The Pennsylvania State University

The Graduate School

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ARC DISCHARGE SYNTHESIS AND MORPHOLOGY CONTROL OF EARLY

TRANSITION METAL CARBIDE NANOPATICLES

A Dissertation in

Chemistry

by

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Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

August 2010

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ABSTRACT

This work is directed to the understanding of the synthesis and morphology control of early transition metal carbides. Chapter 1 gives an introduction to fcc structure nanoparticle synthesis and the parameters controlling nanoparticle morphology. Also the importance of early transition metal carbides is discussed. The experimental methods are described in Chapter 2 including a detailed description of the fabricated arc discharge apparatus employed in this study. In Chapter 3, the results of the synthesis of titanium carbide nanoparticles with different methane concentrations are presented. Titanium carbide nanoparticles prefer a cubic morphology when synthesized with low methane concentrations and cuboctahedron morphology with high methane concentrations. Chapter 4 discusses the synthesis of niobium carbide nanoparticles and how the nanoparticle morphology changes with different reactant gases. Niobium carbide nanoparticles distribution prefer a cubic morphology when synthesized with methane, a mixture of cubic and octahedron morphology when synthesized with ethylene, and a cubic morphology when synthesized with acetylene. Studies of the synthesis of zirconium carbide nanoparticles are given in Chapter 5. The zirconium carbide nanoparticles prefer cuboctahedron morphology when synthesized with methane. The change in nanoparticle morphology for the different early transition metal carbides is attributed to the stabilization of the {111} facet. The stabilization of the {111} facet under different conditions leads to changes in the relative growth rate ratio between the $\{111\}$ facet and the $\{100\}$ fact. The change in the growth rate ratio ultimately leads to changes in the nanoparticle morphology.

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ACKNOWLEDGEMENTS

This work would not have been possible without the help and support of many people. I would like to thank Professor A.W. Castleman for his guidance and the opportunity to work in his lab. All of the members of the Castleman group that I worked with and I would like to especially thank Dr. Ujjwal Gupta for whom I worked closely with to interpret the experimental data. I would also like to thank Erin Goken for her friendship and her help with editing my manuscripts and dissertation. My committee members, Prof Jim Anderson, Prof John Badding, and Prof. Jim Adair for their assistance in completing this dissertation. Barry Dutrow and the machinist from the Penn State Physics Machine Shop who helped me design and build my experimental apparatus. I want to thank my family, friends and future in-laws for their support and encouragement. Finally, I like to thank my future wife Dr. Lisa Dominak for all her love and support. I am very thankful to have gone through this journey with her by my side.

Chapter 1

Introduction

1.1 Background

Throughout history mankind has been innovating and developing new materials from the earliest days of wood and stone to the plastics and alloys of today. In recent times there has been a major push in the direction of nanotechnology. One of the first documented syntheses of metal nanoparticles dates back to Michael Faraday's preparation of gold colloids by reducing gold chloride with phosphorus in water in the 1850's.^{1,2} Since that time there has been a barrage of methods to synthesize colloidal metal nanoparticles. However, most of these methods have been plagued with such problems as polydispersed sizes, poorly defined shapes, and limited morphologies. It has only been within the last few decades that methods have been developed to control the size and morphology of metal particles in colloids. A major theme of this dissertation is to develop a bottom-up approach to synthesize early transition metal carbide nanoparticles with control over nanoparticle morphology.

Nanotechnology is the design, fabrication, and application of nanomaterials and the fundamental understanding of the relationships between physical properties or phenomena with respect to a materials' dimensions.³ A typical definition of a nanomaterial is a material that has at least one dimension that spans from sub 10⁻⁹ meter to several hundred 10⁻⁹ meters. Many of these nanomaterials possess unique physical properties that are distinctly different than their bulk form. For example, nanosized

crystals have lower melting points than their respective bulk material.⁴⁻¹² Bulk semiconductors can become insulators when dimensions are sufficiently small enough.¹³ Gold which is normally inert in the bulk form becomes catalytically active on the nanoscale.¹⁴⁻¹⁸

Many of these unique properties of nanoparticles are a direct result of the large ratio of surface atoms per unit volume. The ratio of surface atoms to interior atoms changes rapidly as the dimensions of the material get smaller. This ratio is shown in Figure 1-1 where the percentage of surface atoms for palladium clusters changes with size.¹⁹ One can see in Figure 1-1 that a small change on the nanoscale range can lead to a large change in the percentage of surface atoms. The increase in surface atoms directly increases the surface energy (γ) of the material. This is due to the atoms on the surface having fewer neighboring atoms or a lower coordination number, thus having a higher number of dangling or unsatisfied bonds. An example of a relationship that gives a rough estimate for the surface energy of a surface is given in Equation 1:²⁰

$$\gamma = \frac{1}{2} N_b \varepsilon p_a$$
^[1]

where N_b is the number of the broken bonds, ε is the bond energy, and p_a is the surface atomic density. Equation 1 does not give an exact value for the surface energy because it does not factor in interactions of higher ordered neighboring atoms,



Figure 1-1. The percentage of surface atoms with respect to the total number of atoms compared to changes with the nanoparticle diameter. (from reference 19)

surface charge, or pressure-volume contributions, while it does assume the bond energy is the same for the surface atoms and interior atoms. Also affecting the surface energy is the nanoparticle morphology. The morphology of the nanoparticle dictates which facets are exposed on the surface of the nanoparticle. Different facets on the same crystal will have different surface energies due to the different coordination states of the surface atoms.

Synthesis methods for producing nanoparticles are typically grouped into two categories: "top-down" and "bottom-up". A top-down approach involves division of a large solid material into smaller portions. This approach typically involves ball milling to grind materials into smaller particles. A few major problems with the "top-down" method are the lack of control over the nanoparticle morphology and the introduction of impurities from the balls. The "bottom-up" approach, the most common method used to synthesize pure metal nanoparticles, involves either decomposition or reduction of a precursor compound to generate zero valent atoms. The nanoparticle size and morphology can be controlled through varying experimental parameters including time, concentration or reducing agent, and capping agent. Arc discharge, chemical vapor deposition, and laser generation are other methods that have also been used to synthesize nanoparticles which typically are not produced through a solution phase. The nucleation and growth of the nanoparticles typically follow the mechanism proposed by LaMer and co-workers.²¹ The concentration of zero valent atoms is generated over a period of time as the precursors are reduced and once the concentration reaches the point of supersaturation, the atoms begin to aggregate into small clusters. The clusters will grow at a rapid rate with a continuous supply of zero valent atoms for growth. The clusters

will continue to grow into nanoparticles of increasing size until the atoms on the surface and the atoms in the vapor or solution come to equilibrium.

The nanoparticles formed from a "bottom-up" method can take on either a singlecrystal, singly twinned, multiply twinned, or a combination of the different structures. The multiple pathways for nanoparticle growth are shown in figure 1-2. The nanoparticles synthesized in this dissertation are all single crystal with a face centered cubic (*fcc*) rock salt-like structure. To achieve the most stable morphology, single crystal seeds follow the Wulf's theorem, which attempts to minimize the surface energy within a given volume.²² As stated in this theorem the seed crystal should be enclosed by $\{111\}$ facets in order to minimize its surface energy. The seed crystal takes on an octahedron shape which is enclosed with eight {111} facets. However, an octahedron shaped seed crystal produces six sharp corners that are high energy due to the number of broken surface bonds. To minimize these high energy contributions from the corners of the octahedron seed crystal the corners are typically truncated. The lowest energy morphology for *fcc* structure seed crystals is therefore a truncated octahedron. The truncated octahedron is enclosed with eight $\{111\}$ facets and six $\{100\}$ facets.

The truncated seed crystal has three different growth pathways depending on the grow rate of the different facets. Figure 2 shows the three possible pathways with the R value needed to produce the final nanoparticle morphology.²³ The R value is the ratio of the growth rate in the {100} direction over the growth rate in the {111} direction. The facet with the highest growth rate typically is not expressed in the final nanoparticle morphology. This is shown in the first and third pathway for a single crystal nanoparticle growth. The first pathway has a larger growth rate in {100} direction and an R value of



Figure 1-2. Reaction pathways for single crystal *fcc* metal nanoparticles to have different morphologies. The green and yellow colors represent the $\{100\}$ and $\{111\}$ facets, respectively. The parameter R is defined as the ratio between the growth rates of the $\{100\}$ and $\{111\}$ facets. (from reference 23)

around 1.73 giving the final nanoparticle morphology as an octahedron with only {111} facets expressed. The second pathway takes place when the growth rates are similar in value and the R value is around 0.87 giving the final nanoparticle morphology as a cube octahedron. The third pathway takes place when the growth rate in the {111} direction is greater than the in the {100} direction and has an R value around 0.58, then the final nanoparticle morphology would be cubic with only the {100} facets being expressed. In solution phase nanoparticle synthesis the growth rate of the different facets can be manipulated by using capping agents that specifically attach to a certain facet.

The main focus of this dissertation will be the synthesis and morphology control of early transition metal carbides using an arc discharge source. The incorporation of main group elements, such as carbon into the lattices of early transition metals, produces compounds with unique physical, chemical, electronic, and catalytic properties.²⁴ These resulting compounds are referred to as transition metal carbides. The carbides are well known for their hardness, strength, and high melting points, which are characteristics of many ceramic materials.²⁵⁻²⁶ Theoretical band calculations indicate that the bonding in carbides involves simultaneous contributions from metallic, covalent, and ionic bonding.²⁷⁻³⁰ Metallic bonding is related to the metal-metal bonds. Covalent bonding arises from the interaction of carbon 2s and 2p orbitals with metal d orbitals. The ionic contribution is related to the charge transfer between metal and nonmetal atoms.

Early transition metal carbides have many potential applications in the fields of catalysis and ceramic materials. Transition metal carbides have attracted considerable attention for catalytic applications since 1973, when Levy and Boudart first reported the Pt-like behavior of tungsten carbide (WC) in the neopentane isomerization reaction.³¹

This class of compounds has shown particularly high potential for use in hydroprocessing reactions.³²⁻³⁴ These processes represent one of the most important steps in petroleum refining. In order to perform as an effective catalyst the material has to have a large specific surface area. The large surface area permits for many active sites, therefore allowing the reaction to proceed at a faster rate. Surface areas can be increased by decreasing the size of the catalyst or by increasing the porosity of the material. The selectivity of the catalyst is dependent on the particle morphology, or which facet is exposed on the surface.³⁵ As mentioned earlier, different facets have different numbers of broken bonds. The broken bonds provide the electrons that interact with the absorbing molecules and promote the catalytic reactions. Also, the atoms on the surface of different facets have different facets. The absorbing molecules may need to be oriented in a certain way in order to interact with the surface atoms.

Morphological control of the transition metal carbide nanoparticles could have very important applications in the field of ceramic and composite materials. One of the desirable properties of early transition carbides is their very high melting points. However, the high melting points of the materials require very high sintering temperatures for micron-sized powders. Nano-sized particles have an advantage because they often have much lower melting points than the bulk material and micron-sized powders.⁴⁻¹² Their low melting points are related to the high surface energy of the nanoparticles. The higher the surface energy of the nanoparticle, the lower the melting point will be for the nanoparticle. The melting point will also change for nanoparticle. For

pure *fcc* structure materials octahedron shaped nanoparticles are enclosed with all {111} facets and cube shaped nanoparticles are enclosed with all {100} facets. The {111} facet has a lower surface energy and therefore would have the higher melting point compared to cube shaped nanoparticles. The ceramic materials themselves are strengthened by using nanopowders due to Hall-Petch strengthening.³⁶ Hall-Petch strengthening is based on the observation that grain boundaries impede dislocation movement. The relationship between yield stress of a material and grain size is described by the Hall-Petch equation shown in Equation 2:

$$\sigma_y = \sigma_o + \frac{K}{\sqrt{d}}$$
[2]

where K is the strengthening coefficient which is unique to each material, σ_o is a materials constant for the starting stress for dislocation movement, *d* is the grain diameter and σ_y is the yield stress. One can see from the Hall-Petch equation that the smaller the grain size the stronger the material. However, experimentally it has been found that the highest yield strength is for a grain size of about 10 nanometers.³⁷ It is believed that grain sizes under 10 nanometers undergo a different strength failure mechanism.

1.2 Thesis Organization

Chapter 2 of this dissertation covers the experimental technique used to study nanoparticle formation though an arc discharge method. Detail is given to dimensions and materials used in the construction of the new instrument. Also included is a short overview of the main analytical techniques used to characterize the nanoparticles synthesized using the arc discharge instrument.

Chapter 3 addresses the synthesis of titanium carbide nanoparticles with the arc discharge instrument. During the arc discharge between two titanium electrodes the methane reactant gas concentration was varied. Under different methane concentrations the titanium carbide nanoparticle morphology was found to change. The various factors leading to this morphology change are discussed.

Chapter 4 discusses the synthesis of niobium carbide nanoparticles with the arc discharge instrument. The morphology of niobium carbide nanoparticles changed under slightly different conditions than for titanium carbide nanoparticles. This chapter explains why it takes a change in experimental conditions to change the nanoparticle morphology for niobium carbide.

Chapter 5 shows the synthesis of zirconium carbide nanoparticles with the arc discharge vessel. The particle morphology of zirconium carbide nanoparticles does not easily change. Also an estimation of the surface energies was calculated in order to compare between titanium, niobium, and zirconium carbide surfaces. The surface energy plays a critical role in the nanoparticle morphology under different conditions.

Chapter 6 presents the results and findings of a side project where the use of the arc discharge instrument to fabricate aluminum nanoparticles. Aluminum nanoparticles have a potential use as a dopant for high energetic fuels. Many different conditions employed in an attempt to form aluminum nanoparticles that did not contain a protective oxide shell.

During the course of my graduate research, the formation of titanium carbide, niobium carbide, zirconium carbide and aluminum nanoparticles were investigated with an arc discharge method. The results of these studies have shown the nanoparticle morphology changes under different synthesis conditions that are unique to each metal system studied. Arc discharge provides a viable synthesis route for making novel nanoparticles. Findings from work I have undertaken has greatly furthered an understanding of how these conditions change the facet growth rates. With this information, conditions can be tuned to produce new nanomaterials with specific morphologies.

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Chapter 2

Experimental Methods

2.1 Introduction

In this chapter the experimental apparatus design and conditions used to synthesize the nanoparticles are explained. This will help future experimentalist repeat the obtained experimental results and be a guide on how to use the apparatus. This chapter is broken down into two sections. The first being the actual experimental apparatus and the second being a review of the most critical analytical techniques used to analyze the synthesized nanopowders.

2.2 Experimental Design

The arc discharge vessel was designed in such a way as to allow particles to be synthesized under various conditions. Nanoparticles can be synthesized under different pressures, gases, flow rates, solutions, metals, and currents. This ability to change the experimental conditions allows the experimentalist multiple pathways to synthesize the desired products.

Figure 2-1 is a top view diagram of the arc discharge vessel apparatus. In Figure 2-1 the metal electrodes are the target materials used to synthesize nanoparticles. In this dissertation the electrodes are made of titanium, zirconium, niobium or aluminum rods as



Figure 2-1. Illustration of the arc discharge apparatus.

specified in each chapter. Each electrode is attached to a lead that is connected to a Craftsman 240AC/180DC arc welder power supply. A direct current of 180 amps is applied to the electrodes. The electrodes are drawn together until an arc discharge is formed between the two electrodes. The distance between the two electrodes is typically only a few millimeters. The arc discharge forms a plasma region where the electrodes are vaporized. Plasmas generated from an arc discharge can reach temperatures of over 3000^oC.¹ Reactant and carrier gases are brought into the vessel through the gas inflow valve. The reactant gases flow into the plasma region where the gas is atomized or forms free radicals. The saturated vapor flows out of the plasma region where it cools, allowing the atoms to nucleate and grow into nanoparticles. The carrier gas propels the nanoparticles out of the arc discharge vessel and to the collection area. The collection area is a bubbler containing HPLC grade acetonitrile. The next few paragraphs give more detail of the materials used in the fabrication and the actual dimensions of the experimental apparatus.

The actual dimensions of the arc discharge instrument are shown in the AutoCAD drawing in Figure 2-2. The figure shows the instrument on its side with the bottom on the left side of the image and the top on the right side. All metal parts are made from stainless steel unless otherwise noted. The main camber of the arc vessel is a cylinder and has the dimensions of 4.5" X 4" with inner dimensions of 1.75" X 4". Figure 3 shows the end view of the main chamber. The inner eight circles are eight 1/4 inch holes drilled through the length of the main chamber to water-cool the vessel. Each cap is fitted with two silicone O-rings; one O-ring is used to seal the inner chamber of the



Figure 2-2. AutoCAD drawings of the side view of the arc discharge apparatus.



Figure 2-3. An AutoCAD drawing of the main chamber from the top showing the position and dimensions of the cooling lines, o-rings, and tapped holes to attach the top.



Figure 2-4. An AutoCAD drawing of the bottom flange, that attaches to the main body of the arc discharge apparatus.



