A Review of LIBS for Real-Time Detection of Trace Silicone Contaminants on CFRP Surfaces

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Introduction

Laser ablation is the removal of material by laser pulses through photochemical, photothermal, or photophysical mechanisms, which is useful to prepare an adherend surface for adhesive bonding. Laser surface treatment is a method that has been under research for the past decade at NASA Langley Research Center (LaRC) to prepare surfaces for adhesive joining of aerospace composite materials [1,2] and metallic alloys [3]. Laser ablation of composite materials increases surface area and removes the surface contaminants introduced during material handling and fabrication processes. By adjustment of laser parameters, it is possible to obtain repeatable surface conditions, and superficial contaminants can be selectively and efficiently removed without damaging the underlying carbon fibers or the carbon fiber reinforced polymer (CFRP) substrate [1,2]. Laser induced breakdown spectroscopy (LIBS) is a surface characterization and inspection technique that can be seamlessly integrated into the laser surface treatment process. At NASA LaRC, a single laser system has been used for both laser surface treatment and LIBS, which enables in-situ monitoring of surface contaminants.

This work focuses on the advancements at LaRC using LIBS to detect surface silicone contaminants on aerospace CFRP materials and to provide surface quality control in adhesive bonding [4].

Laser Induced Breakdown Spectroscopy

LIBS is an elemental characterization technique that utilizes an intense laser source to excite a material (solid, liquid, or gaseous) into a plasma state, and upon relaxation, the chemical species emit light. The optical emission from the plasma plume provides information about the elemental composition of the target material. When LIBS uses short/ultrashort pulses, laser-matter interaction is predominant (i.e. laser-plasma interaction is reduced or non-existent). For polymers, when the laser intensity irradiated on the material is sufficient, mechanical stress is induced by multiphoton transition. If the mechanical stress is sufficient, it will produce bond dissociation, and the polymer material is removed from the target surface by fragmentation [5,6]. There is minimal energy transferred to the regions outside the irradiated material volume, thus, producing less thermal stress in the material [7]. The extension of LIBS toward lower pulse energies, typically below 100 µJ, is known as micro-LIBS (µLIBS) [7]. In this regime, the ablation crater size decreases with lower pulse energies, and thus, µLIBS may be considered nearly nondestructive with enhanced resolution and surface sensitivity [7-10]. µLIBS has been applied to the monitoring of surface quality prior to adhesive bonding [7].

Significant advantages of LIBS measurements are that they can be conducted in open air and without sample preparation, and the results can be obtained near-instantaneously or in real-time. Advancement in the LIBS technique has shown that it can match or exceed the surface sensitivity of X-ray photoelectron spectroscopy (XPS) for detecting the presence of surface contaminants such as silicones [8].

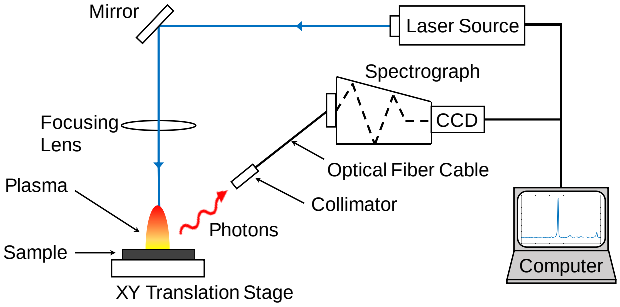

Figure 1. Typical LIBS apparatus comprised of a laser source, a spectrograph, a CCD-based detector, and a computer for data acquisition and laