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ANALYSIS OF LASER INDUCED SPALLATION OF ELECTRON BEAM PHYSICAL VAPOR DEPOSITED (EB-PVD) THERMAL BARRIER COATINGS

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

By

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ABSTRACT

Beeler, David A. M.S.Egr., Department of Mechanical and Materials Science Engineering, Wright State University, 2013. Analysis of Laser Induced Spallation of Electron Beam Physical Vapor Deposited (EB-PVD) Thermal Barrier Coatings.

The use of thermal barrier coatings (TBCs) has been an important factor in the efficiency improvements of jet engines due to their ability to withstand the extreme environments within the engine. With this improved resistance, TBCs have also become more difficult to remove without damaging the substrate. Mound Laser & Photonics Center, Inc. (MLPC) has developed an innovative, laser based technique to spall this coating. The intention of this work was to investigate and better understand the removal mechanism. Through experimentation and analysis (such as high speed video, Scanning Electron Microscopy and Energy Dispersive Spectroscopy, semi-logarithmic analysis, and a numerical thermal model) information supportive of a two stage thermal and rapid vaporization based mechanism has been obtained. The method and analysis presented in this work helps to expand the understanding of thermal and rapid vaporization spallation techniques as well as guide MLPC in optimization of their process.
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Contributions

This thesis contributes to the area of laser and material interaction. Specifically, it introduces a novel method of coating removal to the fields of coating technologies and coating repair. The primary objective of this thesis was to investigate the underlying mechanism utilized by this method.

Although this thesis has benefited from the research performed within the laser cleaning community, it also impacts the current state of research for coating removal as well as particulate removal in the following ways:

1. transition of laser steam cleaning methodology to systems larger and more complex than particulate contamination,

2. identification of a non-hazardous and controllable method of removing thermal barrier coatings from a metal substrate, and the

3. removal of thermal barrier coatings in an effective manner while still maintaining the integrity of the underlying substrate.
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1 Introduction

Thermal barrier coatings (TBCs) are a development based on the need to improve the efficiency and lifetime of turbine engine components. These coatings exist to provide thermal insulation and to protect the metal substrate from the extreme environment within the turbine engine.[1] Through this application, the metal substrate experiences a reduced thermal effect of up to 200°C as compared to substrates without TBCs.[2] These TBCs generally follow a structure of substrate (nickel superalloy), bond coat (nickel-aluminum alloy), thermally grown oxide (TGO) layer (aluminum oxide), and yttria-stabilized zirconia (YSZ).[3] Although there are two main methods of depositing TBCs, plasma spraying (PS) and electron beam physical vapor deposition (EB-PVD), this work focuses on TBC deposited through the EB-PVD process. When the EB-PVD process is used, the YSZ grows in a columnar structure with inter-columnar pores perpendicular to the substrate.[4] As the TBC is intended to survive the caustic turbine engine environment, their removal is not trivial. Currently, the primary methods of TBC removal are grit blasting, autoclave, and water jet.[5] These methods are not highly controllable, do not allow for selective removal, and can be damaging to the substrate. This thesis entails the understanding and analysis of a laser removal process that allows for controllable and selective removal with minimal substrate damage, which is of special interest to the original equipment manufacturers of turbine blades.
1.1 Objective

The primary objective of this thesis is to understand a recently developed laser removal process by Mound Laser & Photonics Center, Inc. and the mechanism it utilizes to remove EB-PVD TBC. Through a better understanding of this mechanism more optimal parameters are hoped to be developed as well as the potential for utilization of the process on other coating types. Experimentation on one-inch circular coupons will be performed in addition to a variety of analyses, including high speed video, scanning electron microscopy and energy dispersive spectroscopy, semi-logarithmic analysis, and basic thermal calculations.
2 Background Information

2.1 Thermal Barrier Coating Structural Information

Although there are a variety of thermal barrier coatings in use, they generally follow a similar structure. Figure 1 below illustrates an idealized structure for the one-inch button coupons that have been used throughout this work. For these coupons, the substrate is a nickel based superalloy with a nickel-aluminum bond coat. Through a pretreatment process, the thermally grown oxide (TGO), which is primarily an aluminum oxide, is grown from the bond coat after the yttria-stabilized zirconia (YSZ) is applied using electron beam physical vapor deposition (EB-PVD). This deposition process results in columnar YSZ with inherent porosity. The porosity and hydrophilic nature of the YSZ allows the fluid to “absorb” into the structure, illustrated with the vertical blue segments. Actual YSZ (shown in the inset image) does not form a columnar structure that is perfectly aligned.
2.2 Spallation

Throughout this work the removal of the YSZ layer will be referred to as spallation. The term spallation refers to the ejection of a coating from a substrate through the means of impact or force being applied to the coating. The phrase laser spallation is most commonly used when describing laser shock processing, which will be described in more depth in Section 3.1.

2.3 Spatial and Temporal Beam Profiles

Depending on the intention of a laser system, different spatial and temporal profiles are commonly utilized. A spatial beam profile refers to a cross sectional view of the beam. Three different examples of spatial profiles are shown below in Figure 2; Gaussian type, flat-top type, and an other type. This view of a laser beam provides information on how the laser will interact with a material. A Gaussian beam has high intensity energy at the very center and uses that portion of the beam during said interaction. A flat-top beam has relatively homogenous energy throughout the profile and

Figure 1: Illustration of an Ideal Coupon Structure
interacts with the surface more evenly than a Gaussian profile. The last image is the profile of the laser system used throughout this work. The highest intensity is neither centered nor homogenous as there is a ring of high intensity with lower intensities both inside and outside of this ring.

![Three Different Laser Beam Spatial Profiles](image)

**Figure 2: Three Different Laser Beam Spatial Profiles (Gaussian, Flat-Top, and Other)**

The temporal profile defines the shape of the pulse with respect to time. In general, there are two different types of pulse shapes, rectangular and Gaussian as shown in Figure 3 below for comparison purposes. The system used in this work has a temporal profile similar to a Gaussian shape. Rectangular pulse shapes apply their energy consistently over the pulse duration; whereas Gaussian pulses are most intense in the middle of the pulse duration.

![Rectangular and Gaussian Temporal Profiles](image)

**Figure 3: Rectangular and Gaussian Temporal Profiles**
2.4 Pulse Energy, Fluence, and Peak Power Density

When using a laser system, the intensity is generally referred to by a measurement of energy or power. For a pulsed laser, that is, a laser system that fires at a consistent repetition rate, pulse energy is a measurement of the energy for each shot (pulse) of the system. For the system used in this work, the repetition rate is 10Hz (1/10 seconds) so every 0.1 seconds a single pulse is emitted. The energy of this pulse is measured in Joules (J), and has variance from pulse to pulse.

The fluence of a laser system is a more specific measurement of energy, specifically the concentration or density. When pulse energy is used, this value only provides information on the pulse itself, not on the amount of energy used at the work surface. By taking the area of the beam at the work surface, fluence can be calculated by dividing the pulse energy by the area, measured in J/cm$^2$.

To describe peak power density, first the peak power must be calculated. Peak power is the pulse energy divided by the pulse duration, but when the temporal profile is of Gaussian shape, this number is multiplied by 0.94 to account for the difference in energy. Similar to fluence, peak power density is more specific as it requires the area of the spot being irradiated. Thus, peak power density is calculated by the peak power divided by the area, measured in W/cm$^2$.

2.5 Reflection and Absorption

Reflection and absorption play a major role in the following work. Mirrors are manufactured specifically to have a very high percent of reflection (as close to 100% as possible). Although reflection naturally occurs on most surfaces, the percentage is
dependent on the wavelength of light and the optical properties of the surface. The idea that dark clothing is warmer in the sun than light colored clothing helps illustrate the concept of absorption. When dealing with the visible spectrum, the color of the material is directly related to the level of absorption. However, the laser used throughout this work has a wavelength that is outside of the visual spectrum (1064nm). Depending on the composition and structure of the material, 1064nm light may have a high absorption coefficient (given in units of cm$^{-1}$), e.g. nickel, or a very low absorption coefficient, e.g. water. For these two materials, if they were of similar thickness, nickel would absorb the most energy whereas water would absorb the least. When a material is referred to as being transparent to a wavelength of light, the absorption coefficient is either zero or sufficiently low such that the loss is negligible. The coupons used in this work and the materials therein have different absorption coefficients and reflection percentages and as such interact very differently with a 1064nm laser pulse.
3 Literature Review

Although there are a variety of potential mechanisms and methods available for coating removal, for the purposes of this thesis, three classes will be discussed as they have similarities to the removal mechanism under investigation. These classes include laser shock processing (LSP), laser-induced thermal removal, and removal by explosive vaporization.

3.1 Laser Shock Processing (LSP)

The basic principal behind Laser Shock Processing (LSP) is illustrated in Figure 4 below. A laser pulse passes through a transparent layer (waterglass is frequently used for its reflection and absorption properties) and interacts with the substrate forming a plasma plume. A plasma plume is generated when the laser intensity is sufficient to ablate (vaporize) a material, which in turn creates a gas with a temperature intense enough that the gas becomes charged. In addition to being transparent, this layer surrounds the formed plasma limiting the expansion and thus a shock wave is generated. The shock wave travels through the substrate until it is reflected by the coating layer, forming a tensile wave. Given that the stress generated by this tensile wave has greater amplitude than the bond strength, the bond is broken.[6]
Removal of the coating at the coating-substrate interface is the ideal failure type of this mechanism. However, depending on the amplitude of the stress pulse and the structure of the coating, other failure modes are possible. This includes fracture inside of the coating, fracture at both the coating-substrate interface and inside of the coating, removal of the coating at the interface, or removal of the coating within the coating layer.[6]

One modification of the LSP method is the addition of a thin aluminum layer (sub-micron thickness) that will melt by sufficiently intense laser energy. The expansion from melting while contained creates a stress pulse that will propagate towards the coating layer. Similarly to the laser induced shock wave, the stress pulse is reflected off the coating, becomes a tensile stress wave, and if it has adequate amplitude, a fracture between the coating and the substrate will be formed.[7]
Due to the efficiency of this method, it has shown to be a popular choice when investigating coating bond strength. The method’s effectiveness is also not limited to a specific material bond type. Various researchers have performed the method on metal-metal, metal-ceramic, and metal-polymer substrate-coating structures.[8–12]

Although not intended for coating removal, but for inducing compressive stresses into the surface, research has also been performed in the generation of shock waves from the coating side. The structure is similar in which there needs to be a containing layer, an absorptive layer, and a substrate which will receive the compressive stress. As the laser energy passes through the containing layer, it rapidly vaporizes the absorptive layer creating a plasma bubble. As the plasma expands but remains trapped, a short pressure pulse is created, part of which travels into the substrate as a shock wave. This shock wave then creates compressive forces in the substrate.[13] Montross et al. studied the shock wave pressure generation and found it can be enhanced with a structure composing of water (the containment layer), paint (the absorptive layer), and substrate. Montross et al. go on to compare the range of energy levels, materials for substrates and containment layers, and more. In their comparison, the range of power density for typical laser shock processing parameters is from $0.1 \times 10^4$ GW/cm$^2$. From the provided values and those using water as the transparent layer, the fluence ranges from $70 – 318$ J/cm$^2$ and with a resultant pressure of $2.5 – 6$ GPa.

3.2 Laser-Induced Thermal Removal

The principal behind laser-induced thermal removal is very similar to LSP but instead of shock wave generation, thermal decomposition and subsequent gas formation
is the basis of the mechanism. Figure 5 below shows the basic layer structure for this type of removal. As an incident laser pulse passes through the coating, the absorptive layer is rapidly heated and goes through a gas-phase decomposition. A bubble is formed between the coating and the substrate and as more gas is created permanent delamination results. Frequently the laser energy is minimized to reduce thermal effects such as melting of the substrate and bond damage.[14], [15]

![Figure 5: Illustration of Laser-Induced Thermal Removal](image)

Depending on the energy level, the extent of the delamination of the coating can be minimal, where the coating requires post-processing cleaning to remove the delaminated section, or it can be explosive, tearing extra coating away from the substrate in the process.[15], [16] Hare, Rhea, and Dlott have also performed experimentation of transmitting the laser energy through the substrate to remove the coating, but this method requires the substrate to be highly transparent to the laser wavelength.
For this removal mechanism, the fluence values range from 0.11 – 2.19 J/cm² across different researchers as well as performing the removal from the coating side and from the substrate side.[14–17] By incorporating an absorptive layer that will outgas during decomposition, the threshold fluence is reduced drastically as compared to the LSP thresholds. This ability enables the process to remove coatings with less concern of damaging the substrate as well as improving the overall laser efficiency in the removal process.

