfa Aesar.
    - ii) 75 mL of sulfuric acid ( $\text{H}_2\text{SO}_4$ ), concentrated, ACS, 96%, Fisher Science Education.
    - iii) Deionized water (DI) with an electrical conductivity  $1.0 \mu\text{S}/\text{cm}$  or less.
  - b) Equipment
    - i) 250 mL round-bottomed flask
    - ii) Reflux condenser
    - iii) Hot plate
    - iv) Stir bar
    - v) Analytical balance
    - vi) Centrifuge
    - vii) 50 mL Centrifuge Tube
    - viii) 250 mL glass beaker
  - c) Procedure
    - i) Weigh 2 g of detonation soot and add to 250 mL round-bottomed flask
    - ii) Separately in beaker mix 75 mL of nitric acid and 75 mL of sulfuric acid
    - iii) Add a stir bar into round-bottomed flask
    - iv) Slowly add acid mixture to 250 mL round-bottomed flask
    - v) Install the round-bottomed flask with reflux condenser on the hot plate (Figure A-7)
    - vi) Open water for the reflux condenser
    - vii) Set the temperature of hot plate  $130^\circ\text{C}$  and speed of rotation 300 rpm
    - viii) After 24 hours, turn off the hot plate and wait for a 1 hour for cooling
    - ix) Add the 100 mL of DI water (slowly) and mix
    - x) Add dispersion from round-bottomed flask to 50 mL Centrifuge Tube (step by step)
    - xi) Centrifuge it and decant to collect the sediment
    - xii) Add another part of dispersion to the same tube with sediment and repeat step (xi) until the entire suspension is treated (Figure A-8)
- 2) Treatment in acid solution ( $\text{HCl} + \text{HNO}_3$ )
  - a) Reagents

- i) Hydrochloric acid (HCl), 36%, w/w aq. soln., Alfa Aesar.
  - ii) Nitric acid (HNO<sub>3</sub>), ACS, 68.0-70.0%, liquid, Alfa Aesar.
  - iii) Deionized water (DI) with conductivity 1.0 μS/cm or less.
- b) Equipment
- i) 250 mL round-bottomed flask
  - ii) Reflux condenser
  - iii) Hot plate
  - iv) Stir bar
  - v) Analytical balance
  - vi) Centrifuge
  - vii) 50 mL Centrifuge Tube
  - viii) 250 mL glass beaker
  - ix) Petri Dish
- c) Procedure
- i) Use the sediment after treatment in H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> and add to 250 mL round-bottomed flask (in case of detonation soot with SiC weigh 2 g of soot)
  - ii) Separately in beaker mix 75 mL of 20% hydrochloric acid and 75 mL of 20% nitric acid
  - iii) Add a stir bar to the round-bottomed flask
  - iv) Slowly add acid mixture to 250 mL round-bottomed flask
  - v) Install a reflux condenser onto the round-bottomed flask (Figure A-7)
  - vi) Open water for the reflux condenser
  - vii) Set the temperature of hot plate 130°C and speed of rotation 300 rpm
  - viii) After 24 hours, turn off the hot plate and wait for a 1 hour for cooling
  - ix) Add the 100 mL of DI water (slowly) and mix
  - x) Add dispersion from round-bottomed flask to 50 mL Centrifuge Tube up to 45 mL (step by step)
  - xi) Centrifuge and decant to collect the sediment
  - xii) Add another part of dispersion to the same tube with sediment and repeat step (xi) until all suspension is treated (Figure A-8)
  - xiii) Add DI up to 45 mL, shake well, centrifuge, and decant
  - xiv) Repeat the washing procedure until pH > 5 in the washing water achieved. This washing procedure was repeated 5-6 times (for samples with SiC more than 10 times).
  - xv) Transfer the solution with sediment to beaker or Petri Dish and dried at temperature about 90°C till to be complete dried (Figure A-9)
- 3) Oxidation
- a) Equipment
- i) Furnace
  - ii) Crucible or boat made from Al<sub>2</sub>O<sub>3</sub>
  - iii) Analytical balance
- b) Procedure
- i) Select the temperature of furnace (in our case it was 450°C)
  - ii) Weigh the detonation soot

- iii) Add this soot to the  $\text{Al}_2\text{O}_3$  crucible, cover with Al foil to prevent contamination and insert the crucible in furnace for 24 hours (Figure A-10)
- iv) Weigh the detonation soot



*a*



*b*



*c*

Figure A-5. A beaker with a suspension of detonation soot before treatment (*a*), during decanting (*b*), and sediment after drying (*c*).



