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Advanced ceramics and composites based on rice hulls

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ADVANCED CERAMICS AND COMPOSITES BASED ON RICE HULLS

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirement for the degree of
Doctor of Philosophy
in
The Department of Mechanical Engineering

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May, 2012
DEDICATION

To my parents
ACKNOWLEDGEMENTS

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ABSTRACT

As a by-product of the agricultural industry, rice hulls are available at large volume across the world. The disposal of the rice hulls itself is a big problem for the rice millers where the rice paddies are peeled off and rice hulls are produced. There have been many disposal methods developed, but the true value of the rice hulls would be more appreciated when they are employed to produce high value-added advanced ceramics.

In this dissertation, advanced ceramics, such as AlN nanowires, SiC whiskers, mullite and SiC/Al₂O₃ nano-sized composites, were developed and studied based on the rice hulls. The SiC whiskers and AlN fibers were successfully prepared at high yield in a process (patent pending) developed by the author. Since the one-dimensional ceramic materials are valuable raw materials for many industrial applications, the study presented in this dissertation is particularly valuable. During the development of the one-dimensional ceramics, some unique morphology, such as the beaded SiC whiskers were also prepared and investigated.

Some potential applications of the prepared ceramics were investigated, such as the application of SiC whiskers as a heat transfer enhancement agent, and the application of beaded SiC whiskers as the reinforcement phase in composites. The heat transfer enhancement by SiC whiskers in a convective flow is promising: an enhancement as high as 27% was achieved by a dispersion of SiC (0.16 wt % in water) at low temperature (300-330 K). The beaded SiC whiskers are confirmed to be an efficient reinforcement phase for plastic-matrix composites, because their special structures would render them a new interlocking mechanism to obtain a much more reliable coupling with the matrix in a composite.
CHAPTER 1. INTRODUCTION TO THE CURRENT CERAMIC FABRICATION FROM RICE HULLS

1.1 An Introduction to the Rice Hulls - a Major Agricultural Waste

1.1.1 The Paddy Production across the World

The rice plant is a grass which can grow to over 1 m tall or to 5 m long in deep water, shown in Figure 1.1. Rice is known to have been domesticated as early as the fifth millennium B.C., and has developed the four major types of rice which grow worldwide: Indica rice, Japonica rice, Aromatic rice and Glutinous rice.\textsuperscript{1} It is normally harvested as an annual plant.

![Figure 1.1 Rice plants](image)

As an important source of food for a large proportion of the human population on the planet, rice is grown on every continent except Antarctica and covers nearly 1% of the planet’s surface. The world paddy gross production was 661.3 million tons in 2008,\textsuperscript{2} and the production is still increasing yearly. From the paddy distribution data for different continents, shown in
Figure 1.2 and Figure 1.3, it is clear that the major production area is in Asia. The paddy production in USA is not as high as some eastern Asian countries, but it is intensively located primarily in the six states: Arkansas, California, Louisiana, Missouri and Mississippi. Based on the data provided by the USA Rice Federation, the total planting area in the six states is over 4 million acres, and Louisiana rice is ranked 2nd in the nation, shown in Figure 1.4.

![Figure 1.2 paddy production by continents](image1.png)

![Figure 1.3 Paddy production by countries](image2.png)

![Figure 1.4 Paddy production by states in USA](image3.png)
To protect the seed during the growing season from the harsh environment, rice hulls, in the form of a hard cover, are formed outside of the seeds. The hulls consist of hard materials, including hydro-form silica, opaline, lignin and so on. The hulls are too hard for human to digest, so before bringing them to the kitchens, the outer shell of paddy must be removed in a mill.

1.1.2 Rice Hulls Produced in the Milling Process

In the milling step of rice industry, a mechanized process is applied to deal with the harvested paddies. At a mill, the harvested raw rice paddies pass through "sheller" machines to remove their inedible hulls. This process yields brown rice with the bran layers surrounding the kernel still intact. Brown rice can be used as it is, or further milled by machines that rub the grains together under pressure. This abrasion process removes the bran layer to obtain the white whole kernels of rice which is directly used in a kitchen.

In small mills, typically found in developing countries, the husk plus bran weigh approximately 25% of the paddy, because the bran (the layer within the husk) is not fully separated from the husk. For larger mills, the husk and bran can be fully separated, thus the husk to paddy ratio is appropriate 20%, which means the total amount of rice hulls is approximately 150 million tons annually in the world.

1.2 Disposal Methods of Rice Hulls and the Pertaining Problems

The large volume of rice hulls coming out every year brings a significant issue: how to dispose these agricultural wastes?

Originally, the rice hulls were simply often disposed as agricultural wastes in landfills. With the science and technology progresses, more disposal methods have been developed and more value of the rice hulls has been recognized. Currently, even more research is still under
conduction to take advantages of the rice hulls. And rice hulls have found applications in multi
industrial sectors: farmers use the rice hulls as compost since they are organic materials and can
provide minerals and nutrient substance to grow new paddies, so they may compensate the soil
back; in some biomass power plants, they are used as fuels; in the chemical industrial, rice hull
can be used to produce meso-porous molecular sieves, which are employed as catalysts for
various chemical reactions, as a support for drug delivery system and as adsorbent in waste water
treatment. 5–6 Rice hulls do burn, but with much difficulty, so they are exploited as building
materials which would retard fire, and insulate heat and moistures as well.7 After burning, the
white ash is left and it primarily consists of amorphous silica, so the rice hull ash could be used
as a silicon source for many purposes, such as fillers in composite materials, production of SiC
ceramic etc. There are some other usages reported,8 such as pillow stuffing, pet food additives,
brewing agent, press aid in juice extraction, etc.

Many current rice hull disposal methods underuse the rice hulls, so the goal of this study is
to develop more value added processes for the rice hull utilization. One of the advanced
applications is for SiC production. SiC is a promising ceramic material, and it has very broad
applications in the modern industry. The preparation of advance SiC ceramic from rice hulls will
be a most important topic in this dissertation.

1.3 The Application for SiC Production

The structure for rice hull is a kind of composites, arranging several components into a
special structure, including opaline, silica and lignin, to protect the inner seeds during growing.
The hardness of the husks is dependent on the silica in them. The very high content (SiO₂ ~ 20
wt %) of silica in hydration form in the hulls confer to them many valuable properties.
Table 1.1 Chemical composition of typical rice hulls ash

<table>
<thead>
<tr>
<th>item</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>TiO₂</th>
<th>SO₃</th>
<th>Loss on ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>90.7</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
<td>0.1</td>
<td>2.2</td>
<td>0.4</td>
<td>0.03</td>
<td>0.1</td>
<td>4.8</td>
<td></td>
</tr>
</tbody>
</table>

The Table 1.1 lists the typical composition of rice hull ash. Silica, the major component in the ash is very fine, which means it has a large surface, thus possesses high activity when involving a chemical reaction. On the other hand, the major raw materials to produce silicon carbide, an advanced ceramic, are silica and carbon element. By Acheson process, SiC has been produced from quartz and petrol coke in open furnaces for more than 100 year. Since the silica in rice hull ash has a fine size and comes with the organic (rich in carbon element), it is an ideal source for the SiC production by carbothermal reduction.

1.4 Literature Reviewing of the Current Research on the Rice Hulls

Since Lee and Cutler\(^{10}\) firstly reported the synthesis of silicon carbide from rice hulls in 1975, the research on this topic has been very active.

Krishnarao et al has published a series work on the formation of SiC from rice husks. Effect of acid treatment on the formation of SiC whiskers was studied by Krishnarao et al,\(^{11}\) and in the study, raw rice husks had been treated by boiling in hydrochloric acid. The boiled rice husks were then directly pyrolysed (without precoking) in argon atmosphere at temperatures of 1350 to 1900 K. With a control of pyrolysis of untreated raw rice husks, it is found that the acid-treated raw rice husks produced more pure and white silica than the untreated control; the silica and carbon from the treated rice husks have lower crystallization degree than untreated husks; the SiC whisker yield is lower for treated husks than the untreated ones; treatment decreased the residual carbon in the final products. Temperature profile and catalysts were also investigated by
Krishnarao et al.\textsuperscript{12} They found that cobalt accelerates the formation of SiC yield in rice husk silica-carbon black mixture. Rapid heating, in the presence of cobalt catalyst, increases the yield of SiC whiskers, while without any catalyst, rapid heating results in the formation of SiC particulates. More other process parameters were studied as well, such as pre-coking, chamber pressure, highest temperature during pyrolysis etc.\textsuperscript{13, 14}

The focus of the research had been directed to the overall yield of SiC and redirected to increasing the whisker yield shortly after the SiC formation was realized. Bhat et al\textsuperscript{15} reported that lower temperatures increases the whisker yield and the whiskers coarsen with longer duration of conversion. Sujirote and Leangsuwan\textsuperscript{16} identified the three stages in the pyrolysis of rice husks: organic decomposition, transformation of silica and condensed organic/graphite, and silicon carbide formation. The C/Si ratio of coked rice husks and raw rice husks was compared in the research and the effect of pretreatment with iron was found to increase the beta-SiC whisker formation.

Although the inherited impurities (Ca, Mg, Fe, Al, K, Na, etc) in rice hulls were found to function as catalysts when the pyrolysis of rice hulls happens, much work has been done to investigate the effect of catalyst addition from external sources. Generally, metals (elements, oxides or hydroxides) are selected to be the external catalysts. Patel and Karera\textsuperscript{17} reported the role of metals (Iron, Cobalt, palladium, Nickel) in the pyrolysis of the rice husks and found that at elevated temperatures the role of catalysts and the reaction mechanism involved in the formation of whiskers are very complex. In the view of this paper, the metals may prompt the reaction between SiO\textsubscript{2} and carbon. Therefore they enhance the formation of SiC. However, the yields with presence of catalysts were not evidently better than that without catalysts.
Besides the metal oxides catalysts, the effectiveness of sodium silicate as a catalyst on maximization of SiC yield was also discussed with the pyrolysis temperature and atmosphere by Janghorban and Tazesh.\textsuperscript{18} It found that multistep pyrolysis to 1650 K produced slightly more SiC whiskers at a cost of reducing the total SiC. The concentration of the catalyst and soaking time are crucial parameters for increasing the SiC yield: soaking in dilute solution of sodium silicate enhanced the formation of SiC whiskers and particles; and a shorter time resulted in a higher yield of SiC.

The formation mechanisms and the general reaction environment for the preparation of SiC from rice hulls have been established so far. However, the major issue left is the relatively low yield of SiC whiskers. Although some work shows that the addition of external catalysts increase the yield of SiC whiskers, the impurity introduced by the addition of catalysts is a major drawback to the improvement, and the catalysts would result in the cost inflation as well.

1.5 Motivation and Goals:

The new technologies developed in the past two decades have been avoiding the underusing of the rice hulls and been finding the true value of the rice hulls. One of the major applications is employed as the raw materials for SiC production, and in several decades, the basic work for the production of SiC from rice hulls has been conducted well. However, some significant issues blocking the commercial event are still unsolved, such as the high pyrolysis temperature, the need for addition of catalysts, and the low yield of SiC whiskers, etc. The realization of high quality SiC whisker yield is most important among them. In this dissertation, new routes will be explored to increase the yield of SiC whiskers as well as improving the purity of the final SiC whisker product. And the final goal is directed to develop an economic process...
to produce high quality SiC whiskers from rice hulls at large scale to meet the industrial demands. New applications of the SiC whiskers will be demonstrated, such as the heat transfer fluid enhancement agent, and the usage of the beaded SiC whiskers as reinforcement phase in composites by a new mechanism.

On the other hand, although some other applications of rice hulls or silica derived from rice hulls have been mentioned and started, the work about recycling the rice hulls intensively falls into the SiC production. As a matter of fact, the white ash of rice hulls is primarily silica, with a 95% or higher purity, which would be used as substitutive where the silica is employed across a broad application spectrum, such as for the industrial production of refractory materials, such as Al$_2$O$_3$/SiC composites. So this research also seeks to broaden the application for rice hulls. Besides the SiC ceramic preparation, more applications of rice hulls were exploited in the dissertation. SiC/Al$_2$O$_3$ composites and mullite are prepared by using rice hulls as raw materials. Thanks to the catalyst effect of the impurities in the rice bran, it was employed as dispersant agent as well as catalyst donors for the preparation of aluminum nitrides by direct nitridation, and the growth mechanism was investigated.

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CHAPTER 2. THE PRETREATMENT OF RICE HULLS AND CHARACTERIZATION

2.1 Purification Treatment of Rice Hulls

Rice hulls are the coating for protecting the seeds of rice plant from exposing to open environment during their growth. Because of the rough surfaces of the rice hulls, mud is usually adhesive to the surfaces. To maximize the purity of the final products, it is necessary to remove the impurities from the beginning. Because mud is usually physically adhesive to the surfaces, it can be cleaned easily. Usually, washing the hulls in water can successfully remove the mechanical impurities.

After washing in tap water, the rice hulls were dried in open air or under sunshine; sometimes in an oven at 380 K, it accelerates the drying process. The dried rice hulls are pale yellow and tens millimeters long, shown in Figure 2.1. The thin flake of husks has an arc-like shape with a length of around 8 mm and around 3 mm in width.

Figure 2.1 the digital image of raw rice hulls
Besides the washing treatment using water, some researchers further treated the rice hulls using acids, such as hydrochloric acids, sulphuric acid, phosphoric acid, boric acid, organic acids. The acids washing process was carried out either at room temperature or at elevated temperatures (boiled in acids). The major enhancement obtained by acids treatment is the better purity. It is reasonable to believe that the metallic ingredients can be effectively removed during the leaching process since most metals and metal oxides (rice hulls may include, shown in Table 1.1) are reactive with acids. Some other effects from acid treatment were reported, such as improved reactivity, larger surface area and pore volume.

The acid treatments resulted in rice hulls with lower impurities, and thus it would produce purer final products. However, the treatment is not environmentally friendly since the acids are involved in the process. Moreover, it inevitably triggers the cost inflation which may pose a barrier to commercialize the technology. Fortunately, for industrial purpose, the impurity level in the rice hulls without acid treatment is acceptable. Especially, when the rice hulls are employed to produce silicon carbide for industrial purpose, the inherited impurities from rice hulls are not a major issue to concern.

2.2 Thermal Pretreatment of the Rice Hulls

2.2.1 Thermal Destruction of Rice Hulls

Usually, before pyrolysis, a preheating process is applied to raw rice hulls, although there are some literatures in which the raw rice hulls were directly pyrolyzed without any precoking treatment. Researchers expected to simplify the pyrolysis process and explore different results by direct pyrolyzing the raw rice hulls, however, some other problems emerge with direct pyrolysis of raw rice hulls, such as the large volume of the raw rice hulls, the water vapor
emitted from the decomposing of cellulose in raw rice hulls, and so on. The high temperature pyrolysis to produce silicon carbide requires inert atmosphere to protect oxidation of the reactants and the final products, so the compacter the raw materials, the easier the process is implemented. Also, the water vapor from the decomposing of the cellulose would harm the pyrolysis furnace system. Another important fact is the ratio of carbon versus silicon in raw rice hulls is not optimized for SiC formation when the raw rice hulls are pyrolyzed directly.

All the problems existing in the direct pyrolysis of raw rice hulls may be overcome by preheating treatment of the raw rice hulls, and no evident data has confirmed direct pyrolysis of raw rice hulls is superior. Usually after the washed rice hulls are dried at 380 K, the preheating of dried raw rice hulls carries out at the temperature range of 500 K to 1000 K in a certain atmosphere, depending on the kind of ash expected.

The thermal destruction of rice hulls in different environments was investigated by several investigators.\textsuperscript{9,10,11} And it is generally accepted that the thermal event of rice hulls has three stages: dying (310 – 420 K), removal of volatile organic components (485 – 620 K) and burning of carbon (620- 960 K).\textsuperscript{12} Markovska et al\textsuperscript{10} reported the thermal destruction of rice hulls in air and nitrogen atmosphere at different temperatures in details and they concluded that the thermal destruction of rice hulls in air initialized at 490 K and completed at 910 K and in nitrogen atmosphere the two temperature points shifted to 510 K and 940 K, respectively. The crystallization of amorphous silica in rice hulls ash started at 1120 K and the silica directly transformed to its high-temperature modification, α- cristobalite.
2.2.2 Preparing Black Ash

The raw rice hulls used in this project was provided by Three H’s, LLC (Crossett AR, USA). The as-received rice hulls were washed and dried at 380 K and then coked in a sealed tube at 670 K, holding for 60 minutes to prepare the black ash (BA). After soaking at 670 K for 60 minutes, the weight of the products would not change anymore and the color was black (the color of carbon). The coked black rice hulls shrunk significantly, and the coked hulls had two major compositions: carbon and silica. The digital image taken for the coked hulls is shown in Figure 2.2.

![Black Ash](image)

Figure 2.2 BA obtained by soaking at 670 K in a sealed tube

2.2.3 Preparing White Ash

To deplete carbon element in the rice hull ash, the rice hulls were coked in air at 830 K. The coking process lasted for around 30 minutes (the time duration depends on the feed of oxygen) until the weight of the ash stayed constant. At the end, the color of ash turned white and the particles became very small (less than 1 mm) and were apt to become smaller under squeezing.
Because of the white color (color of amorphous silica), the ash is called white ash (WA), shown in Figure 2.3.

![Figure 2.3 WA obtained by treatment in air at 830 K](image)

WA is mainly silica, since the organics in raw rice hulls has reacted with the oxygen and gone as gas state. It is recommended to handle the WA in a fume hood because the tiny particles have very small specific gravity and therefore are airborne easily which may be a health hazard.

### 2.3 Characterization of the Rice Hulls and Ashes

#### 2.3.1 Major Composition in the Rice Hull Ash

To determine the composition of the BA and WA, the weight loss of BA in air at 830 K was conducted and XPS (X-ray Photoelectron Spectroscopy) examination of WA was carried out.

Assuming that the weight loss of BA during heating in air is mainly attributed to the oxidation of carbon, based on the weight change during the coking process, the carbon accounts for 56 wt% in BA and the silica and other minor impurities (oxides) which are not volatilize at
high temperature contribute the balance, 44 wt%. The specific composition of WA determined by XPS is listed in the later part of this chapter.

2.3.2 SEM Observation of the Size and Morphologies of Rice Hulls and Ashes

The rice hulls are organic matters filled with super fine silica which is in a hydrated amorphous form to provide the rice seeds inside with a reliable protection from the harsh environment. There are two evident layers consisting of the rice hull. The outer layer has protuberances and the inner surface is smooth, Figure 2.4. Silica is presented intensively in the protuberances on the outer surface of the hulls, whereas, the inner surface of rice hulls is almost free of silica.

The protuberances on the outer surface have a diameter of around 60 microns, and the silica is located inside the protuberances, Figure 2.5. The silica particles are much smaller than the protuberances, and their size is of tens of nanometers scale.

![SEM images of inner and outer surface of a raw rice hull](image)

Figure 2.4 SEM images of inner and outer surface of a raw rice hull
Figure 2.5 SEM images of outer surface of a the rice hull

The SEM observation for WA were also conducted, Figure 2.6. The WA is mainly silica (90 wt% or higher), and it has porous structure and apt to become finer powders. The clusters are very small, at tens of microns and the clusters include sub-particles of silica.

Figure 2.6 SEM images of crushed WA
2.3.3 XRD Analysis for Black Ash and White Ash

The XRD patterns of the ashes were performed by an X-ray diffractometer (MiniFlex XRD, Rigaku Corporation, Japan) with Ni-filtered Cu Kα radiation (λ=1.54178 Å). The results are shown by Figure 2.7. The XRD patterns for BA and WA are very similar, and they do not contain any sharp peaks which are a feature for the existence of crystal phase in the specimen, which means the heat treatment did not make the amorphous silica and carbon in the rice hulls crystalize. The retaining of the amorphous silica and carbon ensures that during the heat treatment, the particles of silica in the rice hulls did not grow and the high energy state of the silica is also retained.

![XRD pattern from rice ash](image)

Figure 2.7 A typical XRD pattern from rice ash

2.3.4 XPS Analysis of the White Ash

The chemical composition of the WA was detected and analyzed by X-ray Photoelectron Spectroscopy (XPS). And the results are shown in the following Table 2.1; the main constituent
in the white ash is amorphous silica, and the trace impurities include K$_2$O, MgO, CaO, Fe$_2$O$_3$, Al$_2$O$_3$, P$_2$O$_5$, etc.

Table 2.1 The chemical composition of the WA used in this dissertation

<table>
<thead>
<tr>
<th>Species</th>
<th>SiO$_2$</th>
<th>K$_2$O</th>
<th>MgO</th>
<th>P$_2$O$_5$</th>
<th>Na$_2$O</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>Al$_2$O$_3$</th>
<th>TiO$_2$, SO$_3$, Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage</td>
<td>92.6</td>
<td>2.3</td>
<td>0.6</td>
<td>0.5</td>
<td>0.2</td>
<td>0.4</td>
<td>0.5</td>
<td>0.3</td>
<td>balance</td>
</tr>
</tbody>
</table>

2.4 Discussion and Conclusion

The raw rice hulls would result in black ash or white ash by different heat treatment programs. The carbon and silica constitute BA and the WA is rich in amorphous silica (concentration more than 90%), with some oxides impurities; the size of the silica particles is at nanometer-scale which is a big advantage for synthesis of SiC; the trace oxide impurities in it would play a catalyst role when the ashes are employed to prepare silicon carbide in the next step.

2.5 References


CHAPTER 3. SYNTHESIS OF SILICON CARBIDE WHISKERS AND THE APPLICATIONS

3.1 Introduction

3.1.1 SiC Whiskers

Because of its excellent properties (high Young’s modulus, high strength at elevated temperature, low density, corrosion durability, high chemical stability, high thermal shock resistance), silicon carbide is a promising material for broad applications. Silicon carbide exists in hundreds of crystalline forms, and it is available in a variety of morphology: including particulate, whisker, fiber, cloth, and bulk forms. Different forms can be further optimized to enhance the intrinsic advantages of SiC for diverse industrial applications. β-SiC (with a zinc blende crystal structure) whiskers have high specific strength, high elastic modulus, high thermal conductivity, good chemical stability and good response to microwave. They have received considerable attentions from both academic and industrial communities. The focus of this research is the synthesis of SiC whiskers and the applications to heat transfer fluids and reinforcement phase in composites.

Many methods have been reported to prepare 1D β-SiC structures. Several forms of 1D Silicon carbide nanostructures were gown in a SiO(g)-CO system, where the partial pressures of the species, SiO(g) and CO(g), were important to control the morphology of the SiC products;\textsuperscript{1,2,3,4,5} silica xerogel was employed to prepare 1D silicon carbide nanostructures by carbothermal reduction;\textsuperscript{6} SiC nanorods and whiskers were reported by thermal decomposition and pyrolysis of

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organic silicon in the presence of certain catalysts;\textsuperscript{7, 8} SiC nanorods were realized by a carbon nanotube template and explained as shape memory synthesis.\textsuperscript{9} Most methods stated in the literatures above are based on the gas phase reaction by either a Vapor-Solid (VS) mechanism or a Vapor-Liquid-Solid (VLS) mechanism. The major issues relating to the failure of reaching a commercialized process are the high cost, poor purity, and low whiskers yield. The raw materials employed in some of the reported routes are expensive and not very readily available; some methods require the selection and employment of complex metal-based catalysts (such as rare-earth metals) to increase the yield of SiC whiskers; consequently, the catalysts themselves are cost-increasing factors and make the method expensive. Since the first report\textsuperscript{10} on the preparation of SiC from rice hulls (agricultural waste available in large scale), there has been a continuous research effort extended in this field, to take advantage of this abundant renewable resource. A better utilization of rice hulls may also pave the way to resolve the disposal problems for farmers and supply advanced ceramics to industrial sectors at low cost. However, the reaction between the intrinsic carbon and silica from rice hulls has the tendency to produce primarily particulate SiC other than whiskers. With the existence of morphologies other than whiskers in the final product, such as irregularly shaped particles, separation of whiskers out of the product is necessary; however, the separation process is usually difficult, time-consuming and incomplete, which therefore brings the cost inflation. In this research, short carbon fibers were screened out of other forms of carbon elements (such as the intrinsic carbon in the rice hulls), to provide carbon source in the thermal reduction of the silica inherited from rice hulls to produce SiC nano whiskers.
3.1.2 Nano-Fluids for Heat Transfer Enhancement

The topics of foreign solid object addition into fluid for heat transfer application have been studied for more than 150 years.\textsuperscript{11} Objects with different sizes can be mixed with a solution to increase the overall thermal conductivity of the suspension. Over the last decade, there has been an exponential increase in Science Citation Index (SCI) publications on the study of nano-fluids, where nano-particles are added to the base fluids.\textsuperscript{12,13,14} By adding up to 4.3 vol\% of nano-particles, a 30\% increase in thermal conductivity has been reported.\textsuperscript{15} A recent study\textsuperscript{16} showed that SiC/water nano-fluid resulted in no particle settling, long term stability, and little agglomeration. Most of the additions in the previous studies are of the spherical shape. Research indicates that the shape of the added nano-particles plays an important role in the level of heat transfer enhancement. Hideo’s group\textsuperscript{17} demonstrated the pulp fibers in paper industry could improve the heat transfer in laminar flow. Under similar conditions, the enhancement of heat transfer coefficient is much higher for the usage of carbon nano-tubes (CNT), whose aspect ratio is >>1,\textsuperscript{18} than that for disc-shaped TiO\textsubscript{2} nano-fluids,\textsuperscript{19} whose aspect ratio is <1. A recent publication by the Stanford University group\textsuperscript{20} shows that only the long aspect ratio CNT-based nano-fluids are promising for micro-fluidic heat exchangers. Due to the large aspect ratio, the thermal conductivity of the CNT nano-fluids increases significantly. However, CNT nano-fluids can cause a clogging problem as well as an abrasion problem in the micro-channel heat exchanger because of the entanglement of CNTs and the formation of large clusters in the base fluid.

The current study in this dissertation is to form SiC whiskers and to demonstrate the improvement of heat transfer. Unlike metallic nano materials, SiC is a ceramic material thus not susceptible to oxidation/corrosion which can lead to degradation. The straight and rigid micro-
sized whiskers are much easier to mix with the base fluid thus avoiding the problem of entanglement; its chemical stability over long period of time and under high working temperature is significantly better than that of metals and CNTs; Also SiC has one of the highest bulk thermal conductivity (300-400 W/Km)\textsuperscript{21} among ceramics. This thermal conductivity value is more than two orders of magnitude larger than that of water (0.6 W/Km).

### 3.1.3 Beaded Whiskers Enhancement of Reinforcement for Composites

The novel silicon carbide structures, beaded SiC whiskers, have drawn interests from researchers, and much work about the synthesis of beaded SiC whiskers and their properties has been done over the decade.\textsuperscript{22, 23, 24, 25} It is found that the unique structure makes the beaded whiskers a promising function material and have a broad applications. Meng’s group reported the synthesis of SiC nano-chains and their Raman/Photoluminescence properties.\textsuperscript{23} The beaded whiskers was prepared by Hao’s group from the carbothermal reduction of a carbonaceous silica xerogel with cetyltrimethylammonium bromide and lanthanum nitrates as catalyst and the whiskers’ enhancement of reinforcement effect to composites was also evaluated by this group\textsuperscript{24}. It is found that the beaded whisker is more effective to reinforce composites compared with the same amount of smooth whiskers.

In this dissertation, a simple method was developed to prepare beaded Si whiskers at low cost by employing rice hull ashes as raw materials. The mechanism of the formation of the beaded SiC was discussed and the application of effective reinforcement phase in composite of the as-prepared beaded SiC was demonstrated as well. The result confirmed that the beaded SiC whiskers are more effective to reinforce the composites compared with its smooth counterpart due to their unique morphologies.
3.2 Experimental Procedure

3.2.1 Raw Materials

Rice hulls, an agricultural waste available at very large scale across the world, contain 15 ~ 20 wt% of silica. The raw rice hulls used in this project were provided by Three H’s, LLC, Crossett, AR, USA.

![Figure 3.1 raw materials, white ash (left), carbon fibers (right)](image)

The as-received raw rice hulls were washed using distilled water to remove mechanical impurities. It is reported that the thermal destruction of rice hulls involves three phases: 26 drying, 310 K ~ 420 K; removal of volatile organic components, 485 K ~ 620 K; and burning of carbon, 620 K ~ 960 K. According to the procedures stated in the previous chapter, the washed rice hulls were preheated. The resultant white ash contains around 92.6 wt% silica and a small proportion of oxides impurities (K₂O, Al₂O₃, CaO, MgO, P₂O₅ etc.), 27, 28 since the organic matters in the raw rice hulls decomposed and pyrolytic carbon from rice hulls had reacted with the oxygen in the air, shown in Figure 3.1 (left). The carbon fibers were purchased from HEXCLE and the diameter is around 5 microns, Figure 3.1 (right).
3.2.2 Preparation of SiC Whiskers

Carbon fibers and white ashes from rice hulls are the carbon source and silicon source to manufacture SiC whiskers, respectively. White ash and carbon fibers, at predefined molar ratios, were milled together to form a homogeneous mixture by ball milling. The typical milling time is several minutes, depending on the mass of the mixture and the mass ratio of the mixture and the balls.

![Electric tube furnace and accessories](image)

Figure 3.2 The electric tube furnace and its accessories (gas tanks and a vacuum pump)

After milling, the mixtures were placed in ceramic crucibles and then the crucibles were heated in a conventional electric tube furnace (a horizontal alumina tube, L: 1000mm; D: 80mm), Figure 3.2. Before heating up, the furnace was purged several times using argon to obtain an inert atmosphere. Then the samples underwent the temperature profile shown in Figure 3.3: heating to 1500 °C (the ramp was 10 °C/min under 1000 °C and 5 °C/min above 1000°C) in a slowly flowing argon atmosphere (30 SCCM), holding at highest temperature for 60 minutes.
Finally, the furnace was programmed to cool down to room temperature at 10 °C/min. During the reaction process, a constant argon flow (at a typical rate of 30 SCCM) was kept to protect the samples from oxidation. To remove the residual carbon in the as-prepared product, it was burned out in air at 700 °C for one hour.

![Temperature profile to prepare SiC](image)

**Figure 3.3** The temperature profile to prepare SiC

### 3.2.3 Characterization of the SiC Whiskers

X-ray diffraction (XRD) measurements were performed using a X-ray diffractometer (MiniFlex XRD, Rigaku Corporation, Japan) with Ni-filtered Cu Kα radiation (λ=1.54178 Å). For all samples, XRD spectra were obtained by scanning at a speed of 2 °/min and step width of 0.02°. The microstructural morphology of the final products was observed by field emission scanning electron microscopy (FESEM) (Model Quanta 3D FEG, FEI Company, USA).

### 3.2.4 Heat Transfer Performance Testing

The prepared SiC whiskers were mixed into water with a concentration of 0.013wt%, 0.04 wt%, 0.08 wt%, 0.12 wt%, 0.16 wt%, 0.2 wt%, and 0.24 wt% respectively. All the SiC-water
mixtures were dispersed by an ultrasonic device (Hielscher, UP100H, 240W) for more than 40 minutes before the heat transfer experiments. The resultant dispersion mixtures (Figure 3.4) are uniform and stable during the test process.

Figure 3.4 The dispersions of different SiC contains (decrease of concentration from left to right)

The experiment setup was built up in the lab and schematically shown in Figure 3.5. A copper block (2 inch in length, 1.5 inch in diameter) was used to provide a stable solid temperature. A 1.5 mm diameter flow channel through the center of the copper block was connected with two linked syringes. Before the test, one syringe was filled with the heat transfer fluid (either pure water or SiC laden water) of room temperature and the second syringe was empty. The copper cylinder was immersed in a hot water bath with an adjustable initial temperature. The connecting tubes between copper and syringes are flexible tube of 1.5 mm inner diameter. Three rubber-air insulation sleeves were used along the connecting tubes to minimize the heat flux from the water bath to the testing fluid. A step motor drove the link which
synchronizes the two syringes (at constant fluid volume rate for both syringes). A displacement sensor logged the speed data of the syringes. Two K-type thermocouples were used to measure the water temperatures entering/leaving the copper block, while a third thermocouple was used to measure the copper block temperature.

Figure 3.5 Experiment setup for the heat transfer performance of SiC laden water
1. computer; 2. displacement sensor; 3. step-motor with links for synchronizing the two syringes; 4. syringes and 3-layered insulating tubes, connecting the copper block; 5. water bath covered by an insulation cover plate. Copper block with thermal couples and a magnetic stirrer are immersed in it; 6. magnetic stirring and heating plate; 7. data acquisition unit

For each testing, the water bath/copper’s initial temperature was set to be 60±0.5°C. Then the SiC/water dispersion inside the syringes was driven through the copper block at a constant speed (by fixing the power input to the motor). The heating to the flow inside the copper block was recorded by the thermocouples. A 1.5-minute waiting time was applied to allow the copper cylinder retrieve homogeneous temperature before the fluid was cycled in between the two syringes. Five cycles were applied for all tests. At least 3 tests were conducted for each SiC concentration group. The heat transfer coefficient could be found by the following equation:
\[ \dot{m}C_p dT = hA (\text{logmean}T) \rightarrow h = \frac{\dot{m}C_p}{A} \frac{dT}{(\text{logmean}T)}; \]

\[ dT = |T_A - T_B|; \quad T_A = T_w - T_1; \quad T_B = T_w - T_2; \quad \text{logmean}T = \frac{T_A - T_B}{\ln(T_A/T_B)}; \]

Where \( \dot{m} \) is the mass flow rate; \( C_p \) is specific heat; \( A \) is surface area; \( T_w \) is wall temperature measured from the copper cylinder; \( T_1 \) and \( T_2 \) are the temperatures at the inlet/outlet of the copper block respectively. The heat transfer coefficient \( h \) is proportional to the slope of \( dT / (\text{logmean}T) \). Under a fixed flow speed, the slope of \( dT / (\text{logmean}T) \) would physically represent the overall heat transfer coefficient between the copper block and the SiC-water mixture.

### 3.2.5 Beaded SiC Whiskers as Reinforcement Phase in Composites

The work was carried out by plastic composite (epoxy as the matrix phase), and the efficiency of reinforcement of beaded whisker was tested and compared with that of traditional SiC whiskers. The samples were designed according to Standard Test Method for Tensile Properties of Plastics (D 638 – 03), as shown in Figure 3.6.

![Figure 3.6](image)

Figure 3.6 The standards for preparation of tensile test samples
To prepare the tensile test samples, the beaded whiskers and epoxy resin were mixed together by the aid of ultrasonic. Then the slurry was cast into a mold, so that the samples were obtained, the whole procedures were shown in Figure 3.7. Three groups of samples were prepared to conduct comparison experiments: one group was fabricated by blank epoxy; the second group was the epoxy matrix reinforced with smooth SiC whiskers and the third one was the epoxy reinforced with the synthesized beaded SiC whiskers. Finally, the tensile tests were conducted on the 810 Material Test System.

![Figure 3.7 The procedure of the tensile test](image)

### 3.3 Results and Discussion

#### 3.3.1 XRD Patterns of the SiC Whiskers

Figure 3.8 shows a typical XRD pattern for the SiC products after depleting the residual carbon fibers. According to the XRD data, the obtained product is β-SiC (cubic, space group F-43m (216)), whose crystal structure is shown in the inset of Figure 3.8. The calculated lattice parameters based on the XPD data is 4.359 Å, which is in good agreement with JCPDS card: No. 29-1129. The silica in rice hulls is amorphous and in the prevalent form of silica gel, but when
the temperature goes higher than 1200 °C, it crystallizes easily; however, there is no any peak which is indexed to any crystal structure of silicon oxide in the XRD pattern of the final product, which means the primary phase in the product is SiC and there is no major residual silica left. The carbothermal reduction was complete by holding the raw mixtures at 1500 °C for an hour.

Figure 3.8 XRD pattern for the β-SiC products (after burning out the residual carbon)

3.3.2 Morphology Observation and the Formation Mechanism

3.3.2.1 Two Morphologies of SiC Whiskers

The high yield of the SiC whiskers was confirmed by the SEM images, shown in Figure 3.9. In the SEM image of the as-synthesized SiC (Figure 3.9 (A), (B)), there were residual carbon fibers with a large diameter of around 6 microns and their surfaces changed by attacking from SiO/CO during the reaction. Part of the surface of residual carbon fibers was coated by SiC, which will be elaborated later. The SiC whiskers were located in the gaps between carbon fibers and the whiskers possessed a diameter of around 300 nm and a length of tens of micrometers.
After heating one hour in air, the residual carbon fiber disappeared and the SiC whiskers were purified consequently, (Figure 3.9 (C), (D)).

![Figure 3.9 SEM images (A) as-prepared SiC fibers (residual carbon fibers appear); (B) as-prepared SiC fibers, higher magnification; (C) SiC whiskers after depleting residual carbon; (D) SiC whiskers after depleting residual carbon, higher magnification; (C/SiO$_2$=5)](image)

As shown above (Figure 3.9), a value of 1/5 for the ratio of C/SiO$_2$ resulted in high quality SiC whiskers at almost 100% percent in the product. However, in this project, it was found that the ratio of C/SiO$_2$ was a very important factor to control the morphology of the final product. With a higher ratio (1/3) of C/SiO$_2$ in the raw materials, a different type of SiC whisker,
the beaded SiC whisker, shown in Figure 3.10, was formed as the dominant morphology in the product.

![Figure 3.10 SEM images of the beaded SiC whiskers (C/SiO₂=3)](image)

3.3.2.2 The Formation of the SiC Whiskers

Except the preparation route via pyrolysis of organic matters, most methods of preparing 1D SiC nano structure involve gas reaction, and either VS (Vapor-Solid) or VLS (Vapor-Liquid-Solid) applies. In this project, the SiC whiskers are believed to grow by VS mechanism, since it lacks the condition (liquid droplets) and features (a cap on the ends of whiskers) for VLS mechanism. The overall reaction forming SiC in a carbon-silica system under high temperature is generally accepted as the reaction (1):

\[
\text{SiO}_2(s) + 3C(s) \rightarrow \text{SiC}(s) + 2CO(g) \quad (1)
\]

And the breakdown of the reaction (1) may include several other reactions which release the volatile species, SiO and CO, and produce SiC and CO₂:

\[
\text{SiO}_2(s) + C(s) \rightarrow \text{SiO}(g) + CO(g) \quad (2)
\]

\[
\text{SiO}_2(s) + CO(g) \rightarrow \text{SiO}(g) + CO_2(g) \quad (3)
\]
SiO\(_{(g)}\) + 2C\((s)\) → SiC\((s,\, particles)\) + CO\((g)\) \hspace{1cm} (4)

\[ \text{CO}_2\((g)\) + C\((s)\) → 2CO\((g)\) \] \hspace{1cm} (5)

\[ \text{SiO}\((g)\) + 3CO\((g)\) → SiC\((s,\, whisker)\) + 2\text{CO}_2\((g)\) \] \hspace{1cm} (6)

The gas species (CO and SiO) which forms then SiC are released through reactions (2), (3), (4) and (5), feeding the system where the CO and SiO are consuming by SiC formation (reactions (4) and (6)). The gas phase reaction (6) is the dominate mechanism for the growth of SiC whiskers, while the solid phase reaction (4) mainly forms the SiC shells on the surfaces of the carbon fibers. Because the silica in the white ash is in the form of high activity,\(^{29}\) the reduction reactions (2) and (3) are apt to occur. It is big advantage over the other silica source employed in conventional process of SiC preparation.

The high yield of SiC whisker is attributed to the morphology of the carbon source in this experiment. Compared with the other forms of carbon (carbon black, intrinsic carbon from rice hulls, particulate carbon, etc.), the carbon fibers used in this process present less surface areas than those of comparable carbon powders. With less area exposed to the gas species, it depresses the contact of SiO gas with solid carbon; therefor, the reaction (4) was depressed. Consequently, more SiO reacted with CO according to reaction (6). As a result of the enhancement of reaction (6), the partial pressure of CO\(_2\) was increased, which would promote the reaction (6) by producing more CO by reaction (5), so the whiskers yield was increased greatly.

According to the overall reaction (1), the perfect ratio of C/SiO\(_2\) for complete reaction is 3, but considering the residual carbon, the system could be in a SiO\(_2\) excessive sate when the ratio of C/SiO\(_2\) in the raw materials equaled to 3. That is why the different morphology of SiC whiskers was formed when decreased the ratio of C/SiO\(_2\) to 3 other than 5. In reality, the reverse reaction (3’) of reaction (3) would happen when the system was in a SiO\(_2\) excessive sate. The
resultant SiO$_2$ from the reverse reaction (3’) deposited onto the surface of the formed SiC whiskers previously in the system, which changed the morphologies of the SiC whiskers from smooth surface to beaded morphology.

$$SiO(g) + CO_2(g) \rightarrow SiO_2(s) + CO(g)$$

(3’)

3.3.3 The Enhancement of Thermal Transfer by Dispersed SiC Whiskers in Water

In the heat transfer tests, SiC whisker laden water dispersion with different SiC concentrations was prepared with the aid of an ultrasonic device.

![SEM image of the SiC drained from dispersion](image)

Figure 3.11 SEM image of the SiC drained from dispersion

To further obtain the information of the morphology and the size distribution of the SiC whiskers, a few drops of the dispersion were collected and drained; then the SEM images were captured, which provided more general information and represented the whole picture of the SiC
whiskers in the dispersion, shown in Figure 3.11. There were some wrecks of the SiC shell which originally coated on the surface of the carbon fiber and survived from the oxidation in air at 700 °C, circled features in Figure 3.11. The whiskers have an average length of 12.3 microns and the length distribution is shown by the inset of Figure 3.11.

The dispersions were pumped at a constant rate through a channel, 1.5 mm in diameter, embedded in the copper block. Due to the high thermal conductivity of copper, during the short testing time (in the order of several seconds) the copper block temperature approximately remained constant. By measuring the SiC/water mixture temperatures at the copper block inlet and outlet, the temperature rise of the SiC/water mixture dT and the logmean temperature can be found, Figure 3.12 (A). The convective heat transfer coefficient between the flow and the channel wall is directly proportional to the dT/(logmean T) values. In Figure 3.12 (B), the instantaneous mean temperature is the average of SiC/water temperatures at copper block inlet and outlet. It is clear that 0.16 wt% group has much higher heat transfer coefficient than the pure water case at the mean temperature range of 37 °C to 43 °C. Due to the selection of initial testing temperatures, the test results are clustered into two distinct groups, Figure 3.12 (B), identified by two temperature regimes (<37°C and >37°C). The heat transfer enhancement plot, Figure 3.13, is based on the averaged data in these two distinct temperature bands. From Figure 3.13 (A), up to 9.3% increase in heat transfer could be achieved by adding 0.16 wt% of SiC whiskers. The large uncertainty bars in the high SiC concentration groups indicate larger variation of performance with high concentrations at the low temperature regime. In this regime, 0.16 wt% group achieved 27.7% increase with respect to the pure water case. By further increase the SiC concentration to 0.2 wt%, the heat transfer performance reduces. It is clear that all the high concentration groups
(0.16%, 0.2% and 0.24%) have a heat transfer enhancement well above the measurement uncertainty range.

Figure 3.12 dT vs Log Mean Temperature; slope vs. mean temperature for different concentration

The increase of heat transfer by the addition of SiC whiskers could have two possible mechanisms: by the rigid rod gyration and by the high thermal conductivity cluster formation. For low concentration groups, the first mechanism would be dominant. The dynamic instability of rod shaped objects could be stimulated by the uneven distribution of shear stress. Such cases are more apparent inside the boundary layer, where large velocity gradient is available. And the rotational motion of the rigid SiC whiskers would lead to the formation of vortexes and thus enhance the mass and energy transfer. With the increase of SiC concentration, space for the whisker free rotation would gradually diminish, thus the enhanced effective thermal conductivity starts to play a dominate role due to the formation of high thermal conductivity SiC clusters/meshes in the channel. It is also observed that in the high temperature regime, the percentage increases in heat transfer for high concentration groups are much higher than the low
temperature cases. At high temperatures, the viscosity of water base decreases and hence assists the first mechanism. At 0.16 wt %, an optimum level for the rigid rod gyration mechanism is achieved. With further increase of concentration, the gyration mechanism is suppressed.

Figure 3.13 Percentage change in slope (convective heat transfer coefficient) with respect to water, within 37-43°C temperature regimes. Error bar indicates 2 standard deviations (95% confidence interval)
3.3.4 The Effective Reinforcement by Beaded SiC Whiskers

Three groups of specimens were prepared by mold cast for tensile tests, epoxy specimens, smooth SiC whiskers reinforced epoxy specimens and beaded SiC whiskers reinforced epoxy specimens, respectively. The tensile test results of the three groups of samples were presented in Figure 3.14: with smooth whiskers (1% concentration), the proof stress increased 33%, comparing to the pure epoxy base level. With beaded whisker reinforcement (1% concentration), the proof stress was improved by an extra 24%. The promising results suggest that there is different mechanism for the more effective reinforcement effect of the beaded SiC whiskers than smooth ones, and the new reinforcement mechanism for the beaded SiC whiskers was proposed as an interlocking mechanism between beaded whiskers and the matrix, shown in Figure 3.15.