### 3.3 Explosive Vaporization

The principal behind explosive vaporization involves the rapid phase change from liquid to gas through a high temperature gradient. Although there is extensive research in the area of explosive vaporization, only two subsets will be briefly discussed here due to their connection with the mechanism under investigation: the Leidenfrost Phenomenon and laser cleaning.

#### 3.3.1 The Leidenfrost Phenomenon

In 1756 Johann Gottlob Leidenfrost published “A Tract about Some Qualities of Common Water” in which he described a phenomenon pertaining to contact between a water droplet and a hot surface.[18] Although Leidenfrost was not able to fully investigate and understand the process, over the years since, many researchers have been investigating this phenomenon. The current state of this research provides the understanding that upon contact with a heated surface, depending on the temperature of said surface, a portion of the water droplet will vaporize and form a “cushion” layer between the droplet and the surface preventing the droplet from rapidly boiling.[18], [19]
In fact, if the temperature of the surface is within the Leidenfrost range for water (250°C to 310°C) the cycle of vaporization, formation of the “cushion” layer, and condensation will allow the droplet to survive on the surface for seconds up to minutes, depending on the size of the droplet and the specific temperature.[19]

As the temperature of the surface increases and / or the lifetime of the droplet decreases, the rapid vaporization of the water can become explosive in nature. In some cases, such as those where a droplet is simply dropped onto a heated surface, the explosive nature is minimal and the droplet simply rebounds from the surface.[20] In principle, if the liquid is contained or has a larger mass to surround the heated surface, the energy from the expanding vapor into the surrounding liquid can be sufficient to drive electromechanical microdevices.[21] In the experiments of Glod et al., a platinum wire was heated at a rate of 86x10⁶ K/s with a heating pulse of 4.5μs resulting in explosive vaporization within 8μs. Another group used parallel plates with a heat rate of 1.8x10⁹ K/s and a heating pulse of 0.2μs, resulting in explosive vaporization within 0.461μs.[22]

These experiments have been performed with a metal surface undergoing a thermal increase due to electrical conduction and as such have been capable of producing explosive vaporization within one microsecond. Heat rates of higher intensity can be generated through the use of a laser and as such should be able to produce similar results. The main difference for a laser based process is that the absorption coefficient of the water and the substrate must be appropriate for the wavelength of the chosen laser. One group used a 248nm, 24ns KrF excimer laser to produce explosive vaporization of water. This group used fluence values of <120 mJ/cm² resulting in the peak surface temperature of a chromium substrate of less than 900K, thus avoiding surface melting but still
sufficient for water vaporization. Through their experiments, they determined a few key factors. Firstly, that fluence values below the vaporization threshold would result in pressure generation due to thermoelastic sources. Secondly, that values above this threshold would result in pressure generation due to bubble generation / growth. Thirdly, as long as the fluence is sufficiently low, no plasma generation would occur to add to the pressure generation. And finally, at 51.3mJ/cm$^2$ a specular reflection analysis showed a drop in the obtained data, due to scattering loss from bubble formation / nucleation, thus identifying the bubble nucleation threshold.[23]

### 3.3.2 Laser Cleaning

Park et al. showed that with relatively low fluence values and an appropriately paired laser source, explosive vaporization can be achieved with water on a metal substrate. Advancements in technology, specifically the reduction in component size, have required the need for removal of small particles (0.1µm).[24] In the experiments of Tam, Ayers, and Ziemlich, the sudden heating of the liquid film results in expansion forces that can be strong enough to overcome the particle-to-substrate adhesion forces of these contaminants.

In order to cause the sudden heating of the liquid film, either the fluid or the substrate itself must be strongly absorptive to the laser wavelength. One group broke down the different techniques utilized in laser cleaning through a discussion of dry and steam cleaning as well as the efficiency differences when the liquid film, substrate, or both film and substrate absorb more strongly. The final result of these experiments
showed that steam cleaning, where the substrate absorbs the laser most strongly, is the most efficient and least damaging method for removing small contaminants. [25]

Figure 6 above illustrates the general concept for steam laser cleaning where the substrate is the absorptive layer. The laser pulse propagates through the water film with minimal losses, is strongly absorbed into the substrate, and rapidly increases the temperature of the film-substrate interface. This temperature gradient can cause the water at this interface to boil and vaporize and if the gradient is sufficient, the generated pressure burst due to the vaporized water will apply force against the particle and overcome the adhesion forces (consisting of Van der Waals, capillary, and electrostatic forces) and eject the particle from the substrate. [25], [26]

Tam et al., found that the particles were being ejected at velocities of greater than $10^4 \text{cm/s}$ producing a jet of water droplets and a shock pulse in the air causing an audible snapping sound. Using a 248nm KrF excimer laser with a pulse duration of 16ns, Tam et
al. found that a fluence range of 30-300mJ/cm² was generally sufficient to remove a variety of contaminants from a silicon wafer (stressing on sub-micron diameter particles). The researchers Hsu and Lin performed similar experimentation with larger particle sizes (10-45μm) on 304 stainless steel with a KrF excimer laser at 248nm and a 30ns pulse duration. Their experimentation showed effective removal when using a fluence range of 305 – 1591 mJ/cm².
4 Efforts to Remove Thermal Barrier Coatings

The purpose of this work was to identify and better understand the underlying mechanism that was developed by Mound Laser & Photonics Center, Inc. (MLPC) to remove EB-PVD thermal barrier coatings from a nickel based substrate. Initial efforts in removing the coating were focused on laser ablation of the YSZ layer. Through spectral monitoring of the plasma plume formed during the ablation, a trigger could be sent to the laser system to stop ablating the coating to minimize substrate damage. Although this process was capable of removing the YSZ, it was determined that the method would be costly both on the capital equipment side as well as required processing time.

Due to the conditions the YSZ layer must withstand while in service, it has proven to be a challenge to remove. Some of the popular methods of removal are focused around caustic etching of the YSZ, water jet stripping, and abrasive grit blasting. [5] In an effort to find an alternative method of removal that would be less damaging to the substrate as well as be more controllable, a method akin to laser shot peening was tested using an in-house system at MLPC. The general requirements of laser shot peening are similar to laser cleaning, but with much higher energies (50-250J/cm², 4-12GW/cm²).[27] The pulse passes through the containing layer, which is frequently water, and then ablates an absorptive layer. The energy of this pulse at the absorptive layer is sufficiently high to generate a plasma bubble between the substrate and containing layer. The containing layer controls the plasma expansion in a manner that causes compressive stress to be imparted into the substrate. The original process developed at MLPC was intended to be...
similar, but performed using significantly lower energies (2-5J/cm$^2$, 0.2-0.5GW/cm$^2$). The original hypothesis of the mechanism was that the generated shock wave was sufficient to disrupt the bond between the TGO and bond coat and remove the coating where the pulse was emitted. Although YSZ removal was found to be repeatable, little was known about the mechanism being utilized. In an effort of investigating the mechanism and thus the ability of improving efficiency and expanding its use, this work was initiated.

The mechanism was first experimented through the use of one-inch coupons with thermal barrier coatings deposited using the EB-PVD process. From the original experimentation, it was thought that a layer of water of approximately 100μm was required to perform the mechanism. Thus, preliminary experimentation was performed by flowing water over the one-inch coupons and through the use of a Spectra-Physics DCR-2A (10Hz, 1064nm, 9ns) laser system, a single pulse was irradiated upon the coupon to spall the coating. By varying the pulse energy while maintaining a focused spot diameter, different fluence values could be compared while maintaining a high level of uniformity of beam quality. Similar experiments were performed with water absorbed into the YSZ porosity. Analyses of the substrate after spallation were performed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS / EDX) to identify the substrate surface morphology resulting from both mechanically removed and spallation removed coatings. A semi-logarithmic analysis similar to that of other researchers was performed on the obtained data. A simplistic thermal model was also coded using MATLAB which uses thermal and optical properties and laser intensity to calculate structural temperatures and compare the results to the experimental data.
5 Experimental

The work in this thesis required additional development of equipment and techniques than were available at Wright State or Mound Laser & Photonics Center, Inc. (MLPC), and what could be obtained from literature review. Throughout the experimentation phase of the work, the theories of the mechanisms were researched to identify similarities to performed experimentation and direct the literature research. Equipment necessary for the experimentation process was engineered and/or integrated from resources available at MLPC.

5.1 Setup of Equipment

All experimentation for this work was performed within a environmentally controlled laboratory at the Mound Advanced Technology facility leased by MLPC. This laboratory consisted of a high quality optical table, the laser system, and all necessary auxiliary equipment which will be described in more detail in the following sections (setup shown in Figure 7 below).
5.2 Laser Description

The laser system used in this work was a Spectra-Physics DCR-2A Nd:YAG model. This system is flash-lamp based, fires at 10Hz and operates at a wavelength of 1064nm. The system is capable of pulse energies up to 350mJ with a 9ns pulse duration. Through the implementation of a 400mm plano-convex lens, the spot diameter at the coupon surface used throughout the work is approximately 2mm. Control of pulse energy was performed through adjustment of a half-wave plate and Glan-Laser polarizer. The half-wave plate changes the percentage of S and P waves within the beam and as the
beam passes through the Glan-Laser polarizer the S waves are reflected out of the polarizer and the P waves pass through. By controlling pulse energy in this manner the beam quality was kept consistent during the experimentation process. Captured by a Spiricon beam profiler, the image shown in Figure 8 below is the spatial profile of the DCR-2A used during the experimentation. As the image shows, the spatial profile is not on the order of a flat-top or Gaussian profile and has inherent in-homogeneity.

![Spatial Profile Image](image)

**Figure 8: The Spatial Profile of the DCR-2A**

### 5.3 Fluid Control / Deposition

Preliminary experimentation was performed by utilizing a water pump to flow water across the surface of the coupon. A Keyence Displacement Sensor (LK-G402) was used to approximate the thickness of the water film. The thickness of the water film was varied by changing the flow rate of the water, the distance of the nozzle to the coupon surface, and / or the nozzle itself. As such, these film thickness measurements have an inherent range. The majority of the experimentation for this work was performed by
applying water to the surface through the use of a misting apparatus to soak the coupon but to have minimal residual “standing” water on the surface. This method was determined to be viable during the preliminary experimentation.

5.4 **Coupon X-Y Movement**

In order to improve the efficiency and consistency of the experiments, a two axis stepper motor and controller (Klinger CC1.2) was integrated to translate the coupons in the X-Y direction (with the beam traveling along the Z axis). This setup allowed for the coupon to be moved in a consistent manner versus moving the beam itself. Figure 9 below shows these stages and their orientation to the beam path (shown by the red dashed line).

![Figure 9: Coupon Movement by Stepper Motors and Controller](image)

**Figure 9: Coupon Movement by Stepper Motors and Controller**
5.5 Pulse Energy Measurement

Pulse energies were measured using a Scientech calorimeter head and display unit (AC2501, Vector D200). The calorimeter head was placed immediately following the focal lens to measure the energy transmitted to the coupon (visible in Figure 9). As the laser system does not produce each pulse with identical energy, ten readings were made and averaged for each set.

5.5 Phantom™ High Speed Video Camera

In an effort to better understand the process, a Phantom V9.1 high speed camera by Vision Research was used to monitor the process. The camera was oriented perpendicular to the beam path as a pseudo cross-sectional view and is shown in Figures 7 and 9. At the lowest resolution of 96 x 8 pixels, the V9.1 has a frame per second rate of 153,846 (6.5 µs). The V9.1 was coupled with a laptop to capture the video and perform any post-processing as required such as brightness/contrast adjustment, trimming, etc.

5.5 Coupon and Sample Identification

The coupons used throughout this work were all coated within a comparable timeframe and with similar processing parameters. The substrate is a nickel based superalloy with a nickel aluminate bond coat and yttria-stabilized zirconia (YSZ) as the thermal barrier coating. The YSZ has an average thickness of 120 µm (as measured by a Wyko NT1100 white-light interferometer). Each of these coupons has a string of alphanumeric characters engraved on the back and this string has been treated as the ID of each coupon. The subsequent numbering scheme for the experiments followed the
pattern of #-- where the first number represents the parameter set and the second number identifies each repeated test.
6 Testing Results

Up to 60 coupons were available for use throughout the experimental process. An attempt was made to keep the number of used coupons at minimum, but maintain an appropriate spacing to avoid data skewing and false reads. As the visual results of the experiments look very similar, only a few images will be shown to illustrate the extent of spallation and the remainder of the results will focus on the obtained numerical data.

6.1 Testing Procedure

As the intention of this work was to determine the underlying mechanism of the spallation process, the variables for this work were pulse energy (and thus fluence), fluid thickness, and fluid type. The method of adjusting the pulse energy and of applying the fluid has been described in previous sections.

