Characterization of Ceramic Composite Materials Using Terahertz Non-Destructive Evaluation Techniques

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CHARACTERIZATION OF CERAMIC COMPOSITE MATERIALS USING TERAHERTZ NON-DESTRUCTIVE EVALUATION TECHNIQUES

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

By

LINDSAY OWENS
B.S., Wright State University, 2010

2012
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION
BY Lindsay Owens ENTITLED Characterization Of Ceramic Composite Materials Using
Terahertz Non-Destruction Evaluation Techniques BE ACCEPTED IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

The characterization of defects such as rust, voids, etc. on materials and the analysis and prediction of strain and stress induced breakdown are well known applications of non-destructive evaluation (NDE) techniques. THz radiation has been suggested as an effective NDE tool for use in the field of ceramics and ceramic matrix composite materials (CMC), via THz spectroscopy and imaging. The goal of this research is to monitor the progression of thermal and mechanical damage applied to the CMC materials using terahertz spectroscopic imaging in order to create a predictive model that will correlate THz imaging data of these materials to environmental stress exposure.
# TABLE OF CONTENTS

I. INTRODUCTION.................................................................................................1  
   Terahertz Imaging............................................................................................1  
   Thermal Protection Systems.............................................................................3  
   Scope..............................................................................................................4  

II. GENERATION AND DETECTION OF THz.........................................................6  
   THz Pulse Generation with Photoconductive Antennas.................................6  
   THz Pulse Detection with Photoconductive Antennas....................................7  

III. NON-DESTRUCTIVE EVALUATION OF MATERIALS..................................15  

IV. EXPERIMENTAL METHODOLOGY...............................................................23  

V. RESULTS: OXIDE...........................................................................................30  

VI. RESULTS: SINC.............................................................................................46  

VII. CONCLUSIONS............................................................................................43  
    Sources of Error..............................................................................................44  
    Future Work..................................................................................................45  

VIII. REFERENCES...............................................................................................46
LIST OF FIGURES

Figure                                                                 Page
1. KT3 Thermal Treated Ceramic.................................................................2
2. X-Scratch Sample....................................................................................3
3. THz image based on Time-Domain maximum amplitude ................................4
4. Generation of THz radiation....................................................................7
5. Hyperhemispherical silicon dome lens......................................................7
6. Detection of THz. .....................................................................................8
7. Detection of THz. .....................................................................................8
8. THz pulse and respective Spectral Amplitude from a reflected THz pulse ....9
9. Teraview Imaging System.........................................................................11
10. PCA Modules Mounted on the Image Gantry.............................................11
11. Images based on TD Max Amplitude, Spectral Amplitude, and Arrival Time......12
12. Frequency Weighted Reflectivity of A-29.................................................13
13. Pitch and Catch Experimental Set Up......................................................16
14. X-Scratch Image of spectral images at different frequencies.....................17
15. Spectroscopic Image at 1.25 THz of 617-A1Q-006 Sample.........................17
16. KT Samples KT2 (left), KT3 (center) and KT4 (right) ............................18
17. Oxide and SiNC Samples........................................................................20
18. Monitoring Damage................................................................................21
19. Time Domain Pulses for Background and Oxide sample and Refractive Index.....22
20. Grid System for Samples..........................................................................23
21. TD Pulses and Spectral Amplitude of Aluminum, Oxide, and SiNC sample......24
22. Heat Treated SiNC sample (left) and Difference in Reflectivity for that sample ....27
23. Difference in Reflectivity Trends............................................................29
24. Reflectivity measurements of A-29R2 sample for P and S polarization rotations...30
25. Difference in reflectivity for A29R2 sample for P and S polarizations............31
26. Reflectivity measurements of A-29R3 sample for P and S polarization rotations...32
27. Difference in reflectivity for (A-29R3) sample for P and S polarizations........32
28. Images based on time domain maximum amplitude of A-29R1 and A-29R3........33
29. Reflectivity measurements of A-30R2 sample for P and S polarization...........34
30. Difference in reflectivity for A-30R2 sample for P and S polarizations...........34
31. Reflectivity measurements of A-31R2 sample for P-polarization...................35
32. B-29R2 Samples for P and S polarization configurations..........................36
33. Difference in reflectivity for SiNC heat treated sample for P and S polarizations...37
34. B-32R2 Samples for P and S polarization configurations..........................38
35. Difference in reflectivity for SiNC heat treated sample for P and polarizations...38
36. SiNC Heat Treated Samples for P and S polarization configurations............39
37. SiNC Fatigue Treated Samples for P and S polarization configurations..........39
38. Difference in reflectivity for SiNC heat treated sample for P and S polarizations.....40
39. Spectral Images of the B-30R1 sample at 250 GHz and 1.25 THz ..................40
40. Spectral Images of the B-30R2 sample at 250 GHz and 1.25 THz ..................41
41. Reflectivity measurements of oxide dwell fatigue treated sample.....................42
LIST OF TABLES

Table                                      Page
1.  Sample Chart.................................................................26
2.  Difference Calculations.................................27
3.  Reflectivity of Samples................................................44
I. INTRODUCTION

TERAHERTZ IMAGING

The Terahertz (THz) range of the spectrum has received considerable attention for the development of standoff imaging systems for non-destructive evaluation applications \[1\]. THz radiation is highly transmissive through dielectrics and highly reflective off of metallic surfaces. These properties are similar to those associated with the microwave region. A THz imaging system can provide a non-destructive standoff imaging technique capable of detecting corrosion on metallic surfaces through obscurants and defects in composite materials.