![Figure 3.14 Typical stress-strain curves for tensile test with different reinforcement groups](image)

Compared with the traditional reinforcement phase (such as particulate shapes, smooth fibers), the beaded whiskers have a much more efficient mechanism by which the force transfer
between reinforcement phase and matrix would be much more reliable. The simple synthesis route developed herein would produce the beaded SiC whiskers at low cost and large scale, which would promote the application of this kind of effective reinforcement materials.

Figure 3.15 Functional scheme for interlock mechanism

3.4 Conclusion

Large scale high quality SiC whiskers were successfully obtained at low cost by employing carbon fibers and white ashes from rice hulls as carbon source and silicon source, respectively. The whiskers possess a diameter of hundreds of nanometers and a mean length of 12.3 microns. The SiC whiskers grew by VS mechanism and the carbon fibers increased the opportunity of gas phase reaction of SiO and CO, therefore the yield of whiskers increased dramatically. Potential applications of the SiC whiskers are demonstrated.

Based on the experimental tests, the addition of SiC has a strong effect on the heat transfer performance. Gyration induced vortex and cluster formation mechanisms were proposed to explain the heat transfer enhancement by the addition of SiC whiskers. The micro scale flow-rigid rod interactions lead to the gyration of SiC whiskers in the shear region (such as within the
boundary layer) of flow and provide an effective mass and energy transfer mechanism. A maximum heat transfer increase was achieved at 37-43°C temperature range, with the 0.16wt% of SiC laden water, based on the experimental measurements. It is worth to explore the detailed thermo fluid physics in order to optimize the whiskers’ shape and concentration for heat transfer fluid applications.

The beaded SiC whiskers are confirmed to be an efficient reinforcement phase for plastic-matrix composites, because their special structure would render them a new interlocking mechanism to obtain a much more reliable coupling with the matrix in a composite. The example was designed to demonstrate the enhancement of the tensile strength of the composite reinforced by beaded SiC whiskers. Sampling and test procedures were adopted from ASTM D 638-03, three groups of specimens were prepared by mold cast for tensile tests, epoxy specimens, smooth SiC whiskers reinforced epoxy specimens and beaded SiC whiskers reinforced epoxy specimens, respectively. The results were promising: with smooth whiskers (1% concentration), the proof stress increased 33%, comparing to the pure epoxy base level. With beaded whisker reinforcement (1% concentration), the proof stress was improved by an extra 24%.

3.5 References


CHAPTER 4. THE FORMATION OF FIBROUS SiC IN SiC\_β/Al\_2O\_3 COMPOSITES FROM THE SILICA-CARBON-ALUMINUM SYSTEM

4.1 Introduction

In the ceramic family, SiC-Al\_2O\_3 composites represent a promising class of materials due to their excellent refractoriness, low susceptibility to oxidation, good mechanical properties at elevated temperature and complex chemical environments. The addition of nano-sized SiC may give a significant increase in creep resistance, strength and toughness of Al\_2O\_3 ceramics;\textsuperscript{1,2,3} the SiC-Al\_2O\_3 composites have been also employed to fabricate mullite/mullite composites with engineered structures;\textsuperscript{4,5,6} in addition, because of its unique combination of good thermal, mechanical and electric properties, the SiC-Al\_2O\_3 composite finds applications in Micro-Electro-Mechanical Systems (MEMS).\textsuperscript{7} As a result, SiC-Al\_2O\_3 composites have been received considerable attentions. In addition to the conventional powder metallurgical method,\textsuperscript{8,9,10,11} there are several other routes for the synthesis of SiC-Al\_2O\_3 composites: such as carbothermal reduction of silica-alumina-containing precursors,\textsuperscript{12,13,14,15} high-energy milling,\textsuperscript{16} Sol-Gel route,\textsuperscript{17} alumina body with polymer infiltration,\textsuperscript{18} in situ formation of SiC particles,\textsuperscript{19,20} combustion synthesis,\textsuperscript{21,22,23,24} electrophoretic deposition\textsuperscript{25} and so on. The in situ synthesis from the silica-carbon-aluminum system has unique characteristics because of the simplicity and low cost; however, several aspects of this process, including the detailed system composition evolution path and the morphologies of the products, have not been addressed thoroughly. In this project, a series of experiments were conducted, to obtain the detailed information about the chemical reactions involved in the evolution of the silica-carbon-aluminum system, and the factors affecting the final morphologies of the product. In this study, the rice hull-based carbon
and silica were used. The super fine silica and carbon with high activity derived from rice hulls make the process more economic and environmentally friendly. The formation of fibrous SiC in the SiC-Al₂O₃ composites could enhance the mechanical strength of the composites.

4.2 Experimental Procedure

4.2.1 Raw Materials

The raw rice hulls used in this project was provided by Three H’s, LLC, Crossett, AR, USA. The as-received raw rice hulls were processed according the procedures stated in the chapter 2. This would give the so-called black ash (BA) and white ash (WA). The WA contains around 92.6 wt% silica and a small proportion of oxides impurities (K₂O, Al₂O₃, CaO, MgO, MnO, P₂O₅ etc)²⁶, ²⁷. The BA consists of 56 wt% carbon and the balance of amorphous silica. The aluminum source is aluminum powder, -325 mesh, purity 99.5% (from sigma Aldrich).

4.2.2 β-SiC₆/Al₂O₃ Preparation

To prepare the starting powder, the WA, BA and aluminum powder were mixed thoroughly by ball milling at two compositions: (molar ratio: Al: SiO₂: C=4:3:3 and Al: SiO₂: C=4:3:4). The milling process was carried out in a Spex 8000 high energy ball mill using 5mm-diameter stainless steel balls; the weight ratio of the mixture and the milling balls was 1:20 and a milling time of 10 minutes (5 minutes + 5 minutes with a time gap to avoid overheating) gave well dispersed fine powders. After milling the mixture was pressed into compact discs by means of binderless cold pressing under different pressures (up to 750MPa). A little chunk of the compact was firstly put into DSC (NETZSCH Differential Scanning Calorimeter, Model DSC 404 F1 Pegasus, NETZSCH Group, Germany) to investigate the reaction thermodynamics of the mixture system, 10K/min under an argon flow. The bulk disc-shaped samples were placed into a
conventional electric tube furnace (a horizontal alumina tube, L: 1000mm; D: 80mm) heating to 1450 °C and 1500 °C (the ramp was 10 °C/min under 1000 °C and 5 °C/min above 1000°C) in a slowly flowing nitrogen atmosphere (30 SCCM), holding at highest temperature for 60 minutes, respectively. Finally, the furnace was programmed to cool down to room temperature at 10 °C/min. In addition, to obtain the onset temperature of the reaction between silicon and carbon, pure silicon and carbon were mixed and underwent the DSC examination.

4.2.3 Characterization

X-ray diffraction (XRD) measurements were performed using a X-ray diffractometer (MiniFlex XRD, Rigaku Corporation, Japan) with Ni-filtered Cu Kα radiation (λ=1.54178 Å). For all samples XRD spectra were obtained by scanning at a speed of 2 °/min and step width of 0.02°. The microstructural morphology of the final products was observed by field emission scanning electron microscopy (FESEM) (Model Quanta 3D FEG, FEI Company, USA).

4.3 Results and Discussion

In materials engineering processes, the particle size of the starting powder mixture may affect strongly on the synthesized composite, and a homogeneous and defect free composite microstructure is critical to guarantee the mechanical performance of the final products. In this paper, the selection of the rice hulls derived silica and carbon is an energy-saving and low cost method to obtain very fine starting powders with high activity. The rice hulls are organic matters with super fine silica which is in a hydrated amorphous form to provide the rice seeds inside with a reliable protection from the harsh environment. Silica is presented intensively in the protuberances on the outer surface of the hulls, Figure 4.1 (a); 10 minutes milling produced the very fine particle mixture system Figure 4.1 (b), which consists of particles at sub-micron scale.
The small size of the silica and carbon inherited from rice hulls ash renders this process a major advantage over the conventional methods where the mineral powders are employed as silicon and carbon supplies.

Figure 4.1 SEM image of raw rice hull surfaces (a), featuring the tiny protuberances located on the outer surface and the as-milled fine powder mixture (b)

To obtain more information on the reactions before large-scale synthesis using a tube furnace, the system was examined by DSC, Figure 4.2 (a). On the heating line, there are three apparent thermal events: 662 °C, melting of aluminum; 760 °C, exothermal reaction between silica and aluminum; and 1410 °C, melting of silicon reduced by the last exothermal reaction (between silica and aluminum). Because the tiny silica particle is of high activity, it may react with aluminum at a temperature as low as 760 °C. The exothermal reaction peak of SiO₂: Al: C=3:4:4 is weaker than that of SiO₂: Al: C=3:4:3, which is not only caused by the different weight ratios of the carbon in the reactant, but also by the connectivity of the silica and aluminum in the reactant (i.e. the exothermal reaction in the system of SiO₂: Al: C=3:4:4 was not complete at 760 °C). The melting point of the silicon in this experiment (1410 °C) is slightly lower than 1414 °C,
which is resulted from the impurities in rice hull ashes. Also, the extent of reactions was investigated for different treatment temperatures, Figure 4.2 (b). After heating to 800 °C, the silicon element dominates. There are weak peaks indexed to the aluminum phase in the XRD pattern of the system, but no evident peaks for alumina were observed, which means the exothermal reaction between aluminum and silica is not complete at 800 °C, and the produced tiny alumina particle may be in amorphous form and entrapped by the residual aluminum. As the temperature goes up to 1100 °C, the reaction between the residual aluminum metal and the silica almost completes and alumina proves its existence by very strong XRD peaks. β-SiC starts to appear from 800 °C, even though its XRD peaks are very unobvious, which is in agreement with the previous reports. 28 Although the temperature goes up to 1100 °C, the SiC phase is still not evident in the system; as a matter of fact, the formation of silicon carbide via solid-solid reaction between silicon and carbon is controlled by the diffusion of Si to the SiC/C interface, and the Si diffusion rate through bulk SiC is extremely slow in the temperature range of 800 ~ 1000 °C. 29 Heating to a higher temperature (1450 °C), the silicon carbide phase in XRD result is very evident and the silicon element fades away. As the temperature goes higher, the reaction mechanism between the silicon element and carbon element also changes, which will be explained later based on the SEM results of the morphology of the SiC products. In addition, besides the temperature and the holding time, the ratio of Si/C in the initial reactant mixture is also important to the completion of the reaction between silicon and carbon to obtain silicon carbide. With more carbon in the system, the connectivity of silicon and carbon is weaker than that of the system with less carbon, so the silicon peaks of SiO₂:Al:C=3:4:4 are lower than that of SiO₂:Al:C=3:4:3 (Figure 4.2 (b)). Lee et al 21 reported the similar result about the Si/C ratio,
but in their SHS process (self-propagating high-temperature synthesis) experiment, the SiO\textsubscript{2}/C ratio of $\frac{1}{2}$ was found to deplete the silicon in the final product.