6.2 Visual Description of Spallation

Figure 10 below shows the stages of the spallation process as the pulse energy (and thus fluence) is increased. The pulse energies of these samples are 28.2mJ (A), 33.6mJ (B), 47.1mJ (C), and 50.1mJ (D). When the pulse energy is lower than the spallation threshold, discoloration of the layer can occur as shown in images A-B. This discoloration is challenging to capture through a picture, but is centered in the image and of similar size to the removed area shown in image D. As the energy crosses the spallation threshold, the YSZ is spalled from the surface as shown in images C-D. As the energy increases, more YSZ is removed following a logarithmic progression. The
spallation has been analyzed through a process of capturing an image of the removal (or lack thereof) using a microscope at 52.1X and calculating the area removed with an ImageJ macro (included in Appendix A). This macro takes the appropriate inch / pixel scale and determines the area of the substrate (through a simple contrast / brightness difference algorithm). These areas were then plotted against the pulse energy for a graphical representation of the results.

Figure 10: Microscopic Image of the Spallation for Pulse Energies of 28.2mJ, 33.6mJ, 47.1mJ, and 50.1mJ, Respectively (Magnification: 52.1X)
6.2  Flowed and Absorbed Water

The first set of experiments performed utilized a water pump to flow water across the coupon surface to a thickness of 120-130μm. By adjusting the pulse energy from 7.8mJ to 179.7mJ and taking that value against the resultant removal area, the plot shown in Figure 11 below was obtained. This data shows that approximately from 0-60mJ the coating does not spall from the surface. As previously discussed, there is a discoloration effect that occurs, but it is not easily quantified and therefore is only noted but not used in analysis. Approximately from 60-80mJ the coating starts to be spalled from the substrate, and the removal area increases rapidly. Beyond 80mJ the rate at which the area increases is reduced. Error bars following normal standard deviation are shown on all data points, but for most, they are smaller than the marker. The experiments within the 60-80mJ range had the highest amount of variation due to the difficulty in accurately controlling the water thickness.

After performing the experiment sets with flowed water, it was accidentally observed that water absorbed into the porous structure of the YSZ would also allow the mechanism to occur. Because of the ease and improved consistency of this method, it was used for all following experiments. As previously mentioned, this method is performed by misting water on the coupon, enough to soak the structure. “Standing” water, that is, a water layer remaining on top of the YSZ is kept at a minimum. These experiments resulted in the plot shown in Figure 11 below. This data follows a similar form as the flowed water with transitions at 30mJ for initial spallation and 50mJ for full spallation. Error bars following normal standard deviation are shown on all data points, but for most,
they are smaller than the marker. Unlike the flowed water plot, the error bars within the 30-50mJ region are reasonably low.

![Figure 11: Plot of Removal Area versus Pulse Energy using Absorbed Water](image)

### 6.3 Other Fluids

With the translation in pulse energy between flowed water and absorbed water, further experiments were performed with other absorbed fluids. Figure 12 below shows the results when using water, mineral oil, ultrasound gel, and methanol. The shape of the data is similar between all four fluids, although they again show a translation along the pulse energy axis. The large error bars for the methanol experiments are thought to be due to the rapid evaporation (as compared to the other fluids) methanol experiences in ambient temperature and pressure. Because of this, it proved to be challenging to keep the amount of fluid within the pores consistent from test to test.
6.4 No Fluid

A final set of experiments were performed without any fluid within the porous YSZ structure. These experiments did not result in spallation over the pulse energy range of $0 - 143.7 \text{mJ}$. 

**Figure 12: Plot of Removal Area versus Pulse Energy for Different Fluids**
7 Discussion of Testing Results

In order to understand the mechanism utilized to spall the YSZ, a number of different analysis of the experimental data was necessary. High speed video of the process was analyzed to observe the stages of the mechanism. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) was performed to better understand the substrate after the spallation has occurred. A semi-logarithmic analysis was used to break down the plots shown in the previous section. Finally, a mathematical model was coded with MATLAB to theoretically look at the process and the thermal aspects involved.

7.1 High Speed Video

All the following high speed stills were obtained with the Phantom V9.1 high speed camera described previously and the CV 2.0 software available from Vision Research. This software simply acts as an enhanced player for the video files providing the ability for frame-by-frame viewing and some limited distance and speed measurements.

7.1.1 Flowing Water

While flowing water over the coupon face, the V9.1 camera was oriented in a way to view the surface from the side as a pseudo cross-sectional view. As the flowing water
caused disruptions in the view, video was generally only recorded while closest to the camera as shown in Figure 13 below.

![Figure 13: Setup of Phantom Camera and Coupon](image)

Figure 14 below shows a side-by-side comparison of three different pulse energies and the spallation response (left – 96.8mJ, middle – 142.4mJ, right – 179.7mJ). Although the frame to frame interval is 156μs for these three tests, the first frame is not perfectly timed between the individual tests. Row A is the frame closest to the initial laser pulse with rows B – E showing the ejection of the YSZ. Through the CV 2.0 software, the velocity of the YSZ particulates ejected from the surface was estimated by selecting a start and end point. Because the frame per section rate is not fast enough, the parts blur as they move through the frame, increasing the error in these measurements. As such, five measurements for each set were taken on different particles to obtain an average speed. The pulse energy results in a spallation speed of 496 ± 113 kpixels / second, 633 ± 132 kpixels / second, and 675 ± 37 kpixels / second for 96.8mJ, 142.mJ, and 179.9mJ pulse energies respectively.
Figure 14: Frames from High Speed Video of 96.8mJ, 142.4mJ, and 179.9mJ Pulse Energies
Table 1 below compares the speed with the area removed by the spallation process. By normalizing both the speed and the area to the 96.7mJ pulse energy, the three values can be more readily related. Through this analysis the data is supportive of higher pulse energies resulting in faster ejection speeds and larger removed areas. However, as the plots in the previous section illustrated, this process is not linear, but follows an exponential form. With such a form, continually increased pulse energy will not provide a beneficial increase in removal area. Increased pulse energy also increases the likelihood and extent of thermal damage (thermal impact and implications are discussed in Section 7.2). For reference, the scale of these frames is approximately 0.035 mm / pixel, which gives a range of 17.4 – 23.6 m/s for the speed of the particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Speed (kpixels / second)</th>
<th>Speed Normalized to 96.mJ</th>
<th>Actual Area (cm²)</th>
<th>Area Normalized to 96.8mJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.8mJ</td>
<td>496 ± 113</td>
<td>1.00</td>
<td>0.0372</td>
<td>1.00</td>
</tr>
<tr>
<td>142.4mJ</td>
<td>633 ± 132</td>
<td>1.28</td>
<td>0.0463</td>
<td>1.24</td>
</tr>
<tr>
<td>179.7mJ</td>
<td>675 ± 37</td>
<td>1.36</td>
<td>0.0543</td>
<td>1.46</td>
</tr>
</tbody>
</table>

Table 1: Comparison of Speeds and Removed Areas for 96.8mJ, 142.4mJ, and 179.7mJ Pulse Energies

### 7.1.2 Absorbed Water

Although the previous analysis was helpful in the regard that it defines the range in which the particles are travelling, it does not reveal much information on the mechanism. Because of this, additional high speed video was recorded with some improvements. The coupon was cut in half, providing a real cross-sectional view, the misting method was used as to avoid any flowing water disruptions, and the resolution of the camera was reduced (and thus reducing the interval time between frames). Figure 15
below shows the frames from four tests on this cross-sectioned sample (using pulse energies of 79.9mJ, 79.9mJ, 57.1mJ, and 135.6mJ respectively). The time between each frame is 20µs with row A representing the frame closest to the pulse of the laser. Rows B – D show the response of the YSZ layer. According to Figure 11, the tests that used pulse energy of 57.1mJ and 135.6mJ responded as expected and caused spallation. The two tests that used a pulse energy of 79.9mJ however should have also produced spallation. Row B, column 2, shows the YSZ bowing away from the substrate. Row B, column 1 however only shows water vapor and droplets leaving the YSZ. This researcher is of the opinion that this difference is due to the amount of water within the porous structure of the YSZ not being consistent between the tests. In all of these tests, a curved mist is generated during the process and the intensity of this mist corresponds to the energy level, given similar quantities of water within the porous structure. However, once the YSZ layer is fractured, the pieces are ejected from the substrate.
Figure 15: Frames from Cross-Sectional High Speed Video of Various Pulse Energies (79.9mJ, 79.9mJ, 57.1mJ, and 135.6mJ)

As was mentioned, the second test of 79.9mJ (column 2) shows the YSZ layer can be delaminated from the substrate, but not fractured and subsequently ejected. Figure 16 below shows optical microscopy images of this test. Although the YSZ was not sufficiently fractured to eject the layer, upon further investigation, the far left of the layer has been vertically fractured. The rest of the delaminated layer appears to be whole and undamaged.
The information obtained from the high speed video of the absorbed water and the high magnification images support a mechanism that occurs between the YSZ layer and substrate, forcing the two apart. If this force is sufficiently high, the YSZ layer will fracture and be ejected away from the substrate. However, if it is not sufficiently high, it may cause delamination, discoloration, or no obvious visible effect.

7.2 Scanning Electron Microscopy / Energy Dispersive Spectroscopy

Inspection of the substrate surface using a standard optical microscope did not provide significant detail or information regarding morphology. However, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analyses were able to provide higher magnification and detail and thus have supplied vital information regarding the thermal aspect of the process and resulting morphology.

7.2.1 Scanning Electron Microscopy

Using the Topcon Aquila scanning electron microscope (SEM) at Wright State University, images were taken of the structure of the cross-sectioned sample, the YSZ from the top down, and the substrate after mechanical removal and spallation at different locations across the substrate surface.
7.2.1.1 Cross-Sectioned Samples and YSZ Structure

A coupon similar to that used for the high speed cross-sectioned analysis was mounted and polished for investigation under SEM. Although there were multiple independent experiments conducted on that sample, the focus for this discussion is one experiment that had a response similar to that discussed in Section 7.1.2; where the YSZ bowed outward and was delaminated, but was not ejected from the substrate. Figure 17 below shows one of the spallation boundaries where the delamination is prevalent as well as a vertical fracture through the YSZ. This figure shows that the YSZ is delaminated cleanly from the substrate and the general structure from a cross-sectional view is consistent with the nearby untouched YSZ. Although this is a small section for comparison, both of these items are supportive of a mechanism that acts semi-consistently across the interface and does not appear to cause obvious structural change to the YSZ.
Figure 17: SEM of a Cross-Sectioned Coupon where the YSZ has been Delaminated

Images were also taken of the YSZ from the top down as shown in Figure 18 below. The left image shows the structure immediately surrounding a spalled section. The right image shows the YSZ structure away from any spallation experiments and is considered to be unaltered. The main difference between the YSZ structure near a spalled section and an untouched section is the compression of the YSZ columns, decreasing some of the initial porosity. This compression of the columns supports an observation from the high speed video (Section 7.1.2); in which, during the removal process, the YSZ is delaminated in such a manner that it bowed away from the surface in a curved manner.
SEM images were taken of the substrate after mechanically removing the YSZ to view an unaltered surface. Once a section of YSZ has been removed through the spallation process, the surrounding YSZ can be mechanically removed by applying force with a lever upon the lower side of the coating. This process was used to remove the YSZ from the substrate at least one beam diameter from a spalled surface, to negate spallation based surface modifications. Figure 19 below shows two images of the substrate after mechanical removal of the YSZ. These substrates show a consistently uneven surface as would be expected from a surface that is often grit blasted to produce sufficient roughness for proper adhesion. The roughness from grit blasting is generally not intended to be overly aggressive and results in an $R_q$ (root mean squared roughness) in the micron range.
Figure 19: SEM Images of the Substrate after Mechanical Removal of the YSZ

7.2.1.3 Substrate after Spallation

Approximately 50 experiments were captured on the SEM resulting in 339 individual images. These images show consistent surface morphology in relation to the energies used. In general, each individual experiment has between 10 and 12 images, split between 2000x and 7500x. Figure 20 below shows two experiments (using absorbed water with pulse energies of 46.9mJ and 141.9mJ respectively) and the approximate locations of these scans. As the second experiment was sufficiently larger in diameter than the first, an additional scan was required to reach the approximate center. Starting from the center, the distance from scan to scan is 250μm. The distance between 1 and 2 is varied as it gives the location of the edge of the YSZ layer. In order to compare these substrates, similar distances from the center are used to minimize differences in the spatial profile of the beam. A post analysis of SEM location and experimental diameter
information resulted in a center deviation of ±16µm with diameters of 2075.4µm (left image) and 2591.8µm (right image).