Figure 2-5. An AutoCAD drawing of the fittings used to insert the electrodes into the arc discharge apparatus.

vessel from the cooling water, and the other is used to seal the cooling water from the outside of the vessel. Silicone O-rings are used because of their ability to handle high temperatures, up to 500° C, and because they are chemically inert. The eight outer holes are tapped to attach the top and bottom caps to the main chamber. Figure 2-3 shows the bottom cap that is 1/2 inch thick with a channel cut on the inner side to transport the cooling-water in and out of the main chamber. Each cap is tapped for an eighth inch national pipe thread tapered thread (NPT) fitting that is used to hook up water lines for cooling the arc vessel. The center of the bottom cap is also tapped for a 1/8 inch NPT fitting, which is used as a drain for arc experiments done under a solution environment. The top cap is equipped with a glass watch glass, which permits monitoring the arc discharge in the vessel. Figure 2-4 shows that a one-inch plug is placed in the bottom of the main chamber to decrease the volume within the vessel. The decrease in volume was desired for arc discharge experiments preformed under a solution environment. The electrodes are brought into the middle of the vessel through 1/2 inch holes. In the experiments reported in this thesis the electrodes for the early transition metal carbides were 1/4 inch in diameter and the aluminum electrodes were 1/4 and 1/8 inch in diameter. Figure 2-5 shows how the fittings were designed to get the electrodes into the arc vessel and keep the vessel sealed from the outside atmosphere. A 1-1/2 inch Teflon fitting is screwed into the side of the vessel with a 0.492 inch hole going through the fitting. A Viton O-ring is fitted between the Teflon fitting and the arc vessel. A macor or a boron nitride ceramic insert is placed in the Teflon fitting and goes through the outer shell of the vessel. Use of the boron nitride ceramic pieces was discontinued because they were too brittle and would fall apart. A viton O-ring was also placed under the lip of the ceramic

piece to make a seal between the ceramic and Teflon fitting. The ceramic and Teflon pieces allow the electrodes to be completely insulated form the vessel. The metal electrodes are then placed into the ceramic pieces and a viton O-ring

The helium and the reactant gases (ethylene, methane or acetylene) are mixed together inside a stainless steel mixing chamber. The reactant gas concentration is calculated from the partial pressure of each gas in the mixing chamber. The gas mixture then goes through a flow controller in order to keep the flow rate constant. Pure helium is run through the whole instrumental setup before each run to purge out any oxygen. During the experiment the nanoparticles are entrained within the gas flow and exit the arc vessel through the gas outlet line. The gas outlet line is attached to a collection bubbler. The collection bubbler is a simple setup comprised of a glass tube with a check valve, rubber stopper, and an Erlenmyer flask. The bubbler is filled with 20-30mL of acetonitrile; acetonitrile was used because it was believed that it might help keep the nanoparticles from oxidizing. The check valve in the glass tube was needed to make sure that no acetonitrile would get sucked back into the arc vessel.

2.3 Analytical Techniques

Once the arc discharge experiment is complete the solution containing the synthesized nanoparticles is transferred to a 40mL scintillation vial and capped. The main analytical techniques used to characterize the synthesized nanoparticles were transmission electron microscopy (TEM), selected area electron diffraction (SAED), and energy dispersive X-Ray spectroscopy (EDS).

A TEM works by accelerating a focused beam of electrons through a sample. Information about the sample that is obtained depends on how the elections interact with the sample. The thicker and more electron-dense the sample, the more the electron beam will be scattered. The TEM typically gives information about particle morphology, composition, and structure.

Morphology information is obtained by one of two methods. One method is the capturing of an image of the unscattered electrons on a phosphorous screen. This method is called bright field mode, where the dark regions in the image are where the electrons scattered the most. The enhanced scattering can either be from a thick part of the sample or from elements with a high atomic number. The second method is where the scattered or diffracted electrons are captured and imaged, called dark field mode, and the dark regions in the image are where the electrons are not scattered. This method is accomplished by either tilting the electron beam with respect to the sample or by inserting an aperture to only allow the scattered electrons to pass.

After obtaining a TEM image, a selected area electron diffraction (SAED) pattern can be obtained from the nanoparticles imaged. SAED is accomplished by either inserting a selected area aperture between the sample and the detector or by focusing down the beam size to only interact with the area of interest. The aperture makes sure that only electrons diffracted from the area of interest are used for the diffraction pattern. The instrument can be switched to diffraction mode from image mode. If the nanoparticles are crystalline their periodic structure acts as a diffraction grating for the electron beam scattering the electrons in a predictable manner. The diffraction pattern is focused and then is recorded on a CCD camera. Polycrystalline materials or many single crystals oriented in different directions display diffraction patterns that are rings. A single crystal oriented with a low index plane perpendicular to the electron beam will give a spot diffraction pattern. The diffraction pattern of crystalline samples can then be compared to tabulated values for various known materials.

To determine the elemental composition of the synthesized nanoparticles, energy dispersive X-ray spectroscopy (EDS) was utilized. The high energy electrons from the electron beam inelastically scatters with some of the core electrons from the elements within the sample. One of the outer shell electrons relaxes into the hole created from the displacement of the core electron. An X-ray is released during this process that is characteristic of a specific element. While the metal electrodes and reactive gases are well known substances, their atomization and combination can form different products. The EDS spectrum gives information on the elemental composition of nanoparticles within the electron beam. The relative intensities of the elementals obtained on a spectrum can give the abundance of the element within the nanoparticle. The EDS spectra are used with the obtained SAED pattern to properly identify the element of composition, structure and phase of the nanoparticles. The sample starts out perpendicular to the electron beam, and in order to obtain an EDS spectrum the sample needs to be rotated 20 to 30 degrees. This is because the X-ray detector is located perpendicular to the electron beam.

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Chapter 3

Effect of Carbon Concentration on Changing the Morphology of Titanium Carbide Nanoparticles from Cubic to Cuboctahedron

Adapted with permission from [Grove, D.E. et al, ACS Nano 2010, 4, 49-50]

3.1 Introduction

Early transition metal carbides are well known for their high melting points, high degree of hardness, and thermal and electrical conductivity.¹⁻⁶ These properties make early transition metal carbides very useful in coatings, tools, machine parts, and as reinforcements in composites.¹⁻⁶ They often adopt simple crystal structures, such as face-centered cubic (fcc), body-centered cubic (bcc), or simple hexagonal (hex) structure, with the nonmetal elements occupying the interstitial spaces between metal atoms.⁷ Theoretical band-structure calculations indicate that the bonding in carbides involves simultaneous contributions from metallic, covalent, and ionic bonding.⁸⁻¹¹ Metallic bonding is related to the metal-metal bonds; covalent bonding arises from the interaction of carbon 2s and 2p orbitals with metal d orbitals; and the ionic contribution is related to the charge transfer between metal and carbon atoms.

The properties of a nanoparticle are determined by a set of physical parameters that include its size, shape, composition, and structure. In the case of catalysis, it is wellestablished that for certain systems the activity of a nanoparticle can be enhanced by reducing its size, thereby increasing the surface area and the availability of defects.¹²⁻¹⁵ Transition metal carbides have attracted considerable attention for catalytic applications since 1973, when Levy and Boudart first reported the Pt-like behavior of WC in the neopentane isomerization reaction.¹⁶ Some advantages that early transition metal carbides have over their parent metal include activity, selectivity and durability.^{17,18} The selectivity is most sensitive to the packing of atoms on the surface or exposed facets of a nanoparticle.^{19,20} Different crystal surfaces exhibit different physical and chemical properties due to their packing and coordination state. For example the {111}, {100}, and {110} surfaces of a face centered cubic (fcc) metal have different surface atom densities, electronic structures and chemical reactivities. The TiC {111} surface was shown to be highly active for dissociative adsorption of hydrogen at room temperature.²¹ The TiC {100} surface has the ability to adsorb several different molecules including water, methanol, ethanol, 2-propanol, NH₃, CO, and methyl formate.²²⁻²⁶ Also adsorption and dissociation of O₂ and SO₂ has been studied on the TiC {100} surface.²⁷⁻³²

Traditionally, titanium carbide (TiC) has been synthesized either as thin films or micron sized particles. TiC thin films can be deposited through the reaction of TiCl₄ with gaseous hydrocarbons or magnesium reduction of TiCl₄ and CCl₄.³³ Early transition metal carbide micron sized particles are commercially made by carbothermal reduction of metal oxide.³⁴ The shape and size of the metal carbides particle depends on the shape and size of the starting metal oxide particle. Titanium carbide nano-powders have been formed through thermal plasma processing with an average size less than 100nm.⁵ The preparation of nanoparticles with different shapes and surface facets is therefore

important for controlling their properties. The role of carbon concentration on how it affects titanium carbide nanoparticle morphology will be presented and discussed.

3.2 Experimental Methods

Materials. Pure metal Ti (purity 99.7%) rods (6.4 mm in diameter) were purchased from Alfa Aesar. Methane (purity 99%) and helium (purity 99.999%) were purchased from BOC Gases and Praxair, respectively. The arc discharge vessel was homemade and the power supply for the arc discharge was a Craftsman 240AC/180DC arc welder.

Nanoparticle Synthesis. Various combinations of methane in helium ranging from 5% to 100% methane were used as reactant gas mixtures. The gas mixture flow rate was maintained at 40 standard cubic centimeters per minute (sccm) with a flow controller and an arc discharge acquired by applying an 180A direct current for 10 minutes. Titanium and methane were atomized within the arc discharge generated plasma. Once the metal and carbon vapor are sufficiently cooled or the concentration is high enough, nucleation occurs and is followed by nanoparticle growth. The titanium carbide nanoparticles were entrained in the helium gas flow and collected from the helium flow in a bubbler containing acetonitrile.

Characterization. The synthesized nanoparticles were characterized by powder X-ray diffraction (XRD) using Cu–K α radiation (λ =1.5405 Å). A couple of drops of solution were place on a 200 mesh lacey carbon coated copper grids for TEM analysis. The morphology, size, and composition of the nanoparticles were characterized using Philips EM-420T transmission electron microscopy operating at an accelerating voltage

of 120kV equipped with Energy Dispersive Spectroscopy (EDS) and Selected Area Diffraction Patterns (SADP) capabilities.