The characterization of defects such as rust, voids, etc. on materials and the analysis and prediction of strain and stress induced breakdown are well known applications of non-destructive evaluation (NDE) techniques \[2\]. The use of terahertz radiation as an analysis and monitoring tool for novel materials has increased rapidly in recent years \[1\]-\[3\]. While suggested as a potential NDE tool for use in the field of ceramic and ceramic matrix composite materials, the use of THz spectroscopy and imaging in the examination of the effects of mechanical and thermally induced strain on ceramic composite materials is not well established. In order to validate whether or not THz imaging will be useful in assessing ceramic composite material health, it is necessary to determine if THz spectroscopic imaging can clearly highlight areas of the samples that have been affected by mechanical and thermal stress.
Previous work using THz-NDE was performed on fiberglass composite materials, referred to here as the KT samples. Fig 1-1 shows the KT-3 sample which was burned at 830°F for 4 minutes in the circular area as marked. The right side shows a THz image of that sample where the burn region is clearly made visible.

In addition, scans were also done on metallic samples with surface corrosion hidden under a layer of paint. Fig 1-2 shows one such sample, where an “X” was scratched into the surface of the metal. The sample was covered with a layer of paint with two distinct air bubbles present. The air bubbles and the scratch are clearly visible in the THz image, and it also noteworthy that there are five defects present in the image that are not seen upon visual inspection of the sample. Three of these defects are outlined in both pictures.
THERMAL PROTECTION SYSTEMS

Thermal Protection Systems (TPS) are used in applications where materials must undergo extended periods of thermal and mechanical strain. Thermal Protection Systems are necessary in order to protect the internal structure of an aerospace material from the extensive heat changes and mechanical stresses occurring on the external surfaces. The design of such a system is based on the requirement that the energy released by the aerodynamic heating must be either absorbed or rejected by the material. [4, 5].

The first generation of TPS consisted of heat sinks, however, after long term exposure to heat, these materials failed quickly and required constant replacement. The second generation used heat shields, however, their extremely heavy design made them impractical. The next generation of TPS are based on Ceramic Matrix Composite Materials [6]. These materials are lightweight but can sustain long term exposure to high
levels of thermal and mechanical strain. Aerospace components, turbine engines, and high performance brake disks are common applications.

SCOPE

In this thesis, the generation and detection of THz radiation will be discussed as well an elaboration of different reflection imaging modalities. Work on non-destructive evaluation of various materials including composites will be referenced before discussion of the ceramic matrix composite materials. Details on the imaging and data analysis process of the collected data on the ceramic matrix composites will be presented. Fig 1-3 shows a sample of a THz image of one of the ceramic matrix composite materials (right) along with the aluminum reference piece (left).

[Image: Fig. 1-3 THz image based on Time-Domain maximum amplitude. The aluminum reference piece is shown on the left, and the CMC sample is shown on the right.]

Imaging of the Oxide materials showed no measurable change in reflectivity when exposed to high levels of thermal stress. However, SiNC samples showed measurable and consistent changes in reflectivity when exposed to thermal treatments. In addition,
fatigue treatments resulted in measurable changes in reflectivity over certain portions of both types of CMC samples.

In this thesis, the method of generation and detection of THz radiation that was used in this experiment will be discussed as well as specific details of THz imaging. Past work using THz radiation as a non-destructive technique is presented as foundation and justification for using these techniques on ceramic matrix composite materials that have been exposed to high levels of thermal and mechanical strain. The details of data acquisition and analysis, including statistical analysis are outlined. The results of both the oxide and SiNC samples are discussed in depth specifically looking at measuring changes in reflectivity. The goal of this research is to monitor the progression of thermal and mechanical damage applied to the CMC materials using terahertz spectroscopic imaging in order to create a predictive model that will correlate THz imaging data of these materials to environmental stress exposure.
II. GENERATION AND DETECTION OF THZ RADIATION

THZ PULSE GENERATION WITH PHOTOCONDUCTIVE ANTENNAS

There are several methods of generating and detecting THZ, and this chapter will outline the method used in this experiment involving photoconductive antennas (PCA). Details about the antennas, laser system, and imaging set up are also outlined.

An 800 nm center-wavelength laser with an 80 MHz repetition rate and a pulse width of 100 fs is incident upon a semi-insulated GaAs substrate. The 1.55 eV of photon energy in the incident pump pulse excites the electrons from the valence to the conduction band, which has a bandgap of 1.42 eV, allowing the GaAs to behave like a conductor. An antenna structure, as depicted in Figure 2-1, is photolithographically defined on one surface of the GaAs substrate. The incident laser pulse is focused on the dipole antenna gap at the center of the electrode structure made of Ti/Au. The gold electrodes are DC biased which accelerates the charge carriers yielding a time varying current. This time-varying current produces the emitted THz pulse which is coupled from the GaAs substrate back into air using a hyperhemispherical silicon dome lens.
Fig. 2-1 Generation of THz radiation. The incident ultrafast laser pulse is indicated in red and the emitted THz pulse is depicted in green.

Fig. 2-2 Hyperhemispherical silicon dome lens. The optical probe pulse (800nm, 100fs) is incident on the left, and a sub-ps THz pulse is emitted on the right.

**THZ PULSE DETECTION WITH PHOTOCONDUCTIVE ANTENNAS**

The detection of terahertz pulses is very similar to generation except it is slightly reversed. The probe beam, split-off from the same laser which created the pump pulse, is incident on a Low-Temperature-Grown GaAs substrate with a defined antenna structure similar to that used in the generation antenna. Instead of having a bias on the electrodes,
the THz pulse accelerates the charge carriers which produces a small current detectable using current pre-amplification as seen in Fig 2-2.

![Fig. 2-2 Detection of THz. The optical probe beam is incident from the left and the incoming THz pulse from the right. The THz pulse energy accelerates the charge carriers giving a measurable time-varying current.](image)

THz time-domain images utilized in this work were acquired using a commercial system manufactured by Teraview [7]. Ultrafast laser pulses with an 800 nm center wavelength and 100 fs pulse width triggered a fiber-coupled GaAs photoconductive antenna (PCA). At low power the amplitude increases linearly with increased current. Once too high a
current is reached the PCA will begin to experience dielectric breakdown. Collimated THz light from the PC antenna transmitter was focused via a 50 mm focal length lens (f# = 2) onto the samples at an incident angle of 14°. The reflected radiation was detected by a PCA receiver module, based on LT-GaAs, with an identical lens configuration. When the system is optimized and calibrated using a metal sample target, the typical bandwidth of a detected THz pulse is approximately 4 THz.

For imaging purposes, an object is placed at the focus of the THz beam and raster scanned in two dimensions while a full time-domain waveform is acquired at each spatial location or pixel. The experimental data is gathered in the x-y plane. Images can be generated based on the time-domain data (maximum amplitude, arrival time etc) as well as the spectral amplitude data obtained via a Fast Fourier Transform. In Fig. 2-4 shown above, the time-domain pulse is normalized to zero.

Phase information contained in the THz waveforms can be used to form images that contain different information from those generated based solely on the time-domain
amplitude. This technique becomes even more powerful when the sample is imaged in a reflection geometry, rather than in transmission [8]. In this mode, one takes advantage of the pulse width of the THz pulses to generate three-dimensional representations of layered objects. In this type of experimental set up, the beam reflects off of the sample at near normal incidence (~14 degrees), and that the sample is optically thin compared to the pulse width of the beam. If the sample consists of several layers, the interface between each pair of layers reflects a portion of the THz pulse, so that the entire reflected pulse contains all the isolated pulses. Each pulse in this train contains information about each of the layers through which it propagated, as well as the interface from which it originated. Given the shape of the incident THz pulse and the complex dielectric function of the materials comprising each of the layers, one can predict this output waveform using conventional optics [9]. Using the information embedded in the both the time-domain and frequency domain data, extraction of frequency dependent parameters such as refractive index, conductivity, and absorption coefficients of the tested materials can be determined. In addition, for certain materials, spectral “fingerprints” can be seen via characteristic resonances within the THz pulse associated with that material.

For the imaging work described in this thesis, a commercial THz time-domain spectroscopic imaging system was used. The PCA antennas are attached via fiber-optic coupling as seen in Fig-2-5. The 800nm center wavelength pulse is split between the Pump beam (to the Transmitter) and the Probe Beam (to the Receiver). The probe beam passes through a mechanical delay line such that both the generated THz pulse and the probe pulse will arrive at the receiver at the same time. Fig 2-6 shows the fiber coupled Teraview system used to perform THz imaging. The sample mount sits on a stage that is
able to move along the “x” direction. The fiber modules are attached to the Imaging Gantry which is able to move in the “y” and “z” directions. With this configuration, 2D images can be acquired in any two desired planes. For this experiment, the modules were locked at fixed z-height in order to be focused on the front surface of the CMC’s which were scanned in both the x and y dimensions.

Fig 2-5 Teraview Imaging System

Fig 2-6 PCA Modules Mounted on the Image Gantry
In order to analyze the acquired data, a program was written in MATLAB that generates images based on the maximum amplitude of the time-domain pulse as well as changes in the arrival time of the pulse (time of flight). Time of flight images can be used to acquire topographic information. Images are also generated based on the electric field amplitude at specified frequencies and frequency weighted reflectivity. In this latter case, the amplitude of each pixel is based on the integration of the full spectral content of the detected pulse. In Fig 2-7 images were generated based on the A-29R1 CMC oxide sample, this sample will be discussed in more detail in Chapter 5.

Fig 2-7 Images based on TD Max Amplitude (left) Spectral Amplitude (center) and Arrival Time (right) with the aluminum reference piece on the left and the CMC sample on the right of each image.

TD Maximum Amplitude images are generated by extracting the full waveform for each pixel, finding the maximum amplitude of the time-domain pulse, and formulating a grid based on those values for every pixel position. Images based on arrival time follow the same procedure, however the position in time of the maximum amplitude is extracted and
then compared to the arrival time of a pulse from the aluminum (assumed to be a near-perfect reflector) in order to formulate the grid. Lastly, images based on spectral amplitude are generated via extraction of the time-domain pulse that has undergone a Fast-Fourier Transform and is now represented as spectral amplitude vs. frequency. A specific frequency is chosen, (1 THz in the case of Fig 2-7) and the spectral amplitude at that frequency comprises the grid. Based on the spectral data, if an optical parameter such as reflectivity has been extracted for each pixel, an image can also be generated based on that parameter. Fig 2-8 shows an imaged based on the frequency weighted reflectivity of the image where \( r \) is calculated for each pixel point. The frequency weighted reflectivity is defined below.

\[
r = \sum \frac{E(\omega)_{\text{Sample}}}{E(\omega)_{\text{Reference}}}
\]

Fig 2-8 Frequency Weighted Reflectivity of A-29 [10]

The image shown in Fig. 2-8 is normalized to 1 with the most reflective part of the image being the aluminum reference piece on the left. Due to a slight slope present in the
imaging system (on the order of micrometers), the intensity of reflectivity decreases in all images along the y-axis. Data generated from the difference in pulse arrival time across the image can be used to correct for this feature.
III. NON-DESTRUCTIVE EVALUATION OF MATERIALS

Terahertz imaging offers a non-invasive, non-contact, and non-ionizing method of assessing the condition of composite parts and materials and could overcome some of the short-comings of other non-destructive techniques such as x-rays and ultrasound techniques [11]. THz techniques provide a method of getting the complex optical properties such as index of refraction and absorption coefficients of non-conducting materials.