![Figure 20: Images of two Experiments and the Locations of the Individual SEM Images (46.9mJ – Left and 141.9mJ – Right)](image)

Figure 20 shows six images of the substrates as previously described. Figure 21A-C corresponds to locations 2, 4, and 6 shown in Figure 20 (left) and shows the substrate after spallation using a pulse energy of 46.9mJ. Figure 21D-F corresponds to locations 3, 5, and 7 shown in Figure 20 (right) and shows the substrate after spallation using a pulse energy of 141.9mJ. By comparing these substrates directly in this manner, the surface morphology transformation is obvious. Images A-C (pulse energy of 46.9mJ) show a transition from a surface that looks very similar to that shown in Figure 19 to a surface that appears to have melted and resolidified during the spallation process. The area between A and C shows increasing localized melting until the majority has been altered as shown in C. In comparison, images D-F show very little transition but
consistently have the same melted and bubbled appearance. As D-F is approximately three times the energy than that of A-C, an increase in the amount of change is supported.
Figure 21: SEM (2000X) of the Substrate after Spallation (A-C - 46.9mJ and D-F - 141.9mJ)
7.2.2 Electron Dispersive Spectroscopy

As briefly mentioned in the previous section, these surfaces visually appear to have been melted and resolidified during the spallation process. An attempt at etching the surface with reportedly effective etchants was performed but at the time did not provide any additional information.[28],[29] In order to determine which layer has melted during the process, electron dispersive spectroscopy (EDS) analysis was performed on selected samples.

7.2.2.1 Cross Sectioned Analysis

The fabricator/coater of the coupons used throughout this work has declined to state whether or not the TGO (aluminum oxide) layer has been initiated. As such, a line scan through the structure was performed in attempt of determining the existence of this layer. Figure 22 below shows the results of this line scan, specifically the intensity response of oxygen and aluminum from the YSZ (far left) through the bond coat and into the substrate (far right). Around the 20μm mark, the TGO should theoretically exist, if the necessary steps were performed during the processing of these coupons. By comparing the amounts of aluminum and oxygen (4:1, respectively, at 20μm) this researcher is of the opinion that the amount of aluminum oxide present is either minimal or not existent. In fact, one group that used similar coupons (by physical appearance, YSZ composition, and deposition method) found that the TGO ranged from 0 to 0.15μm depending on the processing steps.[30]
Figure 22: Result of an EDS Line Scan through the YSZ layer, Bond Coat, and Substrate

7.2.2.2 Direct Substrate Analysis

Morphological analysis of the substrate was performed using two methods; the first was a standard average of the image and the second was a specifically chosen region. Figure 23 below shows the results from the first of these sets. In this case, three experiments (pulse energies of 52.8mJ, 98.4mJ, and 141.9mJ) were analyzed at 20kV. For each of these experiments, a scan in the center of the spallation area (location 6 or 7 from Figure 20) and a scan of the outer edge (location 2 or 3 from Figure 20) were performed. To better compare the differences between experiments, the atomic
percentage for each element was normalized against the same element from the mechanically removed substrate. Although there are a variety of other elements present in and on the substrate, as the focus of this data is to determine which layer is melting, only oxygen, nickel, and aluminum are shown. In the center location of the substrate, as compared to the mechanically removed surface, the spallation process results in an increase in measured oxygen, nickel, and aluminum. In comparison to the result at the edge location, the trends are the similar, except for the 52.8mJ test in which there was less oxygen measured. The main difference as noted previously between these two locations is the amount of surface melting that exists. Lower pulse energies tend to result in less melting at the outer edge than the center and due to the beam spatial profile there is also inherently less melting at the edge than the center. However, from this analysis nothing conclusive concerning the composition of the melted regions can be determined.

Figure 23: Plot of EDS of Three Different Pulse Energies (52.8mJ, 98.4mJ, 141.9mJ)

By comparing the oxygen and nickel-aluminum content directly and ignoring all other elements, Table 2 is generated. A transition of 60% oxygen to around 30% is
observed as the pulse energy is increased. These values suggest that there may be an aluminum oxide layer present and that the spallation process possibly removes part of the layer from the substrate. However, when using a pulse energy of 52.7mJ, the edge location has less oxygen present than the higher pulse energies. This could suggest that the effectiveness of removing the aluminum oxide layer might depend on how the YSZ is removed. As the extent of melting varies with pulse energy, there may be differences in how the YSZ near the perimeter is removed; such as rapid delamination and ejection versus a slow delamination / peeling effect.

<table>
<thead>
<tr>
<th></th>
<th>Center</th>
<th></th>
<th>Edge</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxygen Content</td>
<td>Nickel Aluminum Content</td>
<td>Oxygen Content</td>
<td>Nickel Aluminum Content</td>
</tr>
<tr>
<td>Mechanically Removed</td>
<td>0.60</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52.7mJ</td>
<td>0.32</td>
<td>0.68</td>
<td>0.22</td>
<td>0.78</td>
</tr>
<tr>
<td>98.4mJ</td>
<td>0.34</td>
<td>0.66</td>
<td>0.31</td>
<td>0.69</td>
</tr>
<tr>
<td>141.9mJ</td>
<td>0.35</td>
<td>0.65</td>
<td>0.34</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Table 2: Oxygen and Nickel-Aluminum Content for Averaged EDS Scans

As the SEM images have shown, some portion of the surface appears to be melted during the spallation process, but which part of the layered structure is melting was not identifiable through the previous scans. To further investigate this, higher magnification and more selective EDS scans of melted and normal surfaces were performed. Figure 24 below shows the imagery of the specific locations that have been scanned, using absorbed water and a pulse energy of 52.8mJ. The 6kV scan is within 600µm from the outer edge. The main image on the left side is not the exact location of the scans but is shown as a higher quality image of a representative area. The images on the right side contain red outlined boxes which mark the scanned region. The top image labeled as normal represents a scan of the surface that appears to be similar to the mechanically removed
surface as shown previously in Figure 19. The bottom image represents a scan of the surface that appears to be melted.

![Figure 24: SEM Images of EDS of Melted and Normal Substrates](image)

The results from these EDS scans are shown below in Figure 25. In addition to the scans of the 52.8mJ pulse energy experiment, the results from a scan of the substrate after mechanically removing the YSZ is also shown for comparison with all other data normalized to the mechanically removed surface. The normal region has an atomic percentage of oxygen similar to that of the untouched (mechanically removed) substrate. However, the melted region shows a decrease in oxygen (0.196). This decrease is supportive of the melted region not containing aluminum oxide. Comparing the nickel and aluminum content to the mechanically removed substrate, there is an increase in the content of both (11.3 for nickel and 1.6 for aluminum). This increase, especially the significant increase of nickel is supportive of the bond coat melting. Similar to the
previous EDS analysis, only the results for oxygen, nickel, and aluminum are shown as they are the main elements within the TGO and bond coat layers. The other measured elements do not provide beneficial information on the composition of the melted region.

**Figure 25: Results of EDS Scans of Melted and Normal Substrate Surfaces**

The oxygen and nickel-aluminum content is directly compared in Table 3 below, again ignoring any other present elements. The normal region results in high oxygen content and low nickel-aluminum content, supportive of the possible existence of aluminum oxide. The melt region comparison shows the nickel-aluminum content amounts to more than 92% as compared to the mechanically removed surface. Due to the high content of nickel and aluminum, it is this researcher’s belief that the spallation process is capable of inducing some melting of the bond coat.
### Table 3: Oxygen and Nickel-Aluminum Content for Specific EDS Scans

<table>
<thead>
<tr>
<th></th>
<th>Oxygen Content</th>
<th>Nickel-Aluminum Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanically Removed</td>
<td>0.60</td>
<td>0.40</td>
</tr>
<tr>
<td>Edge (normal)</td>
<td>0.82</td>
<td>0.18</td>
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<tr>
<td>Edge (melt)</td>
<td>0.08</td>
<td>0.92</td>
</tr>
<tr>
<td>Edge (average)</td>
<td>0.31</td>
<td>0.69</td>
</tr>
</tbody>
</table>

#### 7.3 Semi-Logarithmic Analysis

In the literature, a number of groups have utilized a semi-logarithmic analysis when dealing with data that follows an exponential growth. Some groups have used this analysis when dealing with laser induced removal of coatings in order to determine the removal threshold level to better understand the required energy and efficiency levels. [15], [31–34]

##### 7.3.1 Concept and Procedure

The semi-logarithmic analysis in this case involves data in the form of pulse energy and the corresponding removal diameter squared. With this data, the energy is plotted on a logarithmic scale while the diameter squared is plotted on a linear scale. When plotted in this format, the exponential data has a linear appearance. The equation of a logarithmic trendline fitting this data (Equation 1) can be solved to calculate both the beam diameter (Equation 2) and fluence threshold (Equation 3).

**Equation 1** \[ y = m \log x + b \]

**Equation 2** \[ D_{Beam} = 2 \sqrt{\frac{m}{2}} \]
Equation 3

\[ F_{Thrs} = e^{\left(\frac{-b}{m}\right)} \]

Where: \( y = (\text{Spallation Diameter})^2 \)

7.3.2 Water: Flowed and Absorbed

The physical method used to estimate the beam diameter consists of using an easily ablative coating and irradiating the coating with a single pulse from the system, resulting in an ablated region that should correspond to the profile of the laser. This method is simple, but can introduce errors due to paper normalcy, heat affected zones, and the ability of defining the appropriate edge. In this section, the data obtained during the water experiments using both flowed and absorbed water will be used. The other tested fluids are analyzed in Section 7.3.3.

Figure 26 below is similar to that shown in Figure 11 but with the data points color coded by result. The blue points represent pulse energies that did not spall, the green points represent pulse energies that result in partial spallation, and the red points represent pulse energies that result in full spallation. The red and green data points will be analyzed separately with the semi-logarithmic method as they are not of the same exponential form. This dual exponential data will provide two different fluence thresholds. Although this process is only shown for this specific data set, the same method has been used for all of the following semi-logarithmic analyses in this work.
With the data for both the flowed and absorbed water, only using the “red” data points as shown in Figure 26, Figure 27 below can be generated according to the semi-logarithmic process. By solving the trendline equations shown for the beam diameter (Equation 2), the calculated beam diameter is 0.267cm and 0.192cm for flowed and absorbed water respectively. The beam diameter determined using the described ablative method was approximately 0.20cm. As the flowed water experiments had more water surface for energy reflection, had inherent turbulence, and the potential for beam diffraction, the calculated absorbed water diameter will be used as the diameter for the following calculations.
Figure 27: Beam Diameter - Semi-Logarithmic Plot of Flow and Absorbed Water for “Red” Data

Figure 28 below is generated by dividing the pulse energies by 0.192 cm to obtain the fluence values. Solving the trendline equations for the fluence threshold (Equation 3) results in 842.8 mJ/cm² and 189.3 mJ/cm² for flowed water and absorbed water respectively.

Figure 28: Fluence Threshold – Semi-Logarithmic Plot of Flowed and Absorbed Water for “Red” Data
Using the same process on the “green” data in Figure 26 for both flowed and absorbed water will produce similar looking plots and data, as shown below in Figure 29. As this portion of the obtained data contains the most potential for inaccuracy, the trendline fits ($R^2$) are not quite as high as the “red” data. By following the same method as previously used, the trendline equations shown in Figure 29 produce diameters of 1.23cm for flowed water and 0.640cm for absorbed water. Both of these values are well above both the estimated beam diameter of 0.2cm and the previously calculated value of 0.192cm. In order to maintain consistency, the fluences in the right plot of Figure 29 were calculated using 0.192cm. Solving these trendlines for fluence threshold results in 2311.7mJ/cm$^2$ for flowed water and 1317.2mJ/cm$^2$ for absorbed water.

---

**Figure 29:** Beam Diameter (Left) and Fluence Threshold (Right) - Semi-Logarithmic Plot of Flow and Absorbed Water for “Green” Data
At the beginning of this analysis it was briefly mentioned that unlike the analyses performed by the majority of the cited researchers, this data incorporates a dual exponential form that results in two different fluence thresholds. Table 4 above shows the fluence threshold results. Not only is there significant difference between the fluence values of flowed and absorbed water, as is expected from the linear plotting method, but Fluence Threshold 2 is 7.0 times higher for the absorbed data and 2.7 times higher for the flowed data.

Converting these fluence thresholds to their pulse energy equivalents, using 0.192cm for the diameter, and then placing these values onto a linear plot of the flowed and absorbed data, Figure 30 below is generated. Markers 3 and 4 align well to where the data visually suggests the spallation starts to occur. However, markers 1 and 2 are where no spallation occurs. Although pulse energies within this range did not spall the coating, they were able to discolor the coating as was shown and discussed in Section 6.2. Even though no change aside from discoloration has been observed using these pulse energy levels, there are two potential explanations on the cause of the discoloration. One possibility is that the mechanism is causing slight delamination in the coating, as was shown in Section 7.1.2. The other possibility is that the pulse energy is sufficient to start to melt the bond coat also resulting in potential delamination. With this data, a dual stage

<table>
<thead>
<tr>
<th></th>
<th>Fluence Threshold 1 (&quot;Red&quot; Data)</th>
<th>Equivalent Pulse Energy</th>
<th>Fluence Threshold 2 (&quot;Green&quot; Data)</th>
<th>Equivalent Pulse Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowed</td>
<td>842.8 mJ/cm²</td>
<td>24.5 mJ (2)</td>
<td>2311.7 mJ/cm²</td>
<td>67.2 mJ (4)</td>
</tr>
<tr>
<td>Absorbed</td>
<td>189.3 mJ/cm²</td>
<td>5.5 mJ (1)</td>
<td>1317.2 mJ/cm²</td>
<td>38.3 mJ (3)</td>
</tr>
</tbody>
</table>

Table 4: Fluence Threshold Values for Flowed and Absorbed Water
mechanism is supported in which the first stage starts with the Fluence Threshold 1 and the spallation of the coating starts to occur once Fluence Threshold 2 has been reached.

Figure 30: Linear Plot of Flowed and Absorbed Water

7.3.3 Other Fluids

Using the same methods and processes as used on the flowed and absorbed water, the different fluids that were briefly included in the experimentation were analyzed resulting in Figures 31 and 32 below. Figure 31 shows the results for Fluence Threshold 1 with values of 166.9 mJ/cm² for mineral oil, 189.3 mJ/cm² for water, 161.3 mJ/cm² for ultrasound gel, and 111.9 mJ/cm² for methanol. Figure 32 shows the results for Fluence Threshold 2 with values of 1805.1 mJ/cm² for mineral oil, 1316.6 mJ/cm² for water,
1424.6 mJ/cm\(^2\) for ultrasound gel, and 1395.6 mJ/cm\(^2\) for methanol. Once again, for best comparison, a diameter of 0.192cm was used for the fluence calculations.

**Figure 31: Fluence Threshold 1 for Other Fluids**

**Figure 32: Fluence Threshold 2 for Other Fluids**

### 7.3.4 Fluence Thresholds

As analysis has shown, the experimental data provides information for two different fluence thresholds. The benefit of using different fluids to perform the spallation process is that their different material properties can provide additional information on how the mechanism may be working as they each result in different fluence threshold levels, although within the same range.

If the mechanism uses a method of fluid vaporization to spall the coating, the vaporization point, heat of vaporization, and specific heat would all play a role in the
amount of energy required to cause said vaporization, which would correspond to Fluence Threshold 1 (FT1) as the first stage in the mechanism. Table 5 below lists these properties, the calculated fluence threshold values, and the theoretical energy required to bring each fluid to its boiling point and vaporize.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>189.3</td>
<td>1316.1</td>
<td>100</td>
<td>2256</td>
<td>4.18</td>
<td>1.0</td>
<td>334.4</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>166.9</td>
<td>1805.1</td>
<td>310</td>
<td>209</td>
<td>1.97</td>
<td>0.8</td>
<td>394.9</td>
</tr>
<tr>
<td>Ultrasound Gel</td>
<td>161.3</td>
<td>1426.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methanol</td>
<td>111.9</td>
<td>1395.6</td>
<td>64.7</td>
<td>1100</td>
<td>2.51</td>
<td>0.79</td>
<td>88.8</td>
</tr>
</tbody>
</table>

Table 5: Properties of the Tested Fluids and their corresponding Fluence Thresholds [35], [36]

As methanol has a low vaporization point, a mid-range heat of vaporization, and a mid-range specific heat, it should require the least amount of energy to reaching boiling and vaporize (FT1 of 111.9mJ/cm<sup>2</sup>). Water has a mid-range vaporization point, the highest heat of vaporization, and highest specific heat; with these properties, it is expected that it would require the most energy to reach boiling and vaporize (FT1 of 189.3mJ/cm<sup>2</sup>).[35] As ultrasound gel is primarily water, alcohol, and glycol, and although values were not obtainable, requiring energy between that of methanol and water is supportive (FT1 of 161.3mJ/cm<sup>2</sup>). Mineral oil however, has a high vaporization point, a low heat of vaporization, and a low specific heat. When the obtained values are used to calculate the energy required to reach boiling point, mineral oil requires only slightly
more than that of water. The vaporization energy for mineral oil however is much lower than that of water. Between these, a FT1 slightly below that of water is supported.

The Fluence Threshold 2 (FT2) value is much higher than that of the FT1 value for all of the fluids tested, ranging from 7-13 times the FT1. Between the FT1 and FT2 values, it can be assumed that the vaporization continues to occur and likely occurs more aggressively. Below the FT2, delamination of the YSZ starts to occur but does not fracture the layer sufficiently. However, when the FT2 point is reached, spallation visibly starts to occur. Because of this, the FT2 represents a change of the vaporization stage where the pressure generated by vaporization is no longer able to relieve itself through the liquid filled porosity of the YSZ. The pressure generated when using values at or above the FT2 is sufficient to fracture the YSZ layer, ejecting the YSZ and fluid vapor/liquid from the substrate.

7.4 Thermal Model

A thermal model based on the equations found in a laser processing book by Dr. Steen was coded within the MATLAB framework to assist in understanding the mechanism.[37] In addition to the book itself, expanded examples on the webpage of the Manufacturing Research Laboratory of Columbia University were also studied.[38] Using these resources, the code in Appendix B was used to calculate the temperature ranges obtained when using certain laser intensities and material properties.

7.4.1 Methodology

This model assumes constant thermal properties, no phase changes, no convection, and that the spatial profile of the beam is homogenous. The model also
makes simplifications in heat transfer, optical effects, and uses an idealized coating structure. The model methodology is a time based transfer of the laser energy from layer to layer at small increments using Equations 4 - 6 shown below, where \( k \) is the thermal conductivity, \( \alpha \) is the thermal diffusivity, \( I_0 \) is the absorbed laser intensity, \( t \) is time, \( t_p \) is the pulse duration, \( z \) is the distance from the top surface, and \( T_0 \) is the initial temperature (room temperature). Equation 5 is the integral of the complimentary error function. The error function of Equation 5 is substituted by the polynomial shown in Equation 6.

**Equation 4**

\[
T(z, t) - T_0 = \frac{2I_0}{k} \sqrt{t \alpha} \cdot ierfc\left(\frac{z}{2\sqrt{t \alpha}}\right)
\]

**Equation 5**

\[
ieri{c}(u) = \frac{e^{-u^2}}{\sqrt{x}} - u \left[1 - erf(u)\right]
\]

**Equation 6**

\[
erf(u) = 1 - \left(a_1 b + a_2 b^2 + a_3 b^3\right)e^{-u^2}
\]

*Where:
\( a_1 = 0.3480242 \)
\( a_2 = -0.0958798 \)
\( a_3 = 0.7478556 \)
\( c = 0.47047 \)
\( b = (1 + cu)^{-1} \)*

![Figure 33: Idealized Thermal Barrier Structure (TBC)](image-url)
Figure 33 above illustrates an idealized TBC structure and the subsequent layers used throughout the model. The first layer consists of electron beam physical vapor deposition (EB-PVD) of yttria-stabilized zirconia (YSZ) which grows in a columnar structure with an inherent porosity. Based on the SEM image shown in Figure 18 (right side) of the YSZ from the top down, this porosity is approximately 6.7%. In addition to this, as has been mentioned, the YSZ has a hydrophilic nature allowing the water to “absorb” into the structural porosity creating a combined YSZ and water layer. On average, this layer is effectively 120µm thick for the one-inch coupons used throughout this work. Table 6 below lists the thermal, mechanical, and optical properties for the YSZ and water layer. [35], [39–43]

<table>
<thead>
<tr>
<th></th>
<th>YSZ</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption Coefficient (cm⁻¹)</td>
<td>6.39</td>
<td>0.15</td>
</tr>
<tr>
<td>Reflection (%)</td>
<td>72.70</td>
<td>2.25</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>6100</td>
<td>1000</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m·K)</td>
<td>1.75</td>
<td>0.58</td>
</tr>
<tr>
<td>Thermal Diffusivity (m²/s)</td>
<td>0.103E-5</td>
<td>0.146E-6</td>
</tr>
<tr>
<td>Melting Point (K)</td>
<td>5273.15</td>
<td>373.15</td>
</tr>
<tr>
<td>Thickness (m)</td>
<td>120E-6</td>
<td>120E-6</td>
</tr>
</tbody>
</table>

*Table 6: YSZ Properties and Settings*

The second layer is the thermally grown oxide (TGO), specifically aluminum oxide. According to one journal, aluminum oxide has an extinction coefficient of zero from 248nm through 1064nm.[44] To reduce the complexity of the model, it was assumed that the laser energy effectively passes through the TGO layer, aside from reflected losses, without losing intensity due to absorption or other optical interactions. Although the fabricator / coater of these coupons declined to state the presence or thickness of the TGO layer, it has been found that similar coupons used by other
researchers had a TGO layer ranging from 0 - 0.150µm.[30] As such, a TGO thickness of 0.150µm has been incorporated into the structure. Table 7 below lists the thermal, mechanical, and optical properties for the TGO.[44–49]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption Coefficient (cm⁻¹)</td>
<td>0.0</td>
</tr>
<tr>
<td>Reflection (%)</td>
<td>7.49</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>3900</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m·K)</td>
<td>30.0</td>
</tr>
<tr>
<td>Thermal Diffusivity (m²/s)</td>
<td>0.12E-6</td>
</tr>
<tr>
<td>Melting Point (K)</td>
<td>2345</td>
</tr>
<tr>
<td>Thickness (m)</td>
<td>0.150E-6</td>
</tr>
</tbody>
</table>

Table 7: TGO – Aluminum Oxide Properties and Settings

The third and final layer in the model is the bond coat, which is an alloy of primarily nickel and aluminum. Similar to the TGO the fabricator of the coupons declined to provide specific material properties for the bond coat for proprietary reasons. It was provided that the bond coat could be treated as nickel aluminide (NiAl). While obtaining the necessary values for the NiAl, there have been some discrepancies on thermal properties. In addition, the absorption coefficient and the reflection percentage were not able to be obtained. Without the appropriate absorption and reflection values, approximations were calculated by taking a ratio of the absorption coefficient and the reflection percentage based on the amount of nickel and aluminum in the bond coat. This ratio was obtained from the EDS of the melt region. Without accurate values for the absorption coefficient and the reflection percentage, the temperature at the bond coat interface will not be calculated with high accuracy. Table 8 below lists the thermal and optical properties that are used for the bond coat within the model.[46], [50–53]
<table>
<thead>
<tr>
<th></th>
<th>Aluminum</th>
<th>Nickel</th>
<th>NiAl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption Coefficient (cm⁻¹)</td>
<td>1.21E6</td>
<td>6.14E5</td>
<td>0.57Ni + 0.43Al</td>
</tr>
<tr>
<td>Reflection (%)</td>
<td>95.02</td>
<td>72.56</td>
<td>0.57Ni + 0.43Al</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td></td>
<td></td>
<td>5860</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m-K)</td>
<td></td>
<td></td>
<td>76</td>
</tr>
<tr>
<td>Thermal Diffusivity (m²/s)</td>
<td></td>
<td></td>
<td>2.027E-5</td>
</tr>
<tr>
<td>Melting Point (K)</td>
<td></td>
<td></td>
<td>1955</td>
</tr>
<tr>
<td>Specific Heat (J/kg-K)</td>
<td></td>
<td></td>
<td>640</td>
</tr>
</tbody>
</table>

Table 8: Aluminum Properties and Settings

Through an iterative process shown below in Figure 34, the temperature is calculated via Equations 4 – 6 within a nested loop of depth (range: 0.001E-6 – 120.20E-6m, step size: 0.001E-6m) and time / pulse duration (range: 1 – 9 ns, step size: 1ns). Within these nested loops are If-Then statements that separate the structure into three sections; YSZ and water, TGO, and bond coat. These If-Then statements follow a similar procedure in which for the first step into each layer the intensity is reduced by both reflection and absorption losses. For each subsequent step within that same layer, absorption is assumed to be the only loss. At the end of each step, the temperature at that depth is calculated and stored. The laser intensity at the end of the step is then used as the initial intensity for the next step into the layer. This procedure continues through the loops until the temperature has been calculated from 0.001E-6 to 120.20E-6m for 1-9ns. With a temperature map for each nanosecond of the pulse duration, the temperatures are plotted with the maximum temperature obtained for each layer.
Figure 34: Flow Chart Illustration of the Thermal Model Methodology
With the model configured as described, the only additional input necessary to obtain the temperature plots is the laser intensity. As the used laser has a Gaussian temporal profile, the peak power density (PPD) must be multiplied by 0.94. The spot size used for the area portion of the PPD is the 0.192cm obtained from the semi-logarithmic analysis.

As an output, the model produces temperature maps of the coupon cross-section. Figure 35 below shows an illustration of the numbering scheme through the structural layers. The very top of the surface is 0μm, the interface of YSZ and TGO is 120μm, and the interface of TGO and the bond coat is 120.15μm. The bond coat only extends for 0.05μm in the model as the absorption rate is sufficiently high that the energy does not continue beyond this value due to the previously mentioned assumptions.

![Illustration of the Structural Depth Numbering Scheme](image)

**Figure 35: Illustration of the Structural Depth Numbering Scheme**

Although the model creates a temperature plot for each nanosecond, only two plots will be shown and discussed. Figures 36 and 37 below show the temperature plot for 1ns and 9ns, respectively, using the maximum PPD used in the tests (5.12x10^{12})
These figures are split into two different cross-sectional views. The top left image represents 119\( \mu \)m through 120.2\( \mu \)m. As was introduced in Figure 35, this distance included a small portion of the YSZ/water, all of the TGO, and a portion of the bond coat. Without having sufficiently high laser intensities, the YSZ/water will remain near 298K and this plot will not provide much information. The second plot on the top right is zoomed in, only showing 120.15\( \mu \)m through 120.17\( \mu \)m, thus only a portion of the TGO and the bond coat.

\[ \text{Energy: } 5.12 \times 10^{12} \text{ W/m}^2 \]

\[ \text{Showing: 1 nanoseconds} \]

\[ \text{Max Temperature of Water (Kelvin): } 288.0037 \]
\[ \text{Max Temperature of TBC (Kelvin): } 288.0414 \]
\[ \text{Max Temperature of TGO (Kelvin): } 298 \]
\[ \text{Max Temperature of Bond Coat (Kelvin): } 367.7109 \]

**Figure 36: Temperature Plot for 1ns (Temperatures in Kelvin)**
These results show that with the material properties provided, assuming no conduction, no phase changes, and no material property changes with temperature, that the bond coat can reach temperatures above the boiling point of water. At the highest PPD, the surface could reach the boiling point within the first nanosecond of the laser pulse. However, the results also show that at the highest PPD used throughout the experiments, the bond coat does not reach the melting point of 1955K.[51]

Table 9 below shows the temperatures of each layer and the corresponding peak power density used (FT1, FT2, and the maximum PPD, respectively). Due to the thermal and optical properties of the YSZ, water, and TGO, these layers do not increase in temperature much from the single pulse. However, according to the model, only 25.8% of the original laser intensity actually reaches the initial layer of the bond coat, resulting in the temperatures shown.
<table>
<thead>
<tr>
<th>Pulse Energy</th>
<th>Gaussian PPD</th>
<th>YSZ Temp</th>
<th>Water Temp</th>
<th>TGO Temp</th>
<th>Bond Coat Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5mJ</td>
<td>1.98e7 W/cm²</td>
<td>298.0K</td>
<td>298.0K</td>
<td>298.0K</td>
<td>308.5K</td>
</tr>
<tr>
<td>38.3mJ</td>
<td>1.38e8 W/cm²</td>
<td>298.0K</td>
<td>298.0K</td>
<td>298.0K</td>
<td>370.8K</td>
</tr>
<tr>
<td>141.9mJ</td>
<td>5.12e8 W/cm²</td>
<td>298.0K</td>
<td>298.1K</td>
<td>298.0K</td>
<td>568.3K</td>
</tr>
</tbody>
</table>

Table 9: Laser Intensity Levels and Resultant Temperatures

Upon further investigation of the equations used to calculate the temperatures, the thermal conductivity as a part of Equation 4 plays a large role in the obtained temperature. According to one group, ternary additions to NiAl can greatly affect the thermal conductivity.[54] The thermal conductivity value used for the reported temperatures was 76 W/m·K, but if a certain ternary addition was made that resulted in a conductivity of 21 W/m·K, the temperature at the highest energy becomes 1276K. Without knowing the actual thermal properties of the bond coat, the model can only provide estimates.

This estimate is furthered because the model assumes a homogenous beam profile, and as was shown in Figure 8, the beam used for these experiments is not homogenous. In fact the profile has a ring of energy that is at least 2.79 times that of the mean energy, as shown in Figure 38 below. This profile shows energy from mean (1.468e3) to max (4.095e3) in arbitrary units. By taking the maximum energy divided by the mean, there is a factor of 2.79 between the outlying blue (equal to the mean energy) and the white peaks (maximum energy). This inhomogeneity can result in certain regions of the irradiated spot to be of much higher PPD than would be estimated by a standard power measurement.
This model makes a number of assumptions (no phase changes, no conduction, material properties remain the same throughout the temperature gradient, the beam is homogenous) as well as simplifications (heat transfer, optical effects while the laser interacts with the complex structure, and simplifying / idealizing the structure) and therefore can only provide estimates. Although the model can only estimate the temperature, it supports the observations from the SEM images that given the right material properties, the used laser intensities could potentially cause limited melting of the bond coat. However, with the material properties found or estimated, the model does not predict the melt observed.

### 7.5 Discussion

With the different types of analyses performed, all of the observed information will be brought together prior to discussing the hypothesized mechanism. These analyses
include high speed video, SEM / EDS, semi-logarithmic analysis of the experimental data, and the thermal model.

- High speed video captured the coating bowing outward causing delamination and if the energy was sufficient, causing spallation.

- SEM analysis showed that the YSZ structure has no obvious alterations due to the delamination, but spallation can cause the columns to become compressed at the outer perimeter.

- SEM analysis also revealed that the substrate morphology changed depending on the location within the spallation area and on the amount of energy used. This morphology change visually looks like melting and solidification.

- EDS analysis was supportive to the theory that the morphology change is due to surface melting and that the main constituents of this melt were nickel and aluminum, which are the main elements in the bond coat.

- The semi-logarithmic analysis identified that the spallation process has two stages with high and low fluence levels. This analysis also introduced the idea that the mechanism partially relies on the thermal properties of the fluid used, e.g. with methanol requiring the least energy and water requiring the most.

- Finally the model, albeit with a number of assumptions and simplifications, confirmed that with appropriate material properties, it could be feasible to melt the bond coat slightly with the laser energies used throughout this work.
In comparison to the literature review section, the observations from this work are supportive of some of the results from other researchers. Laser shock processing has the least amount of support from these observations. According to one group, when using power densities below $1 \times 10^9$ W/cm$^2$ (the maximum used in this work was $5.12 \times 10^8$ W/cm$^2$ for absorbed water) they suggest using an absorptive layer with a low heat of vaporization such as lead or paint.[55] The reasoning behind this is because the shock processing generally requires a layer to be vaporized for the plasma generation and the higher the heat of vaporization the more energy that is required to perform this action. The heat of vaporization of lead is 850 J/g with nickel and aluminum at 5862 J/g and 9462 J/g, respectively.[56] With the heat of vaporization of the bond coat (nickel and aluminum) being significantly higher than that of lead, the power density would certainly need to be higher than $1 \times 10^9$ W/cm$^2$ according to laser shock processing methodology.

The other two processes, thermal based removal and laser cleaning use a similar concept. Thermal based removal requires a layer to be absorbing to the wavelength and then either through expansion or gas formation by decomposition to create enough pressure to remove the coating. Laser cleaning is focused on particulate removal but does involve the vaporization of water to generate sufficient force upon these particles.

Figure 39 below shows an idealized version of the coupon structure with the YSZ columns shown with water absorbed into the structure, the TGO layer (yellow), the bond coat (light gray), and substrate (dark gray). When a laser pulse is emitted upon this structure, as the model has confirmed, the pulse transmits through the YSZ and water with 28% of the original intensity reaching the TGO layer. With the TGO theoretically having a thickness of 0.15 μm but also not absorbing any of the laser intensity only...
reflecting, the remaining energy (25.8% of original intensity) interacts with the bond coat. Although a significant amount of energy is reflected (82%), enough is absorbed to increase the temperature of the bond coat - TGO interface rapidly to and beyond the boiling point of water. As was discussed within Section 3.3, Park et. al. used 51.3mJ/cm² and were able to produce bubbles from the surface of chromium and Hsu and Lin used 305 – 1591mJ/cm² to remove particulate from 304 stainless steel substrates. From the semi-logarithmic analysis, the lowest fluence threshold for absorbed water was 5.5mJ per pulse, resulting in 190mJ/cm² of potentially usable energy. By taking the amount of energy that is available at the bond coat after the described losses from the YSZ, water, and TGO (25.8% of 190mJ/cm², resulting in 49mJ/cm²), the value corresponds very well with the bubble nucleation / formation threshold found by Park et. al. As such, it is this researcher’s opinion that the calculated Fluence Threshold 1 (FT1) represents the vaporization threshold. When using a fluence that is at this threshold, the energy is sufficient to vaporize the fluid, but spallation does not yet occur. The vaporized fluid simply escapes through the porosity into the environment.

Figure 39: Idealized Illustration of the YSZ, TGO, Bond Coat, and Substrate Structure with Laser Pulse
When the fluence is higher than FT1 but still below FT2 delamination and bowing outward as shown in the high speed video footage can occur and is illustrated by Figure 40 below. With the water closest to the TGO vaporizing more rapidly as the fluence increases up to FT2, the vapor burst is generated and expands too quickly to relieve itself through the porosity in the YSZ. The vapor becomes trapped within the structure but continues to build pressure. Once the pressure is sufficiently high, it delaminates the YSZ and TGO from the bond coat bowing the coating out away from the substrate. As long as the fluence is below FT2, the coating does not spall but returns back to the substrate.

![Figure 40: Idealized Illustration of the YSZ, TGO, Bond Coat, and Substrate Structure with Pressure Building](image)

When the fluence reaches and exceeds FT2 the coating is spalled from the surface as shown in Figure 41 below. The buildup of pressure is now sufficient to delaminate and fracture the coating. This could be viewed in an analogous sense of a 3-point bend test. When performing a 3-point bend test, the ends of the sample are held rigid and similarly the outer most portions of the YSZ are held by the surrounding YSZ and TGO, which causes the sharp compression in columns as was shown in the SEM analysis. When the
force at the center of the delaminated YSZ exceeds the strength of the layer, the YSZ fractures to relieve the pressure and depending on the fluence, residual YSZ may be left or all of the coating may be spalled, resulting in the variation of spallation as shown in Figure 10.

Figure 41: Idealized Illustration of Spallation Occurring
8 Conclusion

The intention of this work was to better understand and determine the underlying mechanism that is used by MLPC to remove thermal barrier coatings. The process that was developed by MLPC is capable of spallating EB-PVD YSZ thermal barrier coatings from a nickel substrate with a single pulse from a 1064nm, 10Hz, Nd:YAG laser system. Due to the discovery of the method, there was little understanding on the specifics of the mechanism. Through experimentation and analyses including high speed video, SEM / EDS, numerical, and simplified thermal modeling, numerous observations have been made. By combining these observations with the advancements and understanding from previous work of researchers focusing on laser shock processing, thermal processing, and laser cleaning this researcher believes the following stages are the key aspects to the mechanism:

- **First:** A liquid is introduced onto the YSZ layer. Due to the deposition method of the YSZ, that is, EB-PVD, the structure is columnar, porous, and hydrophilic, allowing the liquid to absorb into the structure. From this work’s experimentation, this liquid can be water, mineral oil, methanol, or ultrasound gel and still exhibit the spallation capability. (Figure 42)

- **Second:** Using a 1064nm, ~9ns laser system with a fluence of >1300mJ/cm² (assuming the liquid is water), the pulse transmits through the water (low reflection and absorption loses), YSZ (68% reflection loss and over the coupon...
thickness, approximately 4% absorption loss), and the TGO (low reflection loss of 2%). (Figure 42)

![Figure 42: Illustration of the First and Second Steps](image)

- **Third:** With a sufficient amount of energy reaching the bond coat (approximately 25.8% of the original intensity is available, only 4.6% is absorbed) it increases in temperature rapidly over the 9ns pulse duration. Depending on the fluence and spatial beam profile, some surface melting occurs. In the case of this work, the TGO is thin enough (0-0.15μm) to allow sufficient heating of the water at the YSZ-TGO interface and cause rapid vaporization of the water. (Figure 43)

- **Fourth:** The water vaporization occurs rapidly and a pressure bubble is generated near the YSZ – TGO interface. As liquid (in this case water) exists throughout the structure, and due to the incompressibility of fluids and the rate at which the process occurs, the pressure bubble continues to expand without relief, delaminating the YSZ coating. (Figure 43)
- **Fifth:** When the fluence is $< 1300 \text{mJ/cm}^2$, the pressure generated is not sufficient to fracture the YSZ. The coating can be delaminated, but the pressure is relieved through the porosity. However, in this case the fluence is more than $1300 \text{mJ/cm}^2$ and the pressure generated fractures the coating. With the pressure suddenly relieved and the coating fractured, pieces of the coating and water (in the form of vapor and liquid) are ejected from the substrate. The severity of this ejection is dependent on the irradiated fluence. (Figure 44)
With this understanding of the mechanism, it follows that although two different fluence thresholds have been identified, for the intention of spallation, only the second fluence threshold (FT2) is significant as it represents the spallation threshold where the pressure generation is sufficient. The first fluence threshold (FT1) however does identify a helpful aspect as it corresponds to the vaporization point of the fluid in use.