3.3 Results and Discussion

Titanium carbide nanoparticles were synthesized by an arc discharge method with varying methane concentrations, described in Chapter 2. A typical XRD pattern of the synthesized ultra-fine, black powder collected in the bubbler is shown in Figure 3-1, clearly confirming the presence of titanium carbide (TiC) without any evidence of impurities such as titanium dioxide or pure titanium metal. The peaks in the XRD pattern are broad due to the scattering effects from the small particle size of the powders.^{35,36} Particle size can be calculated from XRD patterns by using the Scherrer Equation:³⁷

(1) Diameter = $K\lambda/d\cos\theta$

where λ is the wavelength of the X-Ray radiation source, *d* is the full width half maximum (FWHM) of the peak, θ is the Bragg angle and K is a constant with a typical value of 0.9.³⁷ It is desirable to use peaks at smaller diffraction angles to reduce the effect of lattice strain.³⁸ From the peak of $2\theta = 35.55$ in figure 3-1, particle size is calculated using the Scherrer Equation to be 20 nm for nanoparticles produced with 12% methane concentration, which is in good agreement with TEM images from the sample.

Particles formed from gas mixtures of 5% and 12% methane are shown in the TEM images in figure 3-2a and 3-2b, respectively. The images also show that the



Figure 3-1. XRD pattern of titanium carbide nanopowders compared to a library spectrum for bulk titanium carbide.



Figure 3-2. (a)-(b) TEM images of cube shaped nanoparticles synthesized with 5% and 12% methane. (c) A selected area diffraction of the synthesized titanium carbide nanoparticles confirms the nanoparticles are titanium carbide. The three inner rings have a d-spacing measurement of 2.50, 2.16 and 1.53. (d) EDS spectra of the synthesized titanium nanoparticles showing only titanium, carbon and copper present. The copper and a portion of the carbon signal is form the TEM grid.

particles formed are uniform cubes with no excess amorphous carbon. The varying contrast from nanoparticle to nanoparticle is due to different orientations of the particles in the electron beam. Single particle diffraction patterns show that the nanoparticles are single crystals with all six facets on the cube being {100}. A selected area diffraction pattern shown in Figure 3-2c has d-spacings that measure 2.50, 2.16 and 1.53 that match the bulk titanium carbide *fcc* structure.³⁹ Figure 3-2d is a typical EDS spectrum of the synthesized nanoparticles showing peaks corresponding to titanium and carbon from the nanoparticles. The lacey carbon coated grids also contribute to the carbon signal. The copper peaks in the EDS spectra are from the lacey carbon coated copper TEM grids that the particles are deposited on. Another interesting observation is that there is no visible oxygen peak in the EDS spectra.

A TEM image of TiC nanoparticles synthesized under a gas mixture of 30% methane is shown in Figure 3-3a. The image shows a transformation from the cubic morphology to a mixture of cubes and cuboctahedron shaped particles. Selected area diffraction patterns show that both particle morphologies are TiC with the *fcc* structure. Also single particle diffraction patterns show that both morphologies are single crystals.

Figures 3-3b and 3-3c show the TEM images of nanoparticles formed with 60% and 100% methane, respectively. The morphology of the nanoparticles is now dominated by the cuboctahedron shaped nanoparticles. This gives each of the nanoparticles 14 facets that have a combination of six {100} and eight {111} facets. Selected area diffraction patterns confirm that the nanoparticles are TiC with an fcc crystal structure. Some of the



Figure 3-3. (a)-(c) TEM images of titanium carbide nanoparticles synthesized with 30% (a), 60% (b), and 100% methane. (d) Is a bar graph displaying the abundance of different morphologies synthesized with varying methane concentrations. Cubes dominate at low methane concentrations and cuboctahedrons dominate at high methane concentrations

nanoparticles synthesized with 100% methane show an amorphous carbon shell around the nanoparticles. The reproducible ability to effect morphology changes from cubic to cuboctahedron with increasing methane concentration was verified in a number of experiments.

We measured the shape distribution of the titanium nanoparticles from multiple TEM images from various methane concentrations in Figure 3-3d. For each methane concentration we counted between 100 to 160 nanoparticles. Only clearly visible nanoparticles were counted, and large agglomerates where the morphology of the nanoparticles was not clear, were excluded. The large agglomerates made up of less than 10% of the sample and did not affect the morphology trend. Nanoparticles synthesized with 5% and 12% methane concentrations contained 94% and 86% cubes, respectively. With 30% methane the nanoparticles are split with 58% being cubes and 42% being cuboctahedrons. The cuboctahedron morphology dominates with 60% and 100% methane where 93% and 94%, respectively, of the samples are cuboctahedrons.

To understand this phenomenon of changes in morphology with carbon concentration we looked into the relationship of surface energy with the growth rate of the different facets. As clusters grow past a critical size they form seed crystals which have well defined crystallographic facets.⁴⁰ Under thermodynamic control the seed crystal should take on a morphology that minimizes the exposed surface and maximizes the volume. Typically the most stable morphology follows Wulff's theorem⁴¹, which attempts to minimize the total interfacial free energy of a system within a given volume. For an fcc structure material the surface energy (γ) for the different facets follows an energy sequence of $\gamma_{\{111\}} < \gamma_{\{100\}} < \gamma_{\{110\}}$.⁴⁰ Therefore a single crystal seed should take on the shape of an octahedral in order to maximize the number of {111} facets and minimize the surface energy.⁴⁰ However, this shape has a large surface area compared to its volume resulting in the high energy vertices to be truncated. The seed crystals therefore form into a shape of a truncated octahedron enclosed by a combination of {111} and {100} facets.⁴⁰

Referring back to the results section, we notice that at lower concentrations of methane, cubic morphology is dominant and at higher concentrations, cuboctahedrons are dominant. However, irrespective of the carbon concentration, the TiC nanoparticles have 1:1 stoichiometry which rules out the morphology change being due to different stoichiometries. Now, according to Periodic Bond Chain (PBC) theory nomenclature, {100} faces are flat surfaces and are called F-faces.^{42,43} The {111} faces are kinked surfaces and are called K-faces. Each surface site on the K-faces is a kink site and irreversibly incorporates incoming atoms absorbed on the surface. K-faces therefore produce a surface that has many nucleation sites causing a higher growth rate. However impurities and solvent molecules have been shown to interact with the K-faces, thereby decreasing the growth rate of these facets.^{44,45} In our case either the excess carbon or free methyl radicals interacts with the kink sites on the K-faces. The TiC nanoparticles synthesized with 5% and 12% methane concentrations produce nanoparticles that are cubic having six {100} facets. This can be explained within the PBC theory model. The seed crystal is a truncated octahedron which has a mix of {100} and {111} facets. Since at low supersaturation levels (corresponding to 5% and 12% methane), the growth rate for <111> is faster than the <100> direction, they finally end up forming cubic

nanoparticles possessing all six $\{100\}$ facets, as depicted in figure 3-1. At higher carbon concentration (60%, 100%) the TiC nanoparticles are cuboctahedron shaped. The decrease in the growth rate of the $\{111\}$ facet is because of the interactions between excess carbon and the kink sites. The excess carbon leads both <100> and <111> facets to have similar growth rates and the seed crystal truncated octahedron shape becomes only slightly distorted to the cuboctahedron shape.

At 30% methane concentration both processes are playing a part and therefore a mixture of cubic and cuboctahedron particles are observed. This might also be influenced by a localized concentration/pressure gradient produced during the atomization process. The inner region of the metal and carbon vapor promotes the cuboctahedron shaped particles, while in the outer region where the metal and carbon atoms are in lower concentration, the formation of cubes dominates.

3.4 Conclusions

We have shown that titanium carbide nanoparticles can be synthesized through an arc discharge method. The nanoparticle morphology can be controlled by changing methane concentration. TiC cubes are synthesized at a low methane concentration and cuboctahedrons at a high methane concentration. Both the cubes and the cuboctahedrons are formed from a truncated octahedron seed crystal and have *fcc* structure. However, the difference in morphology arises because of the difference in the growth rates between {111} facet and the {100} facet at different carbon levels. There is no capping agent

used to stabilize the titanium nanoparticle surface, therefore the bare nanoparticles could potentially be important for applications in the fields of catalysis and ceramic processing.

3.5 References

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Chapter 4

The Effect of Methane, Ethylene and Acetylene Gas on the Morphology of Niobium Carbide Nanoparticles

4.1 Introduction

Early transition metal carbides are very useful materials with numerous industrial applications due to their properties of high strength, high hardness and high melting points.¹⁻⁶ These properties make early transition metal carbides ideal for industrial applications such as cutting tools and thin film coatings. Early transition metal carbides also have been found to have useful catalytic properties that are similar to noble metal catalysts, such as Pt, Pd, and Ir.⁷⁻¹⁰ In order to produce useful catalysts, the material needs to have a high specific surface area and preferred exposed surface facets. Nano scale particles are desirable in order to increase the specific surface area of a material, and controlling the particle morphology can be critical in achieving the desired exposed surface facets. Also, in some cases the properties are influenced by size.