The system used to acquire the images seen in Figure 3-2 was a Picometrix T-Ray 2000 Terahertz Time-Domain Spectroscopy and Imaging System (Fig 3-1) [7]. Collimated THz light from the photoconductive antenna transmitter module was focused with a 3” focal length off-axis parabolic mirror onto the corrosion samples at a 45 degree angle. THz radiation that was reflected from the sample was collected by a second identical parabolic mirror and sent to a photoconductive receiver module, this system is known as a “pitch and catch”. The largest drawback to this type of imaging geometry is that the THz beam is not normally incident on the sample, and limits the spatial resolution of the imaging system. During the imaging measurement, the sample was placed on an x-y scanning/position stage. Each spatial location during the scan corresponds to one pixel in the image. For each pixel, a full time-domain waveform was acquired.
Fig. 3-2 shows the accumulated images accomplished via a single imaging run of one of the corrosion samples. The area on the sample that was imaged in is the last picture on the bottom right corner, and is a metallic plate covered in a thin layer of paint on the bottom half with an x-shaped score in the center. Each panel shows the change in the spectral amplitude at the specified frequency as a function of spatial position. The differences between these images as the specified frequency changes can be attributed to several causes. The spatial resolution of the system will increase with increasing frequency due to the diffraction limit. There may also be a frequency dependence associated with the corrosion effect or element being imaged. Further analysis such as examining the change in spectral amplitude as a function of frequency is necessary to determine this.
Fig 3-2 X-Scratch Image of spectral images at different frequencies.

Fig. 3-3 Spectroscopic Image at 1.25 THz of 617-A1Q-006 Sample

Fig. 3-3 shows an image, acquired with the Teraview THz imaging system described in Chapter 2, of a completely painted metal sample with a delamination or blistering present on the paint that is clearly present in the terahertz image above. While the “x” and
delamination’s are clearly visible to the eye, there are several scratches present in the THz image that are not able to be seen in the visual image.

Fig 3-4 KT Samples KT2 (left), KT3 (center) and KT4 (right)

Fiberglass composite samples designated as the KT samples were characterized in order to determine if THz imaging was a useful technique for detecting delamination’s, burns, and other defects in composite materials. Fig 3-4 shows imaging results from three of these samples. KT2 and KT3 were both burned in an isolated area. The darkened portion of the sample clearly shows evidence of this. KT4 was a sample composed of five layers of varying thickness. By comparing the arrival time of the pulse through each of the layers, the layer thickness was able to be determined for each section.

In addition, the non-destructive properties of THz have attracted the attention of art historians. In recent years, THz imaging has been used for the evaluation of clay artifacts, namely Terra Cotta and Egyptian artifacts [12, 13]. In addition, because paint and plaster are transmissive at these frequencies, THz imaging is being used to examine
murals hidden beneath these overlays [14]. If, however, the thin layers of paint on the surface of a material are of interest, detailed models of the time domain THz waveforms can be used to measure the varying thickness of paint on sample substrates [15].

The studies on composite materials are becoming an increasingly popular branch of nondestructive testing. This is due to their growing popularity in thermal protection systems (TPS) systems as well high diversity of industrial applications such as high performance brake disks and engine turbines. Recent studies on THz NDE performed on composite materials researched solid laminates and honeycomb sandwich non-conducting polymeric composites and carbon fiber composites. The defects and anomalies investigated were foreign material inclusions, delamination, mechanical damage, thermal damage, and hydraulic fluid ingression [16]. Also, absorption of water in wood plastic composites (WPC) has been studied. The dielectric properties of the samples were determined for varying water contents creating a model for the dielectric behavior depending on the water content [17].

Ceramic Matrix Composite (CMC) materials are fabricated such that the fibers are arranged in a matrix pattern rather than all the fibers running in one parallel direction within the material. Conventional ceramic materials fracture easily under high amounts of mechanical and/or thermal strain. CMC materials are significantly stronger which makes them ideal for the next generation of thermal protection systems due to their high strength and thermal resistance. Fig 3-5 shows a visual image of the two types of CMC materials used in this study, an Oxide-Oxide based sample (top) and a Silicon Nitride Carbide (SiNC) sample (bottom).
The goal of this research is to monitor the progression of thermal and mechanical damage applied to the CMC materials using terahertz spectroscopic imaging in order to create a predictive model that will correlate THz imaging data of these materials to environmental stress exposure. First, a THz spectroscopic image of an undamaged CMC sample was taken. A high level of stress, either thermal or mechanical or both, was applied to each sample which was then imaged a second time. Comparison of the data both in the time-domain and frequency-domain acquired from this imaging of the untreated and treated samples assesses whether or not the magnitude and extent of stress-induced changes could be monitored using terahertz imaging and spectroscopy. If changes were detected, a second CMC sample of the same type was treated with a smaller magnitude of stress. This accomplished two goals: filling in gaps in the predictive model, as well as determining the smallest magnitude of stress able to be detected via THz imaging of a CMC sample. However, if no change was initially seen, a higher magnitude of stress was applied in the second round. Changes in the reflectivity were used to populate a predictive model for these CMC samples. Part of the model will include monitoring the progression of damage as it is applied gradually over a long period of time in comparison to the model of a sample damaged very heavily in a short period. Degradation due to
purely thermal stress, purely mechanical stress, and a combination thereof will also be compared.

Initial research on the CMC samples was performed on small broken segments of materials similar to those used in the study described in future chapters in a THz transmission modality. The SiNC samples were so optically thin, that transmission measurements were ineffective. However, using the time domain data taken from the oxide samples, plots of refractive index as a function of frequency were generated (Figure 3-7).
Note that the time-domain pulse for the oxide sample is greatly attenuated and also delayed in time. The refractive index as a function of frequency (right) shows that while there is mild fluctuation, the real part of the refractive index is consistently between 2.3 and 2.4, with the index rising at the higher frequencies.