![Figure 4.2](image)

**Figure 4.2** (a) DSC curves for different silica/carbon ratios and (b) XRD patterns after different treatment temperatures

Due to DSC’s vulnerability to damage at high temperature, specimens were tested by DSC without long holding time at highest temperature. Instead, the experiments with long holding time at high temperature were conducted in a tube furnace. One hour holding at 1450 °C almost made the reaction between the silicon and carbon complete for the system with a Si/C ratio of $\frac{3}{4}$ (Figure 4.3 (a)), but there is evident residual silicon for the system with Si/C of $\frac{3}{3}$ (Figure 4.3 (c)). Also, the connectivity of the initial powders played a key role in completing the reaction of silicon and carbon; loose powders even with a Si/C ratio of $\frac{3}{4}$ retained the silicon phase (Figure 4.3 (b)) even though experienced a same temperature program as the compact ones (green bodies formed over 50 MPa with a typical XRD pattern in Figure 4.3). DSC tests (Figure 4.4 inset) revealed that the pressures forming the green bodies affected the onset temperature of exothermal reaction and the intensity of the exothermal reaction, which indicates that the

- 50 -
reaction process is a strong function of the green body density. Indeed, the density of the green bodies was found to make substantial differences on the morphology of the end products.

![XRD patterns of resultants in tube furnace, soaking one hour at 1450 °C](image)

Figure 4.3 XRD patterns of resultants in tube furnace, soaking one hour at 1450 °C

The reactions of forming silicon carbide involved in this system are complicated. They are primarily independent on the spatial distribution (determined by the density of the green bodies) of silicon and carbon elements and reaction temperature; the impurity introduced by the rice hulls is also responsible to some SiC growth mechanisms. Direct solid state reaction between silicon and carbon was confirmed by heating the compact (Si/C=1, formed under 100 MPa) of mixture of pure silicon (Aldrich, -325 mesh) and carbon black (Alfa Aesar, S. A. 75 m²/g) to 1450 °C, 1370 °C and 1250 °C in an argon flow, Figure 4.5. From the DSC curves and their corresponding XRD patterns, it is clear that the Si/C system has an exothermal reaction peak centered at 1364 °C, which is the SiC formation reaction. Because it is an exothermic reaction, the temperature is above the programmed one and might melt the silicon (melting point 1414 °C). At 1250 °C, the solid state reaction rate is slow because the Si diffusion rate through the formed SiC layer between carbon and remaining silicon controls the reaction and it is extremely slow in
the temperature range (Figure 4.5 XRD pattern (a)). It is reasonable to infer that as the exothermal reaction between silicon and carbon proceeds, the remaining silicon melts, and in the liquid phase, the mass transfer is much easier than that of diffusion in solid, so the reaction is almost complete once the temperature is high enough to melt silicon (Figure 4.5 XRD pattern (b) and (c)). It is confirmed that the solid state reaction between silicon and carbon starts under 1250 °C, and this information would be helpful to explore the reaction mechanisms in the silica-aluminum-carbon system.

Figure 4.4 DSC curves and the typical XRD patterns for the specimens (Si/C=1) formed under different pressures (75 MPa ~ 750 MPa)
It has been mentioned that the spatial distribution of the initial power would affect the reaction between the silicon and carbon, thus the morphology of the corresponding end products. Green bodies formed under high pressure (larger than 350 MPa) are dense, which would guarantee good connectivity, thus facilitate the reaction between silicon and carbon according to reaction (1). So, more nuclei are expected and fine SiC powders dominate in the end product, shown in Figure 4.6. More interestingly, when the same specimen was heated to 1500 °C and soaked at 1500 °C for 60 minutes, worm-like SiC appears, Figure 4.7. The worm-like SiC is believed to be developed from the fine SiC particles by annealing effect under high temperature, and the same phenomenon was reported by Yang, et al. There is an evolution trace that the size of the diameters for SiC particles and worm-like SiC matches each other. The driving force for this morphology change is from the thermodynamics of the system; the quasi one-dimensional structure lowered the energy of the system at elevated temperature.

\[ Si(s) + C(s) \rightarrow SiC(s) \]  

(1)
Different from the end product (particles) for denser green bodies discussed above, Figure 4.8 shows the typical SEM images for those of green bodies formed under 150 MPa. Long curved SiC fibers dominate in the product. They have a smooth surface, a diameter of around 50 nm, and a length of up to a few tens of microns. The characteristics are really different from the fibers grown by the well-known mechanisms, such as Vapor-Liquid-Solid (VLS), Vapor-Solid (VS) mechanism; and considering the growth environment, the solid-liquid-solid (SLS) growth mechanism\textsuperscript{31, 32, 33} is believed to be the main formation mechanism of SiC fibers. Because the network between carbon and silicon in this specimen is not as compact as those formed by higher pressure, the mass transfer is very limited when all reactants were in solid phase. The mechanism by which the long fibers grew in this experiment is believed to involve liquid phase. When the temperature increased, the silicon became liquid state, and the very fine amorphous carbon particles inherited from the pyrolysis of the organic in rice hulls was infiltrated by the liquid. So, the reaction (2) would occur and the SiC would precipitate because
of its high melting point. Thermodynamically, the SiC fibers are favorable to minimize the Gibbs energy of the system.

\[ Si(l) + C(s) \rightarrow SiC(s) \quad (2) \]

In addition to the prevailing morphologies found in the end products, Figure 4.8, there are two more types of SiC fibers found locally, Figure 4.9 and Figure 4.10. They are not as long as...
the curved SiC fibers grown by liquid silicon and solid carbon reaction discussed above, but they are straight and located mainly in the free voids of the specimens such as crack gaps, pores inside the compact specimens, which avoid the space limit for the fiber growth. The two types of SiC fibers might be explained by the VS (Figure 4.9) and VLS (Figure 4.10) growth mechanisms, respectively. Figure 4.9 shows typical SEM images for the SiC fibers located in a large void, where the SiC grew by vapor species. In this reaction mechanism, residual silica in the system is the key species. It is reasonable that the silica trapped by carbon was not reduced by the aluminum in the system, and as the temperature went up, according to reaction (3), (4), and (5) redox reaction took place and SiC formed. The gas state reaction forming SiC has been well explained by several investigators, and the reaction (4) favors the SiC whisker formation.

Fig. 10 shows SEM images of typical fibers grown by VLS mechanism. Each of the fibers has a spherical cap at the end, and it seems the diameters of the fibers are determined by the size of the caps. A typical VLS mechanism includes three parts: gas species, a small liquid alloy droplet (catalyst site), and the solid phase separated from the liquid droplet. In this experiment, the catalyst consists of the impurities in the rice hulls, and the gas species (SiO, CO) are from the reaction (3), and (5). When the gases were saturated in the liquid droplets, the nucleation of SiC took place; and as the concentration of SiC seeds was supersaturated in the catalyst sites, the separation of SiC occurred, which grew along the thermodynamically favorable direction to grow SiC fibers and the interface of liquid-solid (SiC).

\[ C(s) + SiO_2(s) \rightarrow CO(g) + SiO(g) \]  
\[ SiO(g) + 3CO(g) \rightarrow SiC(s) + 2CO_2(g) \]  
\[ CO_2(g) + C(s) \rightarrow 2CO(g) \]
4.4 Conclusion

By a low cost and energy-saving method, β-SiC₆/Al₂O₃ composites were successfully synthesized using rice hulls which are a kind of largely available agricultural waste. After holding for 60 minutes at 1450 °C, a Si/C molar ratio of 3/4 was found to obtain SiC product without residual silicon; the compacts formed at 150 MPa produced long curved SiC fibers at
large scale by SLS mechanism. The density of green bodies affects the reaction mechanisms between silicon and carbon, thereof affects the morphology of the end products. At high pressures (above 300MPa), the submicron SiC particles dominate the end product, and around the voids in the specimens, straight SiC fibers were found locally because of the micro environment favors the corresponding growth mechanisms.

4.5 References


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CHAPTER 5. MULLITE PREPARATION USING RICE HULLS AND ALUMINUM CANS

5.1 Introduction

During the last decades, the silica and aluminum system has emerged as an attractive topic to preparing ceramic composites,\textsuperscript{1,2,3} and the reactions between molten Al and different silicate substrates, reaction condition has been intensively investigated.\textsuperscript{4} Many useful ceramic/metal composites with interesting structures, such as Net-shape bi-continuous $\text{Al}_2\text{O}_3$/Al composite, $\text{Al}_2\text{O}_3$/Al/Si composite, SiO$_2$/Al composite were successfully manufactured.\textsuperscript{5,6,7} On the other hand, much attention has been paid on the utilization of rice hulls, a major agricultural waste in the past several decades,\textsuperscript{8,9,10,11,12} since Lee and Cutler\textsuperscript{13} first reported the silicon carbide from rice hulls. Rice hulls have high silica content (~20 wt %) with small amount of alkalis and trace elements;\textsuperscript{14} the organic matters, which are mainly celluloses, in the hulls would become amorphous carbon when they are heated, while the silica in the hulls remains unchanged. Furthermore, the silica in the rice hulls is superfine, which gives it much more advantages over large scale silica. Following the initial work of Cutler et al, intense studies in this area have been done, but the work is concentrated on converting rice hulls to silicon carbide and the formation mechanism for different product such as silicon carbide powder and whiskers. Further exploring for composites based on rice hulls has seldom been seen in literatures. In this dissertation, rice hulls and aluminum based composite was explored. The sources for silica and aluminum are from rice hull ash and aluminum cans, respectively, both of which can be obtained economically. The products were characterized by several technologies such as XRD, SEM. The as-prepared ceramic composites have a promising application in modern industry.
5.2 Experimental Section

5.2.1 Pretreating of Beverage Cans

Aluminum cans’ body is usually made of 3104 aluminum alloy,\textsuperscript{15} which is an abundant and economic source for aluminum in this project. In this dissertation, recycled beverage cans were processed using an electrolytic plasma device, developed in our research group, to remove the paints first; then the cans were grinded to powder (~ 100 \( \mu \)m) using a ball miller machine.

5.2.2 \( \text{Al}_2\text{O}_3 / \text{Si} \) Composites Preparation

WA and aluminum powder were put together with a mass ratio of 5:3 for silica and aluminum. The mixture was thoroughly mixed using a ball mill machine for 40 minutes with the ball-to-powder weight ratio of 30:1. Finally, the mixture was cold pressed under 45 MPa to form discs with a diameter of half inch. In a tube furnace with a continuous argon gas flow of 300 mL/min as a protective gas atmosphere, the discs were heated to 750 °C (sample A) and 1400 °C (sample B), respectively, and both the soaking times were 120 minutes.

5.2.3 Mullite and Mullite/\( \text{Al}_2\text{O}_3 \) Composites Preparation:

Because the amount of oxygen changes during the reaction process, only the ratios of the metals were considered carefully. To get a single mullite phase, WA and aluminum powder were mixed together with a mass ratio which can make the metal atoms Al and Si equal to 3:1. The mixture was thoroughly mixed using a ball mill machine for 40 minutes with the ball-to-powder weight ratio of 30:1. Then the mixture was pressed into a disc with a diameter of half inch by means of binderless cold pressing under 55 MPa. Finally, the disc sample (sample C) was sintered in air using a box furnace up to 1450 °C and holding for 200 minutes. At the same temperature program, the WA and aluminum powder mixture with an Al/Si atom ratio 4:1 (more
than 3:1 for 3Al₂O₃⋅2SiO₂) was also sintered and this ratio produced a double composition phases of mullite and Al₂O₃ (sample D).

5.2.4 Characterization of the Composites:

To determine the phase composition of the as-prepared composites, X-ray diffraction (XRD) measurements were performed on a X-ray diffractometer (MiniFlex XRD, Rigaku Corporation, Japan) with Ni-filtered Cu Kα radiation (λ=1.54178 Å). For all samples XRD spectra were obtained by scanning at scanning speed of 2 °/min and step width of 0.02°. The microstructure morphology of the ceramic composites was observed by Scanning Electron Microscopy (SEM).