Figure A-6. Rotavapor R-124 (BUCHI WaterBath B-481).



Figure A-7. The setup for purification of detonation soot.



Before decanting



After decanting

Figure A-8. Sedimentation of suspension.

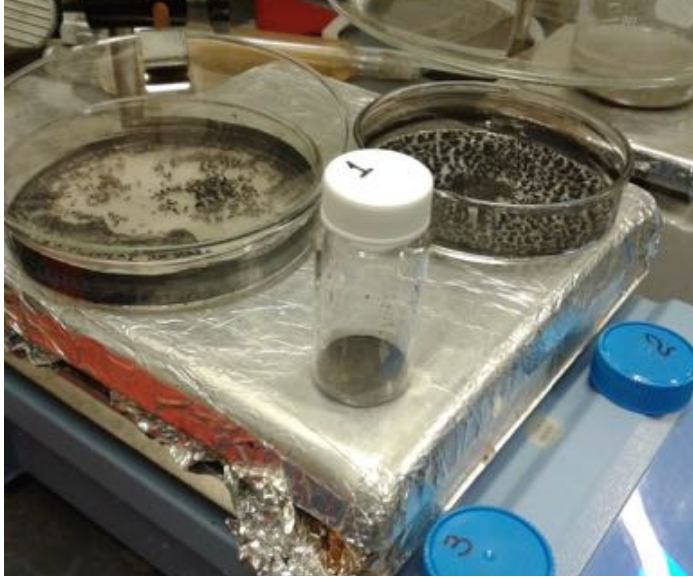


Figure A-9. The final powder after purification – drying in Petri Dish and vial.



Figure A-10. The crucible with detonation soot in furnace.

### **7.3 List of Publications and Presentations**

#### **Given**

1. M. Langenderfer, C. Johnson, W. Fahrenholtz, and V. Mochalin, “Detonation Synthesis of Alpha-Variant Silicon Carbide,” 20<sup>th</sup> Biennial Conference of the American Physical Society Topical Group on Shock Compression of Condensed Matter, St. Louis, MO, July 9-14, 2017.
2. V. Mochalin, “Detonation Nanodiamond: Synthesis, Deaggregation, Modification, Applications,” 20<sup>th</sup> Biennial Conference of the American Physical Society Topical Group on Shock Compression of Condensed Matter, St. Louis, MO, July 9-14, 2017.

#### **Planned**

1. W.G. Fahrenholtz, C. Johnson, V. Mochalin, M. Langenderfer, and S. Chertopalov, “Synthesis of Nanomaterials in Extreme Environments,” Materials Science and Technology Annual Conference and Exhibition, Pittsburgh, PA, October 8-11, 2017.
2. M. Langenderfer, C. Johnson, W.G. Fahrenholtz, V. Mochalin, and S. Chertopalov, “Detonation Synthesis of Nanomaterials: Process Development and Testing,” 44<sup>th</sup> Conference on Explosives and Blasting Techniques, International Society of Explosives Engineers, San Antonio, TX, January 28-31, 2018.

#### **Provisional Patent Applications**

1. “Detonation Synthesis of Nanomaterials” Filed August 8, 2017 by Missouri S&T. Inventors: W. Fahrenholtz, C. Johnson, and V. Mochalin

#### **Students Supported**

1. Martin Langenderfer, PhD student in Explosives Engineering was supported for 9 months as a 50% graduate research assistant (standard graduate appointment).