The foundation for non-destructive imaging techniques using THz radiation has been well established on a variety of materials. Data collected from these images can be used to extract optical parameters such as index of refraction, absorption coefficient, etc. of that material. However, NDE on CMC materials is not yet well established and this thesis is the first examination of both oxide and silicon nitride-silicon nitride carbide samples at these frequencies.
IV. EXPERIMENTAL METHODOLOGY

THz images were taken of both oxide-based and silicon nitride carbon (SiNC) based ceramic matrix composite (CMC) samples. Future work will also include silicon carbide-silicon nitride carbon (SiC-SiNC) based samples. A 5.9 x 17.4 cm area is scanned, containing both an aluminum reference of dimension 15.7 x 1.3 x 0.2 cm and the CMC sample (see Fig 2-7). A full time-domain waveform, 250 ps long, is acquired for each 0.5 x 0.5 mm pixel. The samples are also of dimension 15.7 x 1.3 x 0.2 cm and are segmented into 11 blocks of equal area (Fig 4-1). This allows for comparative measurements to be isolated to the same area of each sample. Certain treatments may only be applied to a specific area of the sample and analysis is focused on those sections rather than on the entire sample.

As seen in Fig 4-1, each of the 11 blocks is 1.1 cm x 1.0 cm. Due to the high spatial resolution of the system at shorter wavelengths, each block is able to be broken down
into 42 sections, and each of those sections is composed of nine 0.5 mm x 0.5 mm pixels. This grid system allows for monitoring the absolute position of the beam on the sample. This is especially important due to the fact that in order to compare the reflected pulses from both the aluminum reference and the CMC sample so as to calculate the reflectivity, the pulses must be at the same relative location on both.

Graphs of normalized reflectivity (for a specific block) are plotted as a function of frequency. In all cases, the reflectivity is based on comparison of a THz pulse reflected from a CMC sample compared to the THz pulse reflected from the aluminum reference,

\[ R = r^2 \]

where

\[ r = \frac{E(f)_{Sample}}{E(f)_{Reference}} \]

Consequently, the changes in the reflectivity of these samples pre- and post- stress treatment were examined over smaller spatial sub-domains. The grid system that was developed allows for point by point comparative analysis of the imaging data. As a result,
it is possible to compare specific spatial points, with a resolution less than 1 mm, on samples prior to and following stress treatments. This analysis approach assesses the spatial variance of any stress induced changes in the terahertz reflectivity.

For this comprehensive study, there were multiple rounds of data acquisition. The first round consisted of spectroscopic imaging of all of the untreated samples. Additional rounds consisted of imaging of all the samples following treatments of either thermally or mechanically induced stress of varying magnitudes and also combinations of the two differing types of stress. Table 4-1 shows a list of all the samples imaged, along with a description of the damage applied to it. Samples which are undamaged are referred to as baselines. Comparison of the data both in the time-domain and frequency-domain acquired from this imaging of both the untreated and treated samples assessed whether or not the magnitude and extent of stress-induced changes can be monitored using THz frequency radiation.

Reflectivity as a function of frequency was plotted for both a damaged sample and its respective baseline. In many cases, the reflectivity data points fell within the standard deviation of each other making it difficult to determine if a measurable change in reflectivity had occurred, thus, a more rigorous statistical-based approach was required.
Table 4-1: Sample Chart

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>CMC Type</th>
<th>Applied Damage</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-29R1</td>
<td>Oxide</td>
<td>Baseline</td>
</tr>
<tr>
<td>A-29R2</td>
<td>Oxide</td>
<td>Heat Treatment: 1000°C for 100 hours</td>
</tr>
<tr>
<td>A-29R3</td>
<td>Oxide</td>
<td>Secondary Heat Treatment: 1100°C for 100 hours</td>
</tr>
<tr>
<td>A-30R1</td>
<td>Oxide</td>
<td>Baseline</td>
</tr>
<tr>
<td>A-30R2</td>
<td>Oxide</td>
<td>Fatigue Treatment</td>
</tr>
<tr>
<td>A-31R1</td>
<td>Oxide</td>
<td>Baseline</td>
</tr>
<tr>
<td>A-31R2</td>
<td>Oxide</td>
<td>Dwell Fatigue Treatment</td>
</tr>
<tr>
<td>B-29R1</td>
<td>SiNC</td>
<td>Baseline</td>
</tr>
<tr>
<td>B-29R2</td>
<td>SiNC</td>
<td>Heat Treatment: 1200°C for 100 hours</td>
</tr>
<tr>
<td>B-30R1</td>
<td>SiNC</td>
<td>Baseline</td>
</tr>
<tr>
<td>B-30R2</td>
<td>SiNC</td>
<td>Fatigue Treatment</td>
</tr>
<tr>
<td>B-31R1</td>
<td>SiNC</td>
<td>Baseline</td>
</tr>
<tr>
<td>B-31R2</td>
<td>SiNC</td>
<td>Dwell Fatigue Treatment</td>
</tr>
<tr>
<td>B-32R1</td>
<td>SiNC</td>
<td>Baseline</td>
</tr>
<tr>
<td>B-32R2</td>
<td>SiNC</td>
<td>Heat Treatment: 1200°C for 10 hours</td>
</tr>
</tbody>
</table>

The difference in reflectivity was calculated by

\[ Diff(f) = R(f)_{baseline} - R(f)_{sample} \]

and plotted with error bars as defined by +/- 2 \( s_e \). This standard error was calculated via

\[ s_e = \frac{\sigma_x}{\sqrt{N}} \]

where \( \sigma_x \) is the standard deviation as shown below, and N is the number of data points comprising the reflectivity curve for the range of interest between 0.05 and 2 THz.

\[ \sigma_x = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x_i - \bar{x})^2} \]