The work described within this thesis and the subsequent analysis has benefited and in a limited degree expanded the research of laser processing as well as the capability of laser thermal removal and steam cleaning. Due to the specifics of this removal mechanism, numerous parameters define the effectiveness of the spallation either resulting in no change to aggressively melting the substrate. These items include but are not limited to the thermal and optical properties of all layers, the amount and properties of the fluid that is absorbed into the structure, and the structure itself. Because of these dependences, fluctuations in these values will drastically change the results.

Potential areas of future research lie in the pressure generation aspect of the mechanism. Experiments could be performed to better understand the changes in pressure with different laser spatial profiles, pulse durations, and beam diameter. Another key aspect for future research focuses on the fluid used. Although water was found to be the most optimal fluid, only a few different fluids were tested. As coating removal efficiency depends on removal rate and energy usage, any improvement will be of benefit.
References


Appendix A: ImageJ Macro Code for Removal Area Calculation

dir1 = getDirectory("Choose Source Directory ");
dir2 = getDirectory("Choose Destination Directory ");
list = getFlist(dir1);
setBatchMode(false);

Dialog.create("Set Scale...");
Dialog.addMessage("Enter the scaling factor in pixel/inch:");
Dialog.addString("-->","Scale");
Dialog.show();
scalefactor = Dialog.getString();

for (i = 0; i<list.length; i++) {
    showProgress(i+1, list.length);
    filename = dir1 + list[i];
    if (endsWith(filename, "png")) {
        open(filename);
        run("Set Scale...", "distance=scalefactor known=1 pixel=1
            unit=inch global");
        run("8-bit");
        setAutoThreshold("Minimum");
        setThreshold(0, 140);
        run("Convert to Mask");
        run("Set Measurements...","area fit redirect=None decimal=6");
        run("Analyze Particles...", "size=0-Infinity pixel circularity=0.00-0.90 show=[Overlay Masks] display exclude summarize");

    selectWindow("Results");
    tbcarea = getResult("Area",0);
    run("Clear Results");

    name = substring(list[i],0,(lengthOf(list[i])-4));

    selectWindow(list[i]);
    run("Flatten");
    saveAs("TIFF", dir2 + name + ",overlay.tif");
    close();
    close();
}
open(filename);

run("Set Scale...", "distance=scalefactor known=1 pixel=1 unit=inch global");
run("8-bit");
waitForUser("Select at least 3 points for the circle fit");
ans = getBoolean("Did you make your selections?");
if (ans == 0)
    waitForUser("Select at least 3 points for the circle fit");
run("Fit Circle");
run("Clear Outside");
setThreshold(100, 130);
run("Convert to Mask");
run("Set Measurements...", "area fit redirect=None decimal=6");
run("Analyze Particles...", "size=25-Infinity pixel circularity=0.00-0.90 show=[Overlay Masks] display exclude");

area = 0;
for (j = 0; j < nResults; j++) {
    area = getResult("Area", j) + area;
}

selectWindow("Results");
run("Clear Results");

waitForUser("Select at least 3 points for the circle fit");
ans = getBoolean("Did you make your selections?");
if (ans == 0)
    waitForUser("Select at least 3 points for the circle fit");
run("Fit Circle");
run("Measure");
circlearea = getResult("Area",0);
setResult("Area",1,area);
updateResults();

selectWindow(list[i]);
run("Flatten");
saveAs("TIFF", dir2 + name + ".overlay-p2.tif");
close();
close();
run("Clear Results");
    setResult("Label",0, name+_melt);
    setResult("Area",0, area);
    setResult("Label",1, name+_diameter");
setResult("Area",1, circlearea);
setOption("ShowRowNumbers", false);
updateResults;

selectWindow("Results");
saveAs("Results", dir2 + name + ".txt");

selectWindow("Summary");
saveAs("Text", dir2 + "SummaryResults.xls");
Appendix B: MATLAB Code for Thermal Model

% Code based on the information provided on
http://www.mrl.columbia.edu/ntm/level1/ch03/html/11c03s04.html

% Coded by David Beeler

tic;
addpath('C:\Users\David\Documents\MATLAB\Thesis Stuff');

clear all; clc;

%%%%
% Initial Settings / Values
T0 = 298; % K (temperature)
Waterrefl = 0.0225; % Percentage of intensity reflected by water
Watertrans = 0.15; % cm^-1 ... Abs Coef for 1064 and water
TBCrefl = 0.72699; % Percentage of intensity reflected by YSZ
1064nm
TBCtrans = 6.3933; % cm^-1 ... Abs Coef for 1078 and YSZ 1064nm
AlOrefl = 0.07491; % Percentage of intensity reflected by Al Oxide
AlOabs = 0.0; % According to sources, does not absorb 1064nm
porsty = .0672; % Percent of water (93.28% TBC)
i_rfl = 0.72558; % Percent reflected at 1064nm
ni_abs = 6.1373e+5; % cm^1 ... Abs Coef for 1064nm and Nickel
al_rfl = 0.95023; % Percent reflected at 1064nm for aluminum
al_abs = 1.2100e+6; % cm^-1 ... Abs coef for 1064nm and Aluminum

%%%%%%% Aluminum Oxide Properties
% density_A12O3 = 3900; % kg/m^3
AA_A12O3 = 1.2e-5; % m^2/s
k_A12O3 = 30; % W/m.K
% Tmelt_A12O3 = 2345; % K
thickness_A12O3 = 0.15e-6; % meters
%%%%%%% Water Properties
% density_H2O = 1000; % kg/m^3
AA_H2O = 0.143e-6; % m^2/s
k_H2O = 0.58; % W/m.K
% Tmelt_H2O = 373.15; % K
thickness_H2O = 120e-6; % meters
%%%%%%% YSZ Properties
% density_YSZ = 6100; % kg/m^3
AA_YSZ = 0.103e-5; % m^2/s
k_YSZ = 1.75; % W/m.K
% Tmelt_YSZ = 5273.15; % K
thickness_YSZ = 120e-6; % meters
%%%%%%% Nickel Properties
% density_Ni = 8908; % kg/m^3
AA_Ni = 23e-6; % m^2/s
k_Ni = 90.9; % W/m.K
% Tmelt_Ni = 1728; % K

%%% Aluminum Properties
% density_Al = 2700; % kg/m^3
AA_Al = 84.18e-6; % m^2/s
k_Al = 237; % W/m.K
% Tmelt_Al = 933.47; % K

%%% BOND COAT
AA_BC = 2.0265e-5; % m^2/s Thermal Diffusivity
(k/(1000*density*specificheat))
k_BC = 21; % W/m.K Thermal Conductivity
refl_BC = (0.5726*ni_rfl + 0.4274*al_rfl); % Percent Reflected
abs_BC = (0.5726*ni_abs + 0.4274*al_abs); % cm^-1

% Laser Specs
tp = 9e-9; % seconds
Ii = 5.12e8*(100*100); % W/m^2 (Starting laser intensity .94 factor, not 2)

tstep = 1e-9; % time step for the time portion ... seconds
cnt = 0;
cnt2 = 0;
count = 0;

TAl2O3 = zeros(150,9);
Ttbc = zeros(120000,9);
Twater = zeros(120000,9);

I0Al2O3 = zeros(150,1);
I0Al2O3t = zeros(150,1);
transAl2O3 = zeros(150,1);

I0bc = zeros(50,1);
I0bct = zeros(50,1);
trans = zeros(50,1);

Tbc = zeros(50,9);

tmap = zeros(50,100);

x = zeros(170,100);
y = zeros(170,100);
c = zeros(170,100);

fileID = fopen('C:\Users\David\Documents\MATLAB\Thesis Stuff\water.txt','w');
fprintf(fileID, '\%4s \%12s \%17s \%10s \n', 't','I0w','transwater','I0wt','temp');
fileID2 = fopen('C:\Users\David\Documents\MATLAB\Thesis Stuff\TBC.txt','w');
fprintf(fileID2, '\%4s \%11s \%15s \%11s \n', 't','I0tbc','transTBC','I0tbct','temp');
fileID3 = fopen('C:\Users\David\Documents\MATLAB\Thesis Stuff\Al2O3.txt','w');
fprintf(fileID3,’%4s %12s %15s %11s %10s
’,’t’,’I0Al2O3’,’transAl2O3’,’I0Al2O3t’,’temp’);

fileID4 = fopen(’C:\Users\David\Documents\MATLAB\Thesis Stuff\BC.txt’,’w’);
fprintf(fileID4,’%4s %12s %15s %11s %10s
’,’t’,’I0bc’,’transbc’,’I0bct’,’temp’);

h = waitbar(0,’Please wait...’);

for t = 1e-9:tstep:tp % time loop (seconds)
cnt2 = cnt2 + 1;
cnt = 0;
cnt3 = 0;
cnt4 = 0;
cnt5 = 0;
waitbar(t / tp)
    for th = 0.001e-6:0.001e-6:120.20e-6 % thickness of structure (in meters)
        cnt = cnt + 1;
        if th <= 120e-6 % for TBC and water
            cnt5 = cnt5 + 1;
            % calculate the temperature at the thickness, at that time
            % calculations for water
            if cnt5 == 1
                I0w = Ii - (Ii*Waterrefl);
                I0wrf1 = I0w;
            else
                I0w = lasttrans;
            end

            transwater = 100*10^((-0.001e-6)*100*Watertrans);
            I0wt = I0w*(transwater/100);
            lasttrans = I0wt;
            I0w = I0w - I0wt;

            depth = 0.001e-6;

            U1  = depth/(2*(sqrt(t*AA_H2O)));

            % for erf(u)1
            A1 = 0.3480242;
            A2 = -0.0958798;
            A3 = 0.7478556;
            C  = 0.47047;
            B  = 1/(1+C*U1);
            erfu1 = 1 - (A1*B + A2*B^2 + A3*B^3)*exp(-U1^2);

            % for ierf(c)1
            ierful = exp(-U1^2)/sqrt(pi) - U1*(1-ierful);

            U2  = depth/(2*(t-tp)*AA_H2O);

            % for erf(u)2
            A1 = 0.3480242;

        end
    end
end
A2 = -0.0958798;
A3 = 0.7478556;
C = 0.47047;
B = 1/(1+C*U1);
erfu1 = 1 - (A1*B + A2*B^2 + A3*B^3)*exp(-U1^2);

%% for ierf(c)1
ierfu1 = exp(-U1^2)/sqrt(pi) - U1*(1-erfu1);

t_trans = T_0 + (2*I_0/k_H2O)*ierfu1*sqrt(t*AA_H2O) - ierfu2*sqrt((t-tp)*AA_H2O));

%% for ierf(c)2
ierfu2 = exp(-U2^2)/sqrt(pi) - U2*(1-erfu2);

T_water = T_0 + (2*I_0/k_H2O)*(ierfu1*sqrt(t*AA_H2O) - ierfu2*sqrt((t-tp)*AA_H2O));

% calculations for TBC
if cnt5 == 1
    I_0tbc = I_1 -(I_1*TBC_refl);
    I_0tbc_refl = I_0tbc;
else
    I_0tbc = last_trans2;
end

trans_TBC = 100*10^((-0.001e-6)*100*TBC_trans);
I_0tbc_trans = I_0tbc*(trans_TBC/100);
last_trans2 = I_0tbc_trans;
I_0tbc = I_0tbc - I_0tbc_trans;

depth = 0.001e-6;

U_1 = depth/(2*(sqrt(t*AA_YSZ)));