Niobium carbide has many useful properties like a very high melting point (3610°C), chemical stability, good wear resistance, and high hardness. Typically, hard metal composite materials usually contain tungsten carbide (WC) or titanium carbide (TiC) with a metal binder like cobalt (Co), nickel (Ni) or iron (Fe) mixed with tantalum

carbide (TaC).¹¹⁻¹² Niobium carbide has been used to replace the costly TaC as cements for TiC and WC based tools.¹³ Adding 0.9wt% NbC to a WC-12wt% Co has been found to greatly improve the hardness and bending strength of the composite.¹⁴ In addition to the beneficial mechanical properties, niobium carbide has been found to be catalytically active for the decomposition of ammonia.¹⁵

In Chapter 3 we developed a method to synthesize titanium carbide nanoparticles with control over the particle morphology.¹⁶ We found that varying the methane concentration during synthesis changed the nanoparticles from dominate cubic at low carbon concentrations to cuboctahedrons at high carbon concentrations. In this chapter, we report the development of a method to synthesize niobium carbide nanoparticles through a plasma generated from an arc discharge. Based on the work reported, we find the morphology of the nanoparticles can be controlled through changing the carbon source gas during the nanoparticle synthesis.

4.2 Experimental Methods

The arc discharge apparatus used in this experiment has already been described in Chapter 2. Pure metal niobium (purity 99.8%) rods (6.4 mm in diameter) were used as electrodes. Various concentrations of methane: 2.5%, 50% and 100; ethylene: 10%, 25%, 50%, 75% and 100%; and acetylene: 10%, 25%, 50%, 75% and 100%; gases were seeded in helium and studied upon interactions with niobium. The gas mixture flow rate was maintained at 40 standard cubic centimeters per minute (sccm) and a discharge was acquired by applying 180A direct current for a period of 10 minutes. The morphology,

size, and composition of the nanoparticles were characterized using a Philips EM-420T transmission electron microscopy equipped with energy dispersive X-ray spectroscopy (EDS) and selected area diffraction patterns (SADP) capabilities operating at an accelerating voltage of 120kV.

4.3 Results and Discussion

Figure 4-1a shows 10 nm sized niobium carbide nanoparticles synthesized with 2.5% methane in helium. Selected area diffraction patterns of the nanoparticles confirmed that the nanoparticles are niobium carbide with the *fcc* structure, and a stochiometry of one niobium to one carbon is displayed in Figure 4-1b. The d-spacings from the obtained diffraction pattern match the literature values for bulk niobium carbide and the three inner rings measure 1.58, 2.24 and 2.58.¹⁷ The nanoparticles are thereby identified as having single crystalline characteristics with all six facets being {100}. Figure 4-1c is an energy dispersive spectra from the nanoparticles which shows that the sample contains niobium, carbon and copper, where the copper peak in the spectra comes from the TEM grids. Also a portion of the carbon signal comes from the TEM grid and from left-over amorphous carbon from the nanoparticles' synthesis. Niobium nanoparticles synthesized with 100% methane shown in Figure 4-1d have cubic morphology seen with the nanoparticles synthesized with 2.5 % and 50% methane. Figure 4-2 is a bar graph that shows the morphology percentage for each methane It displays that when niobium carbide nanoparticles are synthesized with concentration. methane, cubic morphology dominates the nanoparticles morphology distribution. There



Figure 4-1. a) Niobium carbide nanoparticles synthesized with 2.5% methane. b) Selected area diffraction pattern (SADP) of NbC nanoparticles confirms that the nanoparticles are *fcc* structure with a stoichiometry of 1 metal to 1 carbon. The measured d-spacings are 2.58, 2.24, and 1.58.¹⁷ c) Niobium carbide nanoparticles synthesized with 100% methane. d) Energy-dispersive X-ray (EDS) spectra of the synthesized NbC nanoparticles show that only Nb and C are present in the sample. The copper signal comes from the lacey carbon coated copper TEM grid on which the nanoparticles are deposited.



Figure 4-2. Bar graph of NbC nanoparticles comparing particle morphology synthesized with different methane concentrations.

is a small increase in the cuboctahedron morphology with higher methane concentrations. This is slightly different from what was observed with our previous study on methane concentration and its effect on altering the morphology of titanium carbide nanoparticles. The titanium carbide system showed particles with cubic morphology at low methane concentration, with conversion to cuboctahedron morphology at high methane concentrations. Considering the prior work, we believe that if we could increase the carbon concentration then we might be able to shift the percentage of the cube morphology of the niobium carbide nanoparticles to the dominance of cuboctahedron morphology. In order to achieve a higher carbon concentration, in the next series of experiments we used ethylene and acetylene in place of methane as our reactant gas. A series of experiments was run using ethylene and acetylene concentrations of 10%, 25%, 50%, 75% and 100%.

Figure 4-3 is a bar graph comparing the cuboctahedron morphology to the cube morphology synthesized under different ethylene concentrations. Over 500 nanoparticles were counted for each concentration. Particles that were in large agglomerations only made up a small portion of the sample and were not counted. The bar graph shows that niobium carbide nanoparticles synthesized with 10%, 25% and 50% ethylene concentration display a nanoparticle morphology distribution of around 40% cuboctahedron morphology. A TEM image of the nanoparticles synthesized with 50% ethylene is shown in Figure 4-4a. The cuboctahedron shaped nanoparticles are single crystalline with a combination of six {100} facets and eight {111} facets. Also seen in the bottom of the TEM image in Figure 4-4a are two of the niobium particles aligned with the {100} facet perpendicular to the electron beam. This alignment shows the



Figure 4-3. Bar graph of NbC nanoparticles comparing particle morphology synthesized with different ethylene concentrations.



Figure 4-4. a) Niobium carbide cuboctahedron nanoparticles synthesized with 50% ethylene. Also seen in the bottom of the TEM image two of the niobium particles aligned with the {100} facet perpendicular to the electron beam. This alignment shows the truncated corners of the cuboctahedron which is due to the {111} facet scattering the electron beam differently than the {100} facet. b) Niobium carbide cuboctahedron nanoparticles synthesized with 75% ethylene. c) Niobium carbide cuboctahedron nanoparticles synthesized with 100% ethylene. d) Selected area diffraction pattern (SADP) of the nanoparticles confirming that they are NbC.



Figure 4-5. a) Niobium carbide cubic nanoparticles synthesized with 50% ethylene. b) Niobium carbide cubic nanoparticles synthesized with 75% ethylene. c) Niobium carbide cubic nanoparticles synthesized with 100% ethylene. d) Selected area diffraction pattern (SADP) of the nanoparticles confirming that they are NbC.

truncated corners of the cuboctahedron which is due to the {111} facet scattering the electron beam differently than the {100} facet. Niobium carbide nanoparticles synthesized with 75% ethylene displayed a slight increase to 50% cuboctahedrons while nanoparticles with 100% ethylene concentration showed 73% cuboctahedrons. Shown in Figures 4-4b and 4-4c are TEM images of nanoparticles synthesized with 75% and 100% ethylene, respectively. Figure 4-4d displays the selected area diffraction pattern confirming the nanoparticles are niobium carbide. Figure 4-5 displays the cubic morphology for niobium carbide nanoparticles synthesized with 50%, 75%, and 100% ethylene. Also displayed in Figure 4-5d is the selected area diffraction pattern for the cubic nanoparticles confirming that they are niobium carbide.

Figure 4-6 is a bar graph comparing the cuboctahedron morphology to the cube morphology synthesized under different acetylene concentrations. We find that the niobium carbide nanoparticle distribution changes to favor a cuboctahedron morphology when synthesized with acetylene. Nanoparticles synthesized with 10% and 25% acetylene display a morphology distribution around 80% cuboctahedrons. As the acetylene concentration is increased to 50%, 75%, and 100% the percentage of cuboctahedron increases to around 85%. Shown in Figures 4-7a and 4-7b are TEM images of nanoparticles synthesized with 75% and 100% acetylene. Figure 4-7c displays a TEM image of the particles synthesized with 100% acetylene and Figure 4-7d is the selected area diffraction pattern confirming the nanoparticles are niobium carbide.

The results reveal that niobium carbide nanoparticles change particle morphology distributions with different gases, cubic morphology is preferred with methane, a mixture of cubes and cuboctahedrons with ethylene and a cuboctahedron morphology is preferred



Figure 4-6. Bar graph of NbC nanoparticles comparing particle morphology synthesized with different acetylene concentrations.