If Diff(f) +/- 2 \( s_e \) remained above zero, there was a statistically significant difference in reflectivity observed (Fig. 4-3).
Table 4-2: Difference Calculations

<table>
<thead>
<tr>
<th>Frequency: (THz)</th>
<th>Reflectivity: Baseline</th>
<th>Reflectivity: sample</th>
<th>Difference: (Base – Samp)</th>
<th>$\sigma_x$</th>
<th>$s_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.096</td>
<td>0.25893</td>
<td>0.22908</td>
<td>0.02985</td>
<td>0.02626</td>
<td>0.00303</td>
</tr>
<tr>
<td>0.128</td>
<td>0.29045</td>
<td>0.22939</td>
<td>0.06107</td>
<td>0.02626</td>
<td>0.00303</td>
</tr>
<tr>
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<td>0.27068</td>
<td>0.23729</td>
<td>0.03339</td>
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<td>0.21817</td>
<td>0.03846</td>
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<td>0.14564</td>
<td>0.05848</td>
<td>0.02626</td>
<td>0.00303</td>
</tr>
</tbody>
</table>

Fig 4-3: Heat Treated SiNC sample (left) and Difference in Reflectivity for that sample (right). Each plot includes error bars of 1σ.

Fig 4-3 shows reflectivity for both an undamaged SiNC sample (black) and a heat treated SiNC sample (blue) in the S-polarization configuration. Based on this graph alone, it is difficult to determine if a change in reflectivity is seen, because, despite the drop in reflectivity, both reflectivity plots lay within the standard deviation of each other. However, by looking at the difference in reflectivity, it becomes obvious that a statistically significant change (although small in magnitude) in reflectivity is seen.

As a general trend, most of the CMC samples (Fig. 4-4) have frequency bands/regions where a difference in reflectivity can be seen for the top half of the sample. The lower half of the samples tend to have trends where no difference in reflectivity is seen. These changes in reflectivity are tied to optical properties of the material, such as the index of
refraction via Fresnel’s laws. Note however these calculations assume that the only change is in the real part of the refractive index and more analysis will need to be done in order to find changes (if they exist) in the imaginary part as well.

\[ R_s = \left| \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \right|^2 = \frac{n_1 \cos \theta_i - n_2 \sqrt{1 - \left(\frac{n_1}{n_2}\right)^2 \sin^2 \theta_i}}\left| n_1 \cos \theta_i + n_2 \sqrt{1 - \left(\frac{n_1}{n_2}\right)^2 \sin^2 \theta_i} \right|^2 \]

\[ R_p = \left| \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \right|^2 = \frac{n_1 \sqrt{1 - \left(\frac{n_1}{n_2}\right)^2 \sin^2 \theta_i} - n_2 \cos \theta_t}{n_1 \sqrt{1 - \left(\frac{n_1}{n_2}\right)^2 \sin^2 \theta_i} + n_2 \cos \theta_t} \]

where \( \theta_i \) and \( \theta_t \) are the angles of incidence and transmission, respectfully. Allowing \( n_1 \) to be air, \( n_2 \) can be isolated in terms of the other variables and the real part of the index of refraction to be calculated as a function of frequency.

\[ n_2 = \frac{\cos^2 \theta_i \left(\sqrt{R_s} - 1\right)^2}{\left(\sqrt{R_s} + 1\right)^2} - \sin^2 \theta_i \]
While this chapter outlined how the data was acquired and the mathematical process required to calculate reflectivity, the next two chapters will discuss the results of both the oxide and the SiNC materials.

Fig 4-4 Difference in Reflectivity Trends
V. RESULTS: OXIDE

This chapter focuses on the data collected from THz spectroscopic imaging of the Oxide CMC materials. A 5.9 x 17.4 cm area is scanned, containing both an aluminum reference and the CMC sample (see Fig 4-1). A full time-domain waveform, 250 ps long, is acquired for each 0.5 x 0.5 mm pixel. Reflectivity as a function of frequency was then calculated for every pixel within a block and then averaged across the entire block. The following average reflectivity graphs are for Block 3 of the sample, unless otherwise stated.

Fig. 5-1. Reflectivity measurements of oxide heat treated sample for P and S polarization rotations, (left and right respectively). The undamaged baseline is indicated by the black, and the heat treated sample is indicated in red.
The oxide data sets follow a downward trend in reflectivity for higher frequencies. The jagged features between 0-0.25 THz along with the spike in reflectivity at 1.6 THz are characteristic of the oxide samples. Fig 5-1 shows an undamaged oxide sample before and after receiving heat treatment at 1000°C for 100 hours (A-29R1 and A-29R2, respectively). The trend and magnitude of reflectivity do not change following heat treatment, as seen in the figure. In order to determine if there is a statistically significant difference in reflectivity between a damaged sample and baseline, the difference in reflectivity (as described in Chapter 4) can also be examined. For the A-29R2 sample, there is no statistical difference seen in either polarization.

The A-29R2 sample was then exposed to a secondary round of heat treatment, at a higher temperature of 1100°C for 100 hours.
The A-29R3 sample does follow the same general trend as the undamaged baseline in the low frequencies, however around 0.25 THz there is an increase in reflectivity; this trend is not present in the S-polarization. In both polarization configurations there is a significant increase in the standard deviation of this sample in comparison to both the A-29R1 and A-29R2 samples. Looking at the difference in reflectivity of the A-29R3 sample in comparison to the baseline there is not a statistical difference in reflectivity seen for either polarization. The increase in reflectivity of the A-29R3 sample has been
observed in two independent image scans in the P-polarization. Despite the fact that such a significant change in reflectivity is seen, this is not apparent when simply comparing spectroscopic images. Figure 5-5 shows the undamaged A-29R1 sample on the left, and the A-29R3 double heat treated sample on the right. Upon visual inspection of these images, such a dramatic change in reflectivity cannot be seen. Visual inspection of images is not only difficult but time consuming. By using the information contained within the time-domain and spectral data to do comparisons, the process is not only easier, but has a significantly faster throughput.