%% for erf(u)1
A1 = 0.3480242;
A2 = -0.0958798;
A3 = 0.7478556;
C = 0.47047;
B = 1/(1+C*U1);
erfu1 = 1 - (A1*B + A2*B^2 + A3*B^3)*exp(-U1^2);

%% for ierf(c)1
ierfu1 = exp(-U1^2)/sqrt(pi) - U1*(1-erfu1);

U_2 = depth/(2*(t-tp)*AA_YSZ);

%% for erf(u)2
A1 = 0.3480242;
A2 = -0.0958798;
A3 = 0.7478556;
C = 0.47047;
B = 1/(1+C*U2);
erfu2 = 1 - (A1*B + A2*B^2 + A3*B^3)*exp(-U2^2);

%% for ierf(c)2
ierfu2 = exp(-U2^2)/sqrt(pi) - U2*(1-erfu2);

T_tbc = T_0 + (2*I_0tbc/k_YSZ)*(ierfu1*sqrt(t*AA_YSZ) - ierfu2*sqrt((t-tp)*AA_YSZ));
fprintf(fileID, '%6.1e %12.5e %12.8e %12.5e
', t, I0w, transwater, I0wt, Twater(cnt5, cnt2));
fprintf(fileID2, '%6.1e %12.5e %12.8e %12.5e
', t, I0tbc, transTBC, I0tbct, Ttbc(cnt5, cnt2));

end % Water / TBC loop

if th > 120e-6 && th <= 120.150e-6 % for Al2O3
    cnt4 = cnt4 + 1;
    % calculate the temperature at the thickness, at that time
    % calculations for Al2O3
    thAl2O3 = th - 120e-6;
    if cnt4 == 1
        I0Al2O3(cnt4) = (I0wt*porsty+I0tbct*(1-porsty)) - ((I0wt*porsty+I0tbct*(1-porsty))*AlOrefl);
        I0Al2O3t(cnt4) = I0Al2O3(cnt4);
    else
        I0Al2O3(cnt4) = I0Al2O3t(cnt4-1);
    end
    transAl2O3(cnt4) = 100*10^((0.001e-6)*100*AlOabs);
    I0Al2O3t(cnt4) = I0Al2O3(cnt4)*(transAl2O3(cnt4)/100);
    I0Al2O3(cnt4) = I0Al2O3(cnt4) - I0Al2O3t(cnt4);
    depth = 0.001e-6;
    
    U1 = depth/(2*(sqrt(t*AA_Al2O3)));

    % for erf(u)1
    A1 = 0.3480242;
    A2 = -0.0958798;
    A3 = 0.7478556;
    C = 0.47047;
    B = 1/(1+C*U1);
    erfu1 = 1 - (A1*B + A2*B^2 + A3*B^3)*exp(-U1^2);

    % for ierf(c)1
    ierfu1 = exp(-U1^2)/sqrt(pi) - U1*(1-erfu1);
    
    U2 = depth/(2*(t-tp)*AA_Al2O3);

    % for erf(u)2
    A1 = 0.3480242;
    A2 = -0.0958798;
    A3 = 0.7478556;
    C = 0.47047;
    B = 1/(1+C*U2);
    erfu2 = 1 - (A1*B + A2*B^2 + A3*B^3)*exp(-U2^2);

    % for ierf(c)2
    ierfu2 = exp(-U2^2)/sqrt(pi) - U2*(1-erfu2);
    
    TA12O3(cnt4, cnt2) = T0 + (2*I0Al2O3(cnt4)/k_A12O3)*(ierfu1*sqrt(t*AA_Al2O3) - ierfu2*sqrt((t-tp)*AA_Al2O3));
I0Al2O3tf = I0Al2O3t(cnt4);

fprintf(fileID3,'%6.1e %12.5e %12.8e %12.5e%8.1f\n',t,I0Al2O3(cnt4), transAl2O3(cnt4), I0Al2O3t(cnt4), TA12O3(cnt4,cnt2));

end % Al2O3 loop

if th >= 120.151e-6 && th <=120.200e-6 % for Bond Coat
cnt3 = cnt3 + 1;

% calculate the temperature at the thickness, at that time
thbc = th - 120.150e-6;
if cnt3 == 1
    I0bc(cnt3) = I0Al2O3tf - (I0Al2O3tf*refl_BC);
    I0bcrfl = I0bc(cnt3);
else
    I0bc(cnt3) = I0bct(cnt3-1);
end
trans(cnt3) = 100*10^((0.001e-6)*100*abs_BC);
I0bct(cnt3) = I0bc(cnt3)*(trans(cnt3)/100);
I0bc(cnt3) = I0bc(cnt3) - I0bct(cnt3);
depth = 0.001e-6;
U1 = depth/(2*(sqrt(t*AA_BC)));

%% for erf(u)1
A1 = 0.3480242;
A2 = -0.0958798;
A3 = 0.7478556;
C = 0.47047;
B = 1/(1+C*U1);
erfu1 = 1 - (A1*B + A2*B^2 + A3*B^3)*exp(-U1^2);

%% for ierf(c)1
ierfu1 = exp(-U1^2)/sqrt(pi) - U1*(1-erfu1);

U2 = depth/(2*(t-tp)*AA_BC);

%% for erf(u)2
A1 = 0.3480242;
A2 = -0.0958798;
A3 = 0.7478556;
C = 0.47047;
B = 1/(1+C*U2);
erfu2 = 1 - (A1*B + A2*B^2 + A3*B^3)*exp(-U2^2);

%% for ierf(c)2
ierfu2 = exp(-U2^2)/sqrt(pi) - U2*(1-erfu2);

Tbc(cnt3,cnt2) = T0 +
(2*I0bc(cnt3)/k_BC)*(ierfu1*sqrt(t*AA_BC) - ierfu2*sqrt((t-tp)*AA_BC));

fprintf(fileID4,'%6.1e %12.5e %12.8e %12.5e%8.1f\n',t,I0bc(cnt3), trans(cnt3), I0bct(cnt3), Tbc(cnt3,cnt2));
end  % % Bond Coat

end  % % thickness loop

end  % % time loop

fclose(fileID);
fclose(fileID2);
fclose(fileID3);
fclose(fileID4);
close(h);

%% Plot the temperature of the BC
figure(1);
plot(0.001:0.001:0.049,Tbc(1:49,:)); xlabel('Depth in microns');
ylabel('Temperature in Kelvin')

for  i = 1:9
    for  j = 1:100
        tmap(:,i) =  Tbc(:,i);
    end
end

cnt3 = 0;

start = 119000;
endtf = 120200;
arraysize = endtf-start;
final = zeros(arraysize,9);

h = waitbar(0,'Please wait...');
for  k = 1:9
    cnt3 = 0;
cnt2 = 0;
    waitbar(k / 9)
    for  i = start:endtf
        cnt2 = cnt2 + 1;
        if  i > 120150
            cnt3 = cnt3 + 1;
        end
        for  j = 1:100
            if  i <= 120000
                if  mod(j,6) == 0
                    tfinal(cnt2,j,k) = Twater(i,k);
                else
                    tfinal(cnt2,j,k) = Ttbc(i,k);
                end
            end
            if  i > 120000 && i <=120150
                %display('two');
tfinal(cnt2,j,k) = TAl2O3(i-120000,k);

if i > 120150
    %display('three')
tfinal(cnt2,j,k) = tmap(cnt3,k);
end

end

end

close(h);

depthv = (0.001)*start;
depthb = (0.001)*endtf;

for o = 1:9

    for i = 1:100
        for j = 1:arraysize
            x(j,i) = i;
            y(j,i) = depthv + j*0.001;
            c(j,i) = tfinal(j,i,o);
        end
    end

end

MTtbc = max(Ttbc(:,o));
MTwater = max(Twater(:,o));
MTAl2O3 = max(TAl2O3(:,o));
MTbc = max(Tbc(:,o));

% Create figure
figure1 = figure(o+2);
set(figure1, 'Position', [150 50 900 600])

% Create subplot
subplot1 = subplot(2,2,1,'Parent',figure1);
box(subplot1,'on');
hold(subplot1,'all');

% Create plot
pcolor(x,y,c); shading flat; % shading interp;
axis([1 100 depthv depthb ]); axis ij; colorbar; axis square;
ylabel('Structural Depth (microns)'); xlabel('Distance (microns)')

% Create subplot
subplot1 = subplot(2,2,2,'Parent',figure1);
box(subplot1,'on');
hold(subplot1,'all');

% Create plot
pcolor(x,y,c); shading flat; %shading interp;
axis([1 100 120.15 120.17 ]); set(gca, 'YTick',[120.15 120.152 120.154 120.156 120.158 120.160 120.162 120.164 120.166 120.168 120.17]);
\texttt{axis ij; colorbar; axis square;}
\texttt{ylabel('Structural Depth (microns)'); xlabel('Distance (microns)')}
\texttt{I_i_r = I_i/10^{12};}
\texttt{\% Create textbox}

\texttt{\%\% Title}
\texttt{annotation(figure1,'textbox',...}
\texttt{[0.10 0.45 0.35 0.07],...}
\texttt{'String','Energy:',...}
\texttt{'FitBoxToText','on','LineStyle','none','FontSize',14);}
\texttt{annotation(figure1,'textbox',...}
\texttt{[0.24 0.45 0.35 0.07],...}
\texttt{'String',{num2str(I_i_r)},...}
\texttt{'FitBoxToText','on','LineStyle','none','FontSize',14);}
\texttt{annotation(figure1,'textbox',...}
\texttt{[0.31 0.46 0.35 0.07],...}
\texttt{'String','{x \{10\}^{12} W/m}^{2}',...}
\texttt{'FitBoxToText','on','LineStyle','none','FontSize',14);}
\texttt{annotation(figure1,'textbox',...}
\texttt{[0.55 0.45 0.35 0.07],...}
\texttt{'String','Showing: ',...}
\texttt{'FitBoxToText','on','LineStyle','none','FontSize',14);}
\texttt{annotation(figure1,'textbox',...}
\texttt{[0.66 0.45 0.35 0.07],...}
\texttt{'String',{num2str(o)},...}
\texttt{'FitBoxToText','on','LineStyle','none','FontSize',14);}
\texttt{\% Water}
\texttt{annotation(figure1,'textbox',...}
\texttt{[0.20 0.35 0.5 0.07],...}
\texttt{'String','Max Temperature of Water (Kelvin):',...}
\texttt{'FitBoxToText','off','LineStyle','none');}
\texttt{annotation(figure1,'textbox',...}
\texttt{[0.55 0.35 0.35 0.07],...}
\texttt{'String',{num2str(MTwater)},...}
\texttt{'FitBoxToText','off','LineStyle','none');}
\texttt{\% TBC}
\texttt{annotation(figure1,'textbox',...}
\texttt{[0.2 0.3 0.5 0.07],...}
\texttt{'String','Max Temperature of TBC (Kelvin):',...}
\texttt{'FitBoxToText','off','LineStyle','none');}
\texttt{annotation(figure1,'textbox',...}
\texttt{[0.55 0.3 0.35 0.07],...}
\texttt{'String',{num2str(MTtbc)},...}
\texttt{'FitBoxToText','off','LineStyle','none');}
\texttt{\% Al2O3}
\texttt{annotation(figure1,'textbox',...}
\texttt{[0.2 0.25 0.5 0.07],...}
\texttt{'String','Max Temperature of TGO (Kelvin):',...}
\texttt{'FitBoxToText','off','LineStyle','none');}
\texttt{annotation(figure1,'textbox',...}
\texttt{[0.55 0.25 0.35 0.07],...}
'String',{num2str(MTAl2O3)},...
'FitBoxToText','off','LineStyle','none');

%% Bond Coat
annotation(figure1,'textbox',...
[0.2 0.2 0.5 0.07],...
'String',{'Max Temperature of Bond Coat (Kelvin):'},...
'FitBoxToText','off','LineStyle','none');
annotation(figure1,'textbox',...
[0.55 0.2 0.35 0.07],...
'String',{num2str(MTbc)},...
'FitBoxToText','off','LineStyle','none');

end

figure(14);
for i = 1:(tp*10^9)
MTtbc(i) = max(Ttbc(:,i));
MTwater(i) = max(Twater(:,i));
MTAl2O3(i) = max(TAl2O3(:,i));
MTbc(i) = max(Tbc(:,i));
end
xval = 1e-9:1e-9:tp;
plot(xval,MTtbc,xval,MTwater,xval,MTAl2O3,xval,MTbc);
legend('TBC','Water','TGO','BC','Location','NorthWest');
title('Maximum Temperature');
xlabel('Time (seconds)'); ylabel('Temperature (Kelvin)');
toc;