Figure 4-7. a) Niobium carbide nanoparticles synthesized with 10% acetylene. b) Niobium carbide nanoparticles synthesized with 50% acetylene. c) Niobium carbide nanoparticles synthesized with 100% acetylene. d) Selected area diffraction pattern (SADP) of the nanoparticles confirming that they are NbC.

with acetylene. To understand why the niobium carbide nanoparticles change morphology with different gases we look back at the starting seed crystal. Using Wulff's theorem, a seed crystal with fcc structure forms a truncated octahedron morphology in order to minimize the surface energy of the crystal.¹⁸ The truncated octahedron is a combination of six {100} facets and eight {111} facets.¹⁹ According to Periodic Bond Chain (PBC) theory the {111} facets are kinked surfaces that have a higher growth rate than the $\{100\}$ facets.²⁰⁻²¹ Therefore if the $\{111\}$ facets on the truncated octahedron grow out due to the higher growth rate and no longer exists on the surface, then only the {100} facets are left forming cubic shaped particles. However impurities, capping agents and solvent molecules have been found to interact with the kink sites on the {111} facets and slow the growth rate in that direction.²²¹⁻²³ In our case it might be the ethylene and acetylene free radicals or the excess carbon that interacts with the kink sites on the {111} facets, slowing the growth rate to form the cuboctahedron morphology nanoparticles. Another possibility comes from one of the earliest reports of habit modifying from Rome de l'Isle who reported a morphology change of rock salt from cubes to octahedrons in the presence of urea.²⁴ This morphology change for rock salt has also been seen with the presence of formamide or cadmium dichloride.²⁵⁻²⁷ In the {111} direction, titanium and niobium carbide form crystal structures that alternate layers between carbon and metal atoms similar to the growth of rock salt structure crystals.²⁸ This results in alternating layers of cations and anions. The polar surfaces therefore are highly unstable and should not be present in the final morphology of a rock salt structure crystal.²⁹ However, if the surface is stabilized as in the previous reports mentioned, the {111} facet can be expressed in the final morphology. For niobium carbide nanoparticles the ethylene and acetylene free radicals are able to stabilize the {111} facet and therefore allow the facet to be expressed in the final nanoparticle morphology.

In Chapter 3 we found that titanium carbide nanoparticles formed a cubic morphology under low methane concentrations (5% and 12%) and cuboctahedrons with high methane concentrations (60% and 100%). Changing the early transition metal to niobium from titanium, alters the surface energy of the particle and ultimately the growth rates of the facets. Upon changing the methane concentration we did not observe a large nanoparticle morphology distribution change for the niobium carbide system as we did with titanium carbide. Our initial thought was if we increased the amount of carbon available during synthesis, then we could convert the cubic morphology to cuboctahedron. However when ethylene and acetylene were used as the carbon sources, we saw an increase in the percentage of cuboctahedrons being formed even at the same carbon concentration. We believe this enhancement is from the formation of ethylene or acetylene free radicals that leads to the increase percentage of cuboctahedrons. Either the ethylene and acetylene free radicals stabilize the {111} facets more than the methyl free radicals, or another possibility is that since the ethylene and acetylene free radicals are larger molecules than the methyl free radical, they might be more stable and therefore have more time to interact and stabilize the {111} facet.³⁰ The interaction of the ethylene or acetylene free radicals with the {111} facet of niobium carbide provides enough of a barrier to slow the growth rate of that facet to increase the number of cuboctahedrons in the nanoparticle distribution.

4.4 Conclusions

We have shown that niobium carbide nanoparticles can be synthesized through an arc discharge method. The morphology of the nanoparticles can be controlled through the use of different reactant gases. With methane gas, cubes are preferred; with ethylene gas a mixture of cuboctahedrons and cubes are formed, and with acetylene gas cuboctahedrons are preferred. With ethylene either the increase in carbon concentration or the ethylene free radical slows the growth rate of the {111} facet allowing a mixture of cuboctahedron morphology to form. With acetylene either the increase in carbon concentration or the acetylene free radical interacts stronger with the {111} facet causing a higher percentage of cuboctahedrons to be formed. Comparing the niobium carbide nanoparticles to the titanium carbide nanoparticles reveals that the growth rate of the {111} facet for niobium carbide is greater than for the {111} facet for titanium carbide and niobium carbide to see if they correlate with observed findings in this Chapter.

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Chapter 5

Arc Discharge Synthesis of Zirconium Carbide Nanoparticles

5.1 Introduction

Zirconium carbide is among the hardest known compounds with microhardness value of ~ 2600 kg/mm².¹⁻² This property has made ZrC an ideal material for cutting tools and in wear-resistant coatings. ZrC is a candidate material for ultrahigh temperature application because of its high melting point ~3550 °C, solid-state phase stability and good thermomechanical and thermochemical properties.³⁻⁴ Besides high hardness and high melting temperature ZrC exhibits high emissivity and high current capacity at elevated temperatures. Thus, zirconium carbide is a promising material for use in thermophotovoltaic radiators and field emitter tips and arrays.⁵⁻⁶ ZrC also has a low neutron cross-section and thus can be used as a nuclear reactor core material.⁷

Typically zirconium carbide powders are made through a carbothermal process.^{1,8-} ¹⁰ Carbon and zirconium metal are mixed together, the zirconium metal is in the form of either zirconium hydride or zirconium oxide, the mixture is then heated to high temperatures to synthesize zirconium carbide powders. This process leads to zirconium carbide powders with relatively large particle size. This chapter will present a method to synthesize zirconium carbide nanoparticles through an arc discharge method. In this chapter a comparison of nanoparticle morphology between titanium carbide, niobium carbide and zirconium carbide will be presented and discussed.

5.2 Experimental Methods

The arc discharge apparatus used in this experiment has already been described in Chapter 2. Pure metal zirconium (purity 99.8%) rods (6.4 mm in diameter) were used as electrodes. Various concentrations of methane, 2.5%, 12%, 50%, 75% and 100%, seeded in helium were used as the reactant gas mixture. The gas mixture flow rate was maintained at 40 standard cubic centimeters per minute (sccm) and a discharge was acquired by applying 180A direct current for a period of 10 minutes. The morphology, size, and composition of the nanoparticles were characterized using a Philips EM-420T transmission electron microscopy operating at an accelerating voltage of 120kV equipped with energy dispersive X-ray spectroscopy (EDS) and selected area diffraction patterns (SADP) capabilities.

5.3 Results and Discussion

Figure 5-1 shows 30 nm sized zirconium carbide nanoparticles synthesized with 2.5% methane in helium. Selected area diffraction patterns of the nanoparticles confirmed that the nanoparticles are zirconium carbide with *fcc* structure and a stochiometry of one zirconium to one carbon is displayed in figure 5-2. The d-spacings from the obtained diffraction pattern match with bulk zirconium carbide and measure 2.71, 2.35 and 1.66.¹¹ The nanoparticles are single crystalline with six facets being {100} and eight facets being {111}. Figure 5-3 is an energy dispersive spectrum from the nanoparticles and shows that the sample contains



Figure 5-1. Cuboctahedron shaped zirconium carbide nanoparticles synthesized with 2.5% methane.


Figure 5-2. Selected area diffraction pattern (SADP) of the synthesized zirconium carbide nanoparticles. The measured d-spacings are 2.71, 2.35 and 1.66 and match values for bulk zirconium carbide.¹¹



Figure 5-3. Energy-dispersive X-ray (EDS) spectra of the synthesized zirconium carbide nanoparticles show zirconium and carbon are present in the sample. The copper and some of the carbon signal comes from the lacey carbon coated copper TEM grid the nanoparticles are deposited on.

zirconium, carbon and copper. The copper peak in the spectra comes from the TEM grids. Also a portion of the carbon signal comes from the TEM grid and from left-over amorphous carbon from the nanoparticles synthesis. Figure 5-4 displays a TEM image of zirconium carbide nanoparticles synthesized with 100% methane. Figure 5-5 is a bar graph that shows the morphology percentage for each methane concentration. For each methane concentration around 1000 nanoparticles were counted and only clearly visible nanoparticles were counted. The bar graph displays that the zirconium carbide nanoparticles prefer the cuboctahedron morphology for each methane concentration. This is surprising since for the titanium carbide and the niobium carbide systems the nanoparticle morphology to cuboctahedron with increases in methane, ethylene or acetylene concentration. Therefore the intrinsic surface energy of the {111} facet for the zirconium carbide nanoparticles must be lower than for the {111} facet for titanium carbide and niobium carbide.

In order to test this observation out and see if the surface energy for the zirconium carbide system is lower we looked into estimating the surface energies for each system. A crude estimation for surface energy for pure metal *fcc* materials is given in equation $1:^{12}$

$$\gamma = \frac{1}{2} N_b \varepsilon p_a$$
^[1]



Figure 5-4. Cuboctahedron shaped zirconium carbide nanoparticles synthesized with 100% methane.



Figure 5-5. Bar graph of zirconium carbide nanoparticles comparing nanoparticle morphology synthesized with different methane concentrations.

Where N_b is the number of broken bonds, ε is the bond energy between atoms, and p_a is the surface atomic density. In order to estimate the surface energy for the {111} facet, the lattice constant *a* and the number of broken bonds for the {111} facet is incorporated into equation 1 to give equation 2.

$$\gamma\{111\} = \frac{2\varepsilon\sqrt{3}}{a^2}$$
[2]

Table 5-1 displays the values for the lattice constant and the bond energies for titanium carbide, niobium carbide and zirconium carbide and plugging them into equations 2 gives the values for the surface energies for the {111} facets.

	Bond Energy	Lattice constant	Surface energy (111)
	eV	nm	J/m ²
TiC	14.2	0.4328	42.24
NbC	16.62	0.4469	46.08
ZrC	15.58	0.4698	39.04

Table 5-1. Rough estimate of surface energy for the {111} facet for TiC, NbC, and ZrC. Bond energies are from reference 1 and the lattice constants are from reference 11.

The values calculated are not to be taken as the true values for the surface energy, but rather relative values. We are only interested in the trend among the different materials. The surface energy equations are an estimate for pure metal fcc materials and the metal carbides studied in this dissertation are fcc with a rock-salt structured. Therefore this equation does not account for the polarized contribution on the {111) facet, known for rock-salt structured materials. The trend for the {111} facet for the different metal carbides displays a surface energy sequence of NbC > TiC > ZrC. This follows the trend that we would expect to happen from the nanoparticle morphology results. The zirconium carbide nanoparticles developed the cuboctahedron morphology under all methane concentrations evaluated. This means that the {111} facet for the zirconium carbide nanoparticles is lower in energy and is easily stabilized during nanoparticle synthesis. From chapter 3 titanium carbide nanoparticles synthesized with various concentrations of methane displayed cubic morphology with low methane concentration and cuboctahedron morphology with high methane concentrations. This shows that the {111} facet of the titanium carbide nanoparticles is not stabilized with low methane concentrations and therefore displays mostly a cube morphology. With high methane concentrations the titanium carbide {111} facet is stabilized and the nanoparticle morphology displayed is that of a cuboctahedron. In chapter 4 niobium carbide nanoparticles preferred the cube morphology when synthesized with various methane concentrations. Even high methane concentrations were not enough to stabilize the niobium carbide {111} facet. Ethylene gas was able to increase the percentage of cuboctahedrons shaped niobium carbide nanoparticles. When acetylene was used to synthesize niobium carbide nanoparticles, the morphology shifted to a higher number density of cuboctahedrons. The niobium carbide {111} facet is higher in energy and therefore is harder to stabilize to be present in the final morphology.

5.4 Conclusion

To summarize we have been able to synthesize zirconium carbide nanoparticles through an arc discharge method. The zirconium carbide nanoparticles preferred the a cuboctahedron morphology with various methane concentrations. When comparing the $\{111\}$ facet surface energy for zirconium carbide, titanium carbide and niobium carbide we find that they follow the surface energy sequence NbC > TiC > ZrC. This sequence is verified through the experimental data for each carbide.

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Conclusion

6.1 Concluding Remarks

The synthesis of nanoparticles by an arc discharge method has proven to be a successful means to create novel nanomaterials. The arc discharge method allows for the synthesis of nanoparticles from high melting point bulk materials. During the course of experimentation with early transition metal carbides, it was discovered that varying the reactant gas concentration and the type of reactant gas affects the nanoparticle morphology. By studying how the different early transition metal carbide nanoparticles form with different reactant gas conditions, knowledge of the nanoparticle morphology and surface energy of the facets is gained. Once a solid understanding of how reactant gases affect the formation of early transition metal carbide nanoparticles is acquired, methods can be employed to create nanoparticles with tailored properties.

A description of the experimental process was discussed in Chapter 2. The experimental procedure was described in detail to provide other experimentalists with a guide to how the arc discharge instrument was built and used. The experimental setup was designed such that many experimental parameters may be varied. This freedom to change many parameters allows for different possible environments in the attempt to synthesize the desired products. After the nanoparticles were synthesized they were analyzed by a host of techniques including transmission electron microscope (TEM), selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). The electron microscopy techniques were the most useful analytical tools for these studies. The TEM images yield morphological information about the synthesized nanoparticles. Diffraction patterns display the crystal structure. The EDS spectrum gives elemental analysis of the nanoparticles.

The experiments involving the synthesis of titanium carbide nanoparticles described in Chapter 3 have shown that the nanoparticle morphology can be controlled by changing the methane gas concentration. The cube morphology was preferred with low methane concentrations, and the cuboctahedron morphology was preferred with high methane concentrations. The {111} facet is either stabilized by the methyl free radical or the excess carbon blocks the growth sites on the {111} facet surface.

The niobium carbide experiments in Chapter 4 were the next test to see if the nanoparticle morphology would change with varying methane concentration. The experiments showed that changing in the methane concentration did not change the nanoparticle morphology. The niobium carbide nanoparticles preferred cubic morphology when synthesized with methane. When the reactant gas was changed to ethylene there was an increase in the percentage of cuboctahedron shaped particles. Then when acetylene was used as the reactant gas the cuboctahedron morphology dominated the morphology distribution. The change in morphology is due to the stabilization of the {111} facet on the niobium carbide nanoparticles. It was found that ethylene and acetylene were able to stabilize the {111} facet and increase the number of cuboctahedron shaped nanoparticles.

Chapter 5 dealt with the experiments synthesizing zirconium carbide nanoparticles with methane gas as the reactant gas. It was found that the zirconium carbide nanoparticles preferred a cuboctahedron morphology under all methane concentrations used. This means that the methane free radical is able to stabilize the $\{111\}$ facet under all methane concentrations. Also we investigated a model to calculate surface energies for different facets to see if the calculations trend is the same as the experimental trend that is observed for surface facet energy for different carbides. The calculated trend did follow the experimental observations of the $\{111\}$ surface energy sequence of NbC > TiC > ZrC.

6.2 Future Directions

There are many different experiments that can branch off the work that has been presented in this dissertation. There are a variety of experiments that would be very interesting with just a few changes in the experimental apparatus. One could continue studying the other transition metal carbides to develop conditions required for nanoparticles morphology control. One interesting experiment would be to synthesize mixed metal carbides to see how that affects the nanoparticles morphology. Also, instead of studying carbides, nitrides could be synthesized using ammonia in place of carbon containing gases.

Experiments could be performed that might have more direct applications. The catalytic properties of the nanoparticles could be tested by putting the nanoparticles in a tube furnace attached to a gas analyzer. An array of different catalytic reactions could be

performed to study the effects of varied morphologies, different carbides, and mixed metal carbides. The nanopowders could be used to make high aspect ratio ceramic devices and their mechanical properties could be tested. The nanopowders could also be incorporated into composite materials to increase the materials' strength and durability.

Appendix

Arc Discharge Synthesis of Aluminum Nanoparticles

A.1 Introduction

Metal nanopowders have a broad range of applications such as promoters for sintering in ceramics, catalysis for hydrocarbon conversions, hydrogen production and energetic materials as burning rate accelerators.¹⁻⁵ Aluminum is of particular interest because of its high volumetric heat of oxidization. Another benefit of aluminum is that the byproducts of the combustion process are not toxic or harmful to the environment. High energetic materials need to be dense with low melting and boiling points. These properties are important for quick ignition times and complete combustion. Aluminum has a density of 2.70 g/cm³ with a bulk phase melting point of 933 K and a normal boiling point of 2,792 K. Nanoparticles have the significant benefit that their melting points are lower than bulk melting points due to the higher surface energies of the nanoparticles.⁶⁻¹⁴

There are two main barriers that have kept aluminum from achieving its full potential as an energetic fuel additive. First, aluminum has a high affinity for oxygen. The oxide shell formed around the aluminum core slows the ignition time and requires energy to burn off. The second barrier is being able to synthesize aluminum nanoparticles small enough to fully combust. The smaller the nanoparticle the higher the surface energy is which allows for a faster ignition time.

The synthesis techniques for aluminum nanoparticles include gas condensation, plasma processing, chemical vapor synthesis, sol-gel, rapid quenching, crystallization, and mechanical milling.¹⁴⁻²⁹ In this chapter aluminum particles were synthesized through the arc discharge method with a focus on decreasing the nanoparticle size and ligating the aluminum surface to protect the aluminum surface from oxidizing. In the experiments carbon, iodine, fluorine, and acetonitrile were used to passivate the aluminum surface. Aluminum nanoparticles were synthesized with a size of 100 nm down to less than 1 nm.

A.2 Experimental

The experimental setup is basically the same as described in Chapter 2 with a few modifications. One electrode is made of 1/8 inch 99% pure aluminum wire and the other electrode is either a ¹/₄ inch 99.999% pure aluminum rod or a ¹/₄ inch tungsten rod. Modifications of the arc discharge vessel were made to accommodate the 1/8 inch aluminum wire. The 1/8 inch aluminum wire was used to make it easier to generate the discharge between the electrodes. The arc discharge was run at 180 amps under direct current. High purity helium with a flow rate of 40 sccm was flowed into the vessel during the discharge. The aluminum nanoparticles are entrained in the helium flow and are collected in acetonitrile. In some of the experiments different salts are dissolved in the acetonitrile.

try to attach fluorine or iodine to the surface of the aluminum nanoparticles. The aluminum nanoparticles are then analyzed using transmission electron microscopy (TEM) which is equipped with selected area diffraction and energy-dispersive X-ray spectroscopy capabilities. There were two different TEM instruments were utilized to study the aluminum nanoparticles; the Phillips EM420T microscope is a low resolution microscope with an electron acceleration voltage of 120 KeV, and a JEOL 2010 LaB6 is a high resolution microscope with an electron acceleration voltage of 200 KeV.

A.3 Results and Discussion

Aluminum nanoparticles synthesized with 100% helium and collected in acetonitrile show particles that are 10-50nm in diameter. The aluminum nanoparticles are shown in Figure A-1 and a clearly visible 3-5nm oxide shell is seen around the nanoparticles. The source of oxygen was either dissolved in the acetonitrile or from air exposure incorporated while transporting the sample to the TEM facility. Shown in Figure A-2 is a single particle diffraction pattern of an aluminum nanoparticle that measure 2.34, 2.02, and 1.22. The diffraction pattern matches with bulk aluminum and shows that the aluminum nanoparticles are single crystals.³⁰

In order to try to either eliminate or decrease the thickness of the oxide layer we designed a set of experiments to attach molecules or atoms on the surface of the aluminum particles. We have tried to attach succinic acid, iodine, and fluorine to the surface of the particles. There were also a few modifications made to the experimental setup to help eliminate oxygen contamination. The whole instrumental set-up was put



Figure A-1. TEM image of aluminum nanoparticles with 3-5nm oxide shell collected in acetonitrile.



Figure A-2. Single particle diffraction pattern of an aluminum particle collected in acetonitrile. The diffraction pattern measures 2.34, 2.02, and 1.22 and matches the literatures values for pure aluminum.³⁰



Figure A-3. EDS spectra of aluminum nanoparticles synthesized with pure helium gas and collected in acetonitrile. The copper peaks are from the TEM grid the nanoparticles are deposited on. The small oxygen peak is either from the oxide shell around the aluminum nanoparticle or the TEM grid.

into a nitrogen filled glove bag, and dry acetonitrile was used capture the nanoparticles from the vapor.

The hypothesis was that the acid group of the end of the succinic acid would attach to the surface of the aluminum nanoparticle to form a protective monolayer shell around the nanoparticles. Succinic acid would not easily dissolve in acetonitrile, so water was used instead. The water would probably react with the aluminum surface to form an oxide shell; however the succinic acid might attach quickly enough to the surface to prevent oxidative decay. A 0.03 molar solution of succinic acid was prepared and 20 milliliters was put into the collection bubbler. A TEM image of the synthesized aluminum nanoparticles with succinic acid is shown in figure A-4. The image shows that the oxide shell is still present around the aluminum nanoparticles and that the particles are imbedded in some kind of matrix. We believe that the matrix is either the succinic acid or excess carbon.

We then wanted to see if we could passivate the aluminum surface with a coating of amorphous carbon. A mixture of 12% methane seeded in helium was used as the carbon source. The synthesized nanoparticles were carried in the gas mixture and collected in acetonitrile. The collected solution looked cloudy and light grey in color. TEM analysis of the sample shows that instead of the typical smooth spherical aluminum nanoparticles being formed, 10nm sized particulate looking nanoparticles were formed as are displayed in Figure A-5. Diffraction pattern analysis displayed in Figure A-6 of the nanoparticles gives a ring pattern that matches with Al₄C₃. The EDS spectra from the aluminum carbide nanoparticles is displayed in figure A-7 and shows the presence of



Figure A-4. Aluminum nanoparticles collected in water with succinic acid.



Figure A-5. Al₄C₃ nanoparticles synthesized with 12% methane seeded in helium.



Figure A-6. Selected area diffraction pattern of aluminum carbide nanoparticles collected in acetonitrile. The most intense d-spacings for aluminum carbide is 2.83, 1.67, and 2.25 angstoms.³⁰



Figure A-7. EDS spectra from the Al_4C_3 nanoparticles synthesized with 12% methane. The spectra shows enhanced peak for oxygen and carbon.

aluminum, copper, carbon, and oxygen. It is interesting that there is a higher oxygen peak for Al_4C_3 than there is for the pure aluminum nanoparticles. There was no evidence in the pure aluminum nanoparticles when aluminum is ablated with the presence of carbon. Therefore, it is more energetically favorable to form Al_4C_3 than to form pure aluminum nanoparticles with methane present during the arc discharge event.

In order to try to eliminate the synthesis of other aluminum compounds, ligating atoms or molecules were then only introduced in the collection region. This would allow the aluminum atoms to nucleate and grow into nanoparticles without the presence of an impurity. For the next set of experiments we wanted to see if we could attach fluorine or iodide to the surface of the aluminum nanoparticles. Sodium fluoride or sodium iodide was dissolved in acetonitrile and put in to the collection bubbler. We wanted to attach an atom that is either larger in atomic diameter or has a stronger electron affinity than oxygen. Oxygen has an atomic diameter of 120 picometers and an electron affinity of 141 kilojules per mole.³¹ Fluorine has a smaller atomic diameter of 100 picometers and a larger electron affinity of 328 kilojules per mole.³¹ Iodine is larger in both the atomic diameter and electron affinity than oxygen. For iodine the atomic diameter is 280 picometers and an electron affinity of 295 kilojules per mole.³¹ A 0.125 molar sodium fluoride solution was used to collect and to attach fluorine to the aluminum nanoparticles. A 0.125 molar sodium fluoride solution was produced by dissolving 1.312 grams of sodium fluoride in 250 milliliters of acetonitrile. Figure A-8 shows a TEM image of the collected aluminum nanoparticles. The image displays that the nanoparticles still posses an oxide shell ranging from 3 to 5 nanometers. However the EDS spectra shown in figure A-9 do not show any evidence of fluorine in the sample. There was no evidence



Figure A-8. Aluminum nanoparticles collected in a sodium fluoride solution.



Figure A-9. EDS spectra of aluminum nanoparticles collected in a sodium fluoride solution. No sodium or fluorine peak was seen in the spectra. Contamination was present in the electron microscope; the peaks are from tungsten, iron and cobalt.

of fluorine attaching to the aluminum nanoparticles therefore exposing the nanoparticles surface to oxygen and forming an oxide layer.

The sodium iodide solution was made in the same manner as the sodium fluoride solution. In this case 4.68 grams of sodium iodide was dissolved in 250 milliliters of acetonitrile to form a 0.125 molar solution. The TEM image of the synthesized aluminum nanoparticles in Figure A-10 shows that the oxide shell (3 to 5 nm) is still present. Figure A-11 is the EDS spectrum for the aluminum nanoparticles and does show a small signal for iodine. The presence of the oxide shell on the aluminum nanoparticles shows that the iodine did not attach to the surface and protect the surface from oxygen. The iodine signal in the EDS spectra is probably from sodium iodide residue left after evaporating the acetonitrile off. The iodide is either on the surface of the oxide layer or is on the TEM grid. There is also contamination signal in the spectra coming from tungsten, cobalt and iron. The contamination signal comes from within the electron microscope and not from the aluminum nanoparticle sample.

There was one experimental run where the aluminum nanoparticles were synthesized and collected in acetonitrile that did not show any visible oxide layer. The TEM image is from the high resolution microscope. Figure A-12 shows aluminum nanoparticles that are 20 to 30 nm in size with no visible oxide shell. The high resolution microscope was used after no visible oxide layer could be seen in the low resolution microscope. The hypothesis behind the absence of the oxide shell on the nanoparticles is that the acetonitrile attached to the aluminum surface, and therefore protected the surface from oxygen. The EDS spectrum of the particles does not show any evidence of nitrogen, which would have confirmed the presence of acetonitrile on the surface of the aluminum. Since the acetonitrile is not present in the EDS spectrum then it must be weakly bound to the surface of the particle. There are two possibilities that could cause the acetonitrile to desorb off the surface of the nanoparticles. One possibility is due to the very low vacuum pressures in the transmission electron microscope. The other is that once the particle is in the electron beam, it is heated and therefore possibly causing the acetonitrile to desorb from the aluminum surface.

After the aluminum nanoparticles have been exposed to the high resolution electron beam for approximately fifteen minutes, the nanoparticles start to exhibit beam damage. Figure A-13 shows the same aluminum nanoparticles shown in Figure A-12 after being exposed to the electron beam for more than fifteen minutes. The beam current of 200 KeV is therefore high enough to displace atoms within the aluminum nanoparticles. It is also interesting that the beam damage is not uniform on the nanoparticles. It only etches away certain areas, leaving behind islands that are roughly the same size. Currently it is unknown why only certain areas etch out and the islands are about the same size.

A.4 Conclusions

The arc discharge method was able to synthesize aluminum nanoparticles. The aluminum nanoparticles synthesized were typically 100nm or less. Most experiments that tried to passivate the aluminum nanoparticle surface did not work, and an oxide layer of 3-5 nm layer was visible. However one experimental trial did work and no visible oxide layer was present. The nanoparticles were synthesized with pure helium and

collected in acetonitrile. It is believed that the acetonitrile attached to the surface and protected the aluminum nanoparticle surface from oxidizing. Unfortunately after many attempts to repeat these findings they were not reproducible.



Figure A-10. Aluminum nanoparticles collected in a sodium iodide solution.



Figure A-11. EDS spectra of aluminum nanoparticles collected in a sodium iodide solution. Sodium and iodine peaks are seen in the spectra. Contamination was present in the electron microscope; the peaks are from tungsten, iron, and cobalt.



Figure A-12. Aluminum nanoparticles collected in acetonitrile without a visible oxide shell.



Figure A-13. TEM image of aluminum nanoparticles after being exposed for fifteen minutes by 200 KeV electron beam.

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Figure A-13. TEM image of aluminum

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