![Fig. 5-5 Images based on time domain maximum amplitude of A-29R1 (left) and A-29R3 (right). The image on the right shows the A-29R3 sample placed immediately to the right of the aluminum reference piece.](image)
The fatigue treated sample (A-30R2) followed the same general trend of the baseline and no obvious changes in reflectivity can be seen for the P-polarization. The reflectivity difference plots also show no statistical difference in reflectivity. The S-polarization configuration however shows a more pronounced broadening of the reflectivity between 0.6 THz and 1.25 THz than in the P-polarization case. However, statically no changes in reflectivity can be seen in this polarization.

Fig. 5-6. Reflectivity measurements of oxide fatigue treated sample for P and S polarization rotations, (left and right respectively). The undamaged baseline (A-30R1) is indicated by the black, and the fatigue treated sample (A-30R2) is indicated in red.

Fig 5-7. Difference in reflectivity for oxide fatigue treated (A-30R2) sample for P and S polarization rotations, (left and right respectively)
The dwell fatigued oxide sample also showed no changes in reflectivity for P-polarization. Due to lack of time, S-polarization scans have yet to be properly acquired, however there is no expectation to see a change in reflectivity for that polarization. Due to the result that the oxide samples showed no statistical difference between thermal and mechanical treatments applied independently, it is expected that no changes should be seen when treatments are applied simultaneously.

The results from the oxide samples were discussed in this chapter. Oxides samples showed no obvious change in reflectivity after receiving either heat or fatigue treatments. The next chapter will outline the results pertaining to the SiNC materials.
VI. RESULTS: SINC

This chapter focuses on the data collected from the SiNC CMC materials. As with the oxide based samples, a 5.9 x 17.4 cm area is scanned, containing both an aluminum reference and the CMC sample (see Fig 4-1). A full time-domain waveform, 250 ps long, is acquired for each 0.5 x 0.5 mm pixel. Reflectivity as a function of frequency was calculated for every pixel within a block and then averaged across the entire block. The following average reflectivity graphs are for Block 3 of the sample, unless otherwise stated.

Fig. 6-1. SiNC Heat Treated Samples for P and S polarization configurations (left and right respectively). The undamaged baseline (B-29R1) is indicated by the black, and the 100 hour heat treated sample (B-29R2) is indicated in blue.
Fig. 6-1 shows reflectivity as a function of frequency for a SiNC sample before and after undergoing a heat treatment for both the P (left) and S (right) polarization configurations. For the P-polarization, the oscillatory trend from 100 GHz - 0.6 THz is evident in all SiNC samples and is believed to be a characteristic trait of these materials. Following heat treatment of 1200°C for 100 hours, the magnitude of reflectivity maintained the same general trend of the baseline with a decrease in reflectivity by approximately 0.1 for the entire frequency span shown. Measurements done with the S-polarization show no discernible difference between the heat treated sample and the baseline in comparing reflectivity data. Also note the resonant peaks at 125 GHz and 300 GHz, which appear in the P-polarization, but not in the S-polarisation.

In order to determine if there is a statistically significant difference in reflectivity between a damaged sample and baseline, the difference in reflectivity (as described in Chapter 4) can also be examined. For the B-29R2 sample, there is a discernible difference in the reflectivity (as seen in Fig. 6-1) but is further reinforced by examining the difference in reflectivity. In the S-polarization, there is no obvious change in

Fig 6-2. Difference in reflectivity for SiNC heat treated sample for P and S polarization rotations, (left and right respectively)
reflectivity, however examining the difference in reflectivity, a statistical difference can be seen in the band from 0.1 – 1.0 THz.

Fig. 6-3. SiNC Heat Treated Samples for P and S polarization configurations (left and right respectively). The Undamaged baseline (B-32R1) is indicated by the black, and the 10 hour heat treated sample (B-32R2) is indicated in blue.

Fig 6-4. Difference in reflectivity for SiNC heat treated sample for P and S polarization rotations, (left and right respectively)

Since an observable change in reflectivity was seen for a 100 hour treated sample, a second SiNC sample was heat treated at 1200°C for 10 hours in order to determine if a smaller magnitude of thermal treatment would cause a change in reflectivity. Once again, in the P-polarization an obvious change in reflectivity is seen. In the S-polarization there is a slight drop in reflectivity from 0.1 – 1.25 THz. Both of these
changes can be classified as significant based on their respective difference in reflectivity plots (Fig 6-4).

Fig. 6-5. SiNC Heat Treated Samples for P and S polarization configurations (left and right respectively). The undamaged baseline (B-29R1) is indicated by the black, and the 10 hour heat treated sample (B-32R2) is indicated in red, and 100 hour treated sample (B-29R2) in blue.

Fig. 6-5 shows reflectivity for both the 10 hour (red) and 100 hour (blue) heat treated SiNC samples together with the undamaged baseline it is apparent that in the P-polarization there is a correlation between the magnitude of thermal treatment and a decrease in reflectivity.

Fig. 6-7. SiNC Fatigue Treated Samples for P and S polarization configurations (left and right respectively). The undamaged baseline (B-30R1) is indicated by the black, and the fatigue treated sample (B-30R2) is in blue.
Fig. 6-6 is a plot of reflectivity as a function of frequency for a SiNC sample before and after undergoing a fatigue treatment. In the lower frequencies, out to 600GHz there is no apparent change in magnitude of reflectivity. However, in the higher frequencies the reflectivity diverges, with the fatigue treated sample exhibiting a lower reflectivity. The S-polarization shows a slight decrease in reflectivity from 0.1-1.6 THz, this is further evidenced Fig 6-8.