5.3 Results and Discussion

5.3.1 Formation of Al₂O₃/Si Composites

The raw materials and final products were characterized by XRD and the patterns were shown in Figure 5.1. Figure 5.1 (a) indicates the powder from Aluminum cans’ body is mainly composed of aluminum; Figure 5.1 (b) is the typical pattern for amorphous silica with a broad peak centering around 2θ=22°. In inert atmosphere, the following chemical reaction occurs in the silica-aluminum system⁶:

\[
3\text{SiO}_2 + 4\text{Al} \rightarrow 3\text{Si} + 2\text{Al}_2\text{O}_3 \quad (1)
\]
Figure 5.1 XRD patterns for raw materials and Al₂O₃/Si composites

The ratio between SiO₂ and Al plays an important role in the composition of the final product. In these samples, the ratio could promote the completion of the reaction (1) and produce two phases of silicon and alumina in the final composite. However, the sintering temperature is significant for getting the crystal structure. Although the reaction (1) happens as low as the melting point of aluminum, the reaction could not go completely. As the XRD pattern shown in Figure 5.1 (c), after holding 120 minutes at 750 °C, the resultants are composed of silicon and aluminum, which means the reaction was not complete. On the other hand, the alumina resulted from reaction (1) could not create peaks in XRD patterns, which maybe mean the alumina was not in a crystal structure because the holding temperature was too low to make it crystallized.
When the holding temperature was raised up to 1400 °C, there were two composition phases in the resultants, the XRD pattern of resultants, Al₂O₃ and Si, Figure 5.1 (d). At higher temperature, the reaction (1) happened completely and the resultant alumina crystallized.

![Figure 5.2 SEM images for Al₂O₃/Si composites](image)

From the SEM images, shown in Figure 5.2, it is clear that the microstructures are different for high temperature and low temperature sintering. Considering that the sum of the molar amount of the resultants in reaction (1) is less than that of the reactants, it is reasonable that there are more pores created by reaction shrinkage under 1400 °C than that under 750 °C, because the reaction went more completely under higher temperature and the more alumina became crystallized than that under low temperature.

Although in the Al-SiO₂ system, the reaction of silica with aluminum is thermodynamically favored with the reaction product being silicon and alumina, once alumina formed according to reaction (1), there are other two possible reactions would happen: forming mullite, reaction (2), and the reduction of silicon from mullite, reaction (3):

\[ 3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow \text{Al}_6\text{Si}_2\text{O}_{13} \quad (2) \]

\[ 8\text{Al} + 3\text{Al}_6\text{Si}_2\text{O}_{13} \rightarrow 13\text{Al}_2\text{O}_3 + 6\text{Si} \quad (3) \]
According to the previous work, even if mullite or any other aluminosilicate forms as intermediate, it would eventually transform to alumina. Because both silica and mullite are only stable with pure silicon element, and only trace amount of aluminum are enough to stabilize alumina under 800 °C by reaction (1). As the displacement of silicon by aluminum is kinetically controlled by the diffusion of aluminum through the solid aluminum layer, it is hard to complete the reaction (1) under low temperature. At higher temperature, the diffusibility of liquid aluminum through the resultant alumina is enhanced and the silicon reduced from silica dissolves in liquid aluminum. Thus, the bulk of the reaction could be maintained at higher temperature and the in situ reaction could be completed because of the self-sustained nature of the aluminothermic reaction at high temperatures.

5.3.2 Formation of Mullite and Mullite/Al₂O₃ Composites

Figure 5.3 shows the XRD patterns for pure mullite phase (a) and double phases of mullite and alumina (b). The silica and aluminum with the atomic ratio between Al and Si of 3:1 in sample C produced almost single mullite phase after sintered at 1450 °C in air; with more Aluminum composition in sample D, there is the other alumina phase, shown in Figure 3 (b).
The phase formation and development in sample C and D actually are a reaction-bonded process. The chemical reactions involved in the reaction-bonded process are reaction (1), (2), (3) and the following step, which are partially overlapping:

\[ 3O_2 + 4Al \rightarrow 2Al_2O_3 \quad (4) \]

\[ Si + O_2 \rightarrow SiO_2 \quad (5) \]
The apparent linear shrinkage for the two samples C and D is less than 0.2% although the microstructures on the SEM images (Figure 5.4 and Figure 5.5) indicate there are pores in the ceramics. The weight for sample C increased by 46.3% after sintering in air and 51.2% for sample D, both of which are close to the theoretically number 51.06% and 57.14% respectively, when the system totally converted to mullite phase or mullite/alumina composite. There are two possible reasons for the difference between real weight increase and theoretical ones: the oxidation of the metal in the raw materials and the incompletion of metal oxidation in the final ceramics. Along the formation of mullite, the volume shrinkage was compensated partly by the involvement of oxygen, which accounts for the minor linear shrinkage of the samples.

![SEM images for mullite/alumina](image)

Figure 5.5 SEM images for mullite/alumina

It previously reported\(^{16}\) that temperatures higher than 1550 °C are necessary for complete mullite formation in alumina-silica reaction couples. In this experiment, the single mullite phase successfully obtained under 1550 °C, because the nano-sized silica powder derived from rice hulls enhanced the reaction process. The silica in the rice hulls is around 50 nano meters and in amorphous form, which renders more energy to the silica, thus makes the reaction happen at lower temperature.
The SEM images reveal some difference between the microstructures for the single mullite ceramic (Figure 5.4) and the mullite/ Al₂O₃ composite (Figure 5.5). There are more pores in the mullite ceramic than in the mullite/ Al₂O₃ composite, which would account for the shrinkage during the formation of mullite from alumina and silica. This formation shrinkage could be employed to realize porous ceramics for some specific application in industry.

5.4 Conclusion

In this chapter, we extended the rice hulls’ application by introducing aluminum, which is also from a low cost source. The chemical reaction evolution of rice hull ash and aluminum powder from beverage cans under different temperature programs and atmosphere conditions was investigated. Several ceramic based composites were developed and characterized. These high added value ceramics may find application in the modern industry; for instance, mullite has excellent long-term high temperature stability in air and low thermal conductivity, and it displays very good thermal shock and creep resistance, which make this research significant to dealing with the agricultural problem as well provide a new industry opportunity.

5.5 References


CHAPTER 6. FORMATION OF NANO-SIZED AlN BY DIRECT NITRIDATION USING RICE BRAN

6.1 Introduction

Aluminum nitride (AlN) is an important member of the group III nitrides with the highest bandgap of around 6.2 eV. It is a promising advanced ceramic material with many excellent properties, such as high electrical resistivity ($10^{13} \ \Omega \cdot cm$), small dielectric constant (8.8 at 1 MHz), high thermal conductivity (320 W/m K), and low thermal expansion coefficient (which closely matches that of silicon, $4.7 \times 10^{-6}/K$). Therefore, aluminum nitride is a potential candidate for many applications, such as microelectronics packaging where rapid heat dissipation for high-density, high-power, and high-speed integrate circuits is required. It is desirable to form AlN nanofibers, nanotubes and nanowires because of the one-dimensional (1D) quantum confinement geometries, which may dramatically improve the desired properties and make AlN a promising candidate for making novel nano-devices such as field effect transistors, light-emitting diodes, field emission devices (since AlN has a very small value of electron affinity ranging from negative to 0.6eV), as well as for understanding fundamental concepts underlying the observed electronic, optical and mechanical properties of materials. As a result, an overwhelming volume of research is directed towards obtaining high quality 1D AlN nano materials, including combustion synthesis, vapor – solid (VS) process, anodic porous alumina template, directly nitriding aluminum powders under ammonia/nitrogen with or without a catalyst, carbothermal reduction and nitridation of electrospun precursor.
fibers or solid solution precursors\textsuperscript{1,14} direct sublimation method\textsuperscript{15} and so on. In this chapter, AlN nanopowders and AlN nanofibers were synthesized by direct nitridation of Al, and the morphologies of AlN were found to be a strong function of the compaction pressure of the green body. The products were characterized by using several techniques and the AlN formation mechanism was discussed.

6.2 Materials and Experimental Procedure

To assist the direct nitridation of aluminum (-325 mesh aluminum powders from Alfa Aesar, 99.5% purity), raw rice bran (from a local farm in Louisiana, average particle size less than 1 mm) was selected to act as dispersant/catalyst donor. The as-received rice bran was rinsed with distilled water and dried up at 120 °C in a furnace to remove mechanical residuals and moisture. Initial powder mixtures (aluminum + raw rice bran) were prepared by milling aluminum powder and raw rice bran of same weight. The milling process was carried out in a Spex 8000 high energy ball mill using 5mm-diameter stainless steel balls and a customer-designed stainless steel vial with an inert atmosphere at very low temperature provided by liquid nitrogen cooling; the weight ratio of the mixture and the milling balls was 1:20 and a milling time of 15 minutes gave well dispersed fine powders. In an inert atmosphere, the milled powders were used to form a series of compact disc samples (12.7 mm in diameter and ~ 3mm in thickness) under different compression pressures: 160 MPa, 320 MPa, 480 MPa and 640 MPa. Then the nitridation of the disc-shaped samples were performed in a conventional electric tube furnace (a horizontal alumina tube, L: 1000mm; D: 80mm) in a flowing nitrogen atmosphere (30 mL/min). All the samples prepared under different compression pressures underwent the same temperature program: from room temperature to 1300 °C at a ramp of 10 °C /min; and then
immediately cool down at 20 °C /min to room temperature. The nitride disc samples were collected from the furnace and heated up to 650 °C in air for 2 h to deplete the carbon. The disc samples’ color turned from dark black to gray white in this process due to the loss of carbon. A parallel comparative experiment was conducted by replacing the rice bran with commercial carbon black while all the other conditions remained the same. Finally, the products were characterized by XRD (MiniFlex XRD, Rigaku Corporation, Japan; Ni-filtered Cu Kα radiation λ=1.54178 Å, 2 °/min with a step width of 0.02°) and FE-SEM (Quanta 3D FEG, FEI Company, USA).

6.3 Results and Discussion

Cryo-milling of ductile materials, such as aluminum powders, has been proven to be a useful method for making materials with ultrafine microstructures. In this experiment, the cryo-milling process split the original particle into much smaller pieces as well as formed a thoroughly dispersed system. Figure 6.1 shows FE-SEM micrograph of the as-milled Al and rice bran powder mixture that was employed to synthesize AlN. The powder consists of irregular particles and possess a size range of 1 ~ 20 µm, which is much smaller than the original size of Al and rice bran powders. The density of the green bodies was obtained by measuring the weight and thickness of the compact discs, which were 1.640 g/cm³, 1.650 g/cm³, 1.664 g/cm³ and 1.709 g/cm³ for the discs under the compression pressure of 160 MPa, 320 MPa, 480 Mpa and 640 MPa, respectively. The density revealed the porosity difference in the samples, which, we believe, would affect the nitrogen diffusion, in consequence, the AlN formation and their morphology.
Figure 6.1 FE-SEM image of the raw Al-rice bran powder mixture

Figure 6.2 XRD pattern for initial Al-rice bran powder (a) and a typical AlN product (b)

Figure 6.2 shows the XRD patterns for the initial powders and the AlN products. Figure 6.2 (a) is for the initial powders and has only peaks for aluminum phase, indicating that the initial aluminum powders are well preserved by the inert atmosphere from oxidization during the
milling process. The nitridation products were confirmed to be hexagonal AlN by the XRD results. Regardless of the different compaction pressure levels used to form those green bodies, the final products share the same AlN XRD patterns, and Figure 6.2 (b) shows a typical XRD pattern for the products. According to the XRD data, the obtained product is hexagonal AlN with lattice parameters of $a = 3.129 \text{ Å}$ and $c = 4.992 \text{ Å}$, which are in good agreement with JCPDS card: No. 25-1133. The XRD pattern is apparently broadened, which means the AlN crystals are much smaller than those in bulk AlN. Although the compaction pressures in forming the green bodies did not significantly affect the XRD pattern of the AlN products, the compaction pressure was found to affect significantly the morphologies of the products.