Fig. 6-9 Spectral Images of the B-30R1 sample at 250 GHz (left) and 1.25 THz (right).
Dwell fatigue is a simultaneous combination of fatigue and heat treatment induced simultaneously. These treatments are concentrated only on the middle of the sample. Sample reflectivity following a dwell fatigue treatment of Block 5 is represented in Fig. 6-11. Unlike the isolated fatigue treatment, at lower frequencies the magnitude of reflectivity is less than that of the baseline. There is also no divergence at the higher frequencies.

Due to the evidence that fatigue treatments have an effect on reflectivity at these frequencies, the fatigue contribution to the dwell treatment was negligible. For the range of 0.25 - 2.0 THz, the magnitude of change in reflectivity is ~0.1, the same as an isolated heat treated sample. This consistent decrease in reflectivity from the dwell fatigue treated sample leads to the conclusion that the prominent contributing factor is the heat portion.
Fig. 6-11 Reflectivity measurements of oxide dwell fatigue treated sample for P-polarization (left). The undamaged baseline (B-31R1) is indicated by the black, and the dwell fatigue treated sample (B-31R2) is indicated in blue.

Difference in reflectivity for SiNC dwell fatigue treated sample for P-polarization (right)
VII. CONCLUSIONS

In this thesis, the method of generation and detection of time-domain THz radiation was discussed as well as various application of THz imaging from historical artwork through material characterization. THz imaging is ideal for non-destructive evaluation purposes. Non-destructive testing on ceramic materials is still relatively unexplored, specifically in regard to work on CMC materials. This thesis work was the first THz time-domain characterization of both the Oxide and SiNC type CMC materials. The image acquisition process and data analysis (including the statistical analysis) methods were explained in detail as well as methods of extraction of optical parameters from the data.

Imaging of the oxide sample set showed no measurable change in reflectivity when exposed to high levels of thermal stresses. However, when fatigue damage was applied, mild differences were observed, though no changes were seen from application of dwell fatigue on the oxide samples. The SiNC samples on the other hand, showed measurable and consistence changes in reflectivity when exposed to thermal treatments. In addition, fatigue treatments resulted in measurable changes in reflectivity over certain portions of the SiNC samples. Dwell fatigue treatments were the most effective at producing changes in reflectivity for the SiNC samples.
<table>
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<tr>
<th>Sample</th>
<th>Difference in Reflectivity</th>
<th>Magnitude of Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide: (Heat 1000 °C)</td>
<td>No</td>
<td>-</td>
</tr>
<tr>
<td>Oxide: (Heat 1100 °C)</td>
<td>No</td>
<td>-</td>
</tr>
<tr>
<td>Oxide: (Fatigue Treated)</td>
<td>Yes</td>
<td>Mild</td>
</tr>
<tr>
<td>Oxide: (Dwell Fatigue)</td>
<td>No</td>
<td>-</td>
</tr>
<tr>
<td>SiNC: (Heat 100 hours)</td>
<td>Yes</td>
<td>Strong</td>
</tr>
<tr>
<td>SiNC: (Heat 10 hours)</td>
<td>Yes</td>
<td>Strong</td>
</tr>
<tr>
<td>SiNC: (Dwell Fatigue)</td>
<td>Yes</td>
<td>Strong</td>
</tr>
<tr>
<td>SiNC: (Fatigue Treated)</td>
<td>Yes</td>
<td>Strong in 0.75-2.0 THz range</td>
</tr>
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</table>

**SOURCES OF ERROR**

Prior to receiving the samples, all of the CMC materials were all individually labeled with red ink for the Oxides and a graphite pencil on the SiNC samples. Graphite is very reflective at THz frequencies, and as a result sections of almost all the SiNC samples were unusable. This limited reflectivity calculations to the center of the samples to avoid error introduced by the enhanced reflectivity of graphite on the surface of the samples. As THz is very transmissive to thin layers of dried ink, no such restriction was necessary on the oxide samples.

Each of the damaged CMC samples imaged was unique in that no two samples were damaged in the same magnitude or manner. Because there was no case in which two samples were both given the same stress treatments, repeatability of results has yet to be determined. There are some cases, particularly with the A-29 Oxide sample which the calculated reflectivity is unlike any of the other calculated reflectivity trends of the other Oxides. Whether this is an anomaly or accurate representation of the change reflectivity due to these heat treatments cannot be determined unless it were compared to another Oxide sample which received two heat treatments of the same magnitude and duration as those applied to the A-29 sample.
FUTURE WORK

Experimental future work will include imaging of a third set of CMC materials, the silicon-carbide-silicon-nitride carbide (SiC-SiNC), for which the process of imaging and monitoring damage will be the same as on the oxide and SiNC sets. Initially transmission measurements taken at normal incidence were acquired for the CMC materials. The SiNC samples were too optically thick to take advantage of this technique. Despite severe attenuation of the pulse, transmission data was able to be acquired for the outer edge portion of the oxide samples. Transmission through the center of the samples was not feasible due to the length of the samples themselves and the confined space available in the transmission chamber. The PC modules used in the reflection imaging experimental set up can be repositioned on the gantry to do transmission measurements, though it should be noted that such an experimental set up would require a significant amount of time to prepare for data taking. While optical parameters can be derived from reflection data, the ability to compare the calculated values of index of fraction, absorption coefficient, etc. with those calculated from the transmission data of the same sample would provide confirmation of the correctly calculated values.

Further data analysis that quantifies changes in the index of refraction and absorption coefficient as a function of frequency is needed. In an attempt to continuously populate the predictive model for correlating a change in reflectivity to the magnitude of treatment applied, more images will have to be acquired and analyzed on samples of varying degrees of magnitude of thermal damage for the SiNC samples.
REFERENCES