FE-SEM images for AlN products are shown in Figure 6.3. All the images were collected from the cross section of those disc-shaped samples. The compaction pressures under which the green bodies were formed are as following: 160 MPa in Figure 6.3 (a), 320 MPa in Figure 6.3 (b), 480 MPa in Figure 6.3 (c) and 640 MPa in Figure 6.3 (d). It is obvious that the morphologies of the primary products are strongly dependent on the compaction pressure: appropriate pressures (320 MPa ~ 480 MPa) lead to a high yield of fibers; the products for lower or higher pressure levels primarily consist of agglomerated AlN particles, seen in Figure 6.3 (a) and (d). The AlN fibers were found to have an aspect ratio up to 400, diameter in the range of 50-600 nm, and tens of micrometers in length. The AlN fiber diameter is more uniform in the samples prepared under 480 MPa of compression, in comparison to those samples at 320 MPa. In both cases, caps on the tip of the fibers are apparent, which evolved from the liquid catalyst drops involved in the VLS mechanism by which AlN fibers grew$^3$ (more pronounced in Figure 6.3 (c)).
Figure 6.3 FE-SEM images (sample cross-section) for the AlN product under different pre-compression pressure levels (160 MPa, 320 MPa, 480 MPa and 640 MPa)

The XRD results and FE-SEM (Figure 6.4) for the control experiment, using pure carbon black instead of rice bran, were also obtained in the same way. The peaks in XRD patterns for all the samples were originated from AlN and all the products gave nearly the same morphologies, only AlN nano particles and no AlN fibers. The comparative tests using carbon black and aluminum powder testify the importance of both feedstock compositions and the compression pressure of the green body to the formation of AlN nanofibers. The trace metal elements in rice bran may vary based on the locations where the rice bran was grown, it was reported that the
trace elements in rice bran may include K, Ca, Mg, Mn, Cr and others (several to hundreds µg/g in dry weight). The rice bran used in this study was examined by XPS (X-ray photoelectron spectroscopy) to investigate the trace metals. After heated the rice bran to 600 °C in air for 2 h, the ash was analyzed, and the results are shown in table 1. It has 6% CaO, 5% MgO, and about 1% of Fe,Co,Ni. In this experiment, the pre-compression pressures on the green bodies are believed to alter the volumetric density of the AlN nuclei formed in the initial phase of the reaction (low temperature), since the porosities are different, which affected the nitrogen diffusion into the compact samples; and the formation of the AlN fibers was followed when temperature went higher by VLS (Vapor-Liquid-Solid) mechanism. The catalyst-assisted VLS growth is mediated by a liquid-solid interface: a liquid droplet, which is saturated by vapor species and located at the growth front of the fibers, acted as the catalytic active site. In the present study, it is reasonable to believe that only a proper population of AlN nuclei formed under relatively low temperature (< 660 °C) would eventually lead to the growth of fibers by the VLS mechanism. At a temperature as low as 550 °C, the nitridation of the Al and N₂ began. The N₂ diffused into the compacts where reaction between solid Al and nitrogen happened to form AlN on the outside of the aluminum particles. As the temperature went higher, the trace metals in the rice bran agglomerated onto AlN nucleus to form alloy liquid droplets; on the other hand, the tiny aluminum particles trapped by AlN shell melt and this changed the contact opportunity between nitrogen and aluminum. Herein, the amount of AlN formed on the outside of the aluminum particle could make big difference since it remained solid and could control the contact window of the aluminum and the nitrogen. For the samples with plural AlN fibers, it is believed that the population of the AlN seeds formed at lower temperature is desirable to protect the aluminum inside from sufficiently contacting the nitrogen in the gas phase; whereas, the aluminum inside
the AlN shell evaporated to escape into gas phase since the vapor pressure of aluminum is increased due to a big curvature (vapor pressure for small particle size, given by Kelvin equation

\[
\ln \frac{p}{p_0} = \frac{2\gamma V_m}{rRT}
\]

and the high temperature. The evaporation of the aluminum improved the mass transportation for aluminum, and it could move farther than liquid aluminum. The aluminum gas is easy to condense into the alloy liquid droplets adhering to the AlN nucleus formed when the temperature was high. In the liquid droplets saturated by aluminum and nitrogen, the reaction between aluminum and nitrogen happened inside forming AlN as the same time the AlN solidified out from the drops because of a higher melting point and grew on the AlN seeds. In this process AlN grew out of the liquid matrix and elongated continually. When the aluminum element was depleted, the reaction between aluminum and nitrogen ended and the liquid drops remained at the tips of fibers; it finally solidified there as the temperature dropped, which had been confirmed by experimental observation, SEM images in Figure 6.3 (b) and (c).

![Figure 6.4](image) Figure 6.4 a typical FE-SEM image of the AlN powder from nitridation of Al-Carbon Black powder (pre-compression pressure of 320 MPa)
The samples formed at 320 MPa and 480 MPa should induce a proper population of AlN seeds when the temperature was low and just right amount of nitrogen diffused into the disk samples due to the perfect porosity, and the chemical reaction in these samples could be described using the discussions above and finally, AlN fibers were produced. However, under a lower compaction pressure of 160 MPa, more nitrogen diffused into the loosely compacted samples because there were more pores in the compacts. The abundant nitrogen reacted with aluminum to form AlN, which almost depleted the aluminum elements at the lower temperature stage; as a result, when the temperature went high and the growth mechanism was favorable to grow fiber, there was no enough aluminum supply. So the sample produced mainly AlN particles, shown in Figure 6.3a. Under the higher compression pressure of 640 MPa, however, less nitrogen could diffuse into the denser samples at lower temperature stage because there were less pores in the compacts which resulted in less AlN formed on the outside of aluminum particles in the denser samples. Once the temperature went high and the aluminum melted, since there was few AlN shell barrier outside the aluminum droplets, the nitrogen could easily contact liquid aluminum, which resulted into many AlN crystals formed over a very short time; consequently, there was not much Al left for each crystal seed to grow up. So the tiny AlN particles eventually agglomerated other than growing fibers by VLS mechanism, Figure 6.3d. Although the primary product in the sample formed under 640 MPa was nano-sized AlN powder, there were still some nano-sized fibers located near the cracks, which means it formed proper population of AlN crystal seeds in those locations (just like the cases discussed above for the samples formed under 320 MPa and 480 MPa) at a low temperature, and followed the same mechanism the fibers grew.
6.4 Conclusion:

AlN nano-particle and nano-fibers were synthesized by directly nitridation of cryogenic milled rice bran, an abundantly available agricultural byproduct, and commercial aluminum powder mixture. The dependence of the morphologies of the product, AlN, on the compaction pressure levels was investigated and discussed in details. A green body compression pressure range, from 320 MPa to 480 MPa, was identified to promote the AlN fiber yield. The VLS growth mechanism and the importance of rice bran as dispersant/catalyst donor were suggested and discussed for the formation of AlN fiber. This pressure controlled morphology method could be employed to synthesize AlN nano-fibers at large scale and low cost.

6.5 References


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CHAPTER 7. CONCLUSIONS

In this dissertation, based on the silica in rice hulls the advanced ceramics, namely SiC whiskers, SiC/Al₂O₃ nanocomposites, mullite, and AlN nanowires, were developed and studied, and some potential applications of these ceramics were investigated.

The SiC whiskers were successfully prepared at high yield by simple methods (patent pending). Since the one-dimensional ceramic materials are more valuable for many applications than particulate SiC, the study in this dissertation is particularly valuable. During the development of the one-dimensional ceramics, some unique morphology, such as beaded SiC whiskers were also prepared and investigated. The whiskers possess a diameter of hundreds of nanometers and a length of tens of microns. It is believed that the carbon fibers in the raw materials which were employed to synthesize SiC promote significantly the yield of SiC whiskers. The SiC whiskers grew by VS mechanism between SiO and C, and the carbon fibers increased the opportunity of gas phase reaction of SiO and CO, therefore the yield of whiskers increased dramatically.

For thermal application, the heat exchange enhancement by SiC whiskers is promising; an enhancement as high as 27% was achieved by a dispersion of SiC (0.16 wt%) in water, in comparison to the pure water baseline case at a temperature range of 300-320 K. The beaded SiC whiskers are confirmed to be an efficient reinforcement phase for plastic-matrix composites, because their special structure would render them a new interlocking mechanism to obtain a much more reliable coupling with the matrix in a composite. This example was designed to demonstrate the enhancement of the tensile strength of the composite reinforced by the beaded SiC whiskers. Three groups of specimens were prepared by mold cast for tensile tests, epoxy
specimens, smooth SiC whiskers reinforced epoxy specimens, and beaded SiC whiskers reinforced epoxy specimens, respectively. The results were promising: with smooth whiskers (1\% wt concentration), the proof stress increased 33\%, comparing to the pure epoxy base level. With beaded whisker reinforcement (1\% wt concentration), the proof stress was improved by an extra 24\%.

Using a low cost and energy-saving method, β-SiC/Al₂O₃ composites were successfully synthesized by white ashes from rice hulls. The parametric study shows that the density of green bodies affects the reaction mechanisms between silicon and carbon, thereof affects the morphology of the end products. The samples formed at 150 MPa produced long curved SiC fibers at large scale by SLS mechanism. At high pressures (above 300MPa), the submicron SiC particles dominate the end product, and around the voids in the specimens, straight SiC fibers were found locally because of the micro environment favors the corresponding growth mechanisms. The super fine silica and carbon with high activity derived from rice hulls make the process more economic and environmentally friendly. The formation of fibrous SiC in the SiC-Al₂O₃ composites could enhance the mechanical strength of the composites.

In this dissertation, white ashes from rice hulls and aluminum (from beverage cans) based composites were also explored. The chemical reaction evolution of rice hull ash and aluminum powder from beverage cans under different temperature programs and atmosphere conditions was investigated. Several ceramic based composites were developed and characterized. These high value-added ceramics may find applications in the modern industry; for instance, mullite has excellent long-term high temperature stability in air and low thermal conductivity, and it displays very good thermal shock and creep resistance, which make this research significant to dealing with the agricultural problem as well provide a new industry opportunity.
Using rice brans as a dispersant agent, AlN nano-particle and nano-fibers were synthesized by directly nitridation of cryogenic milled mixture of rice bran and aluminum. The morphologies of AlN were found to be a strong function of the compaction pressure of the green body. The dependence of the morphologies of the product, AlN, on the compaction pressure levels was investigated and discussed in details. A green body compression pressure range, from 320 MPa to 480 MPa, was identified to promote the AlN fiber yield. The VLS growth mechanism and the importance of rice bran as dispersant/catalyst donor were suggested and discussed for the formation of AlN fiber. This pressure controlled morphology method could be employed to synthesize AlN nano-fibers at large scale and low cost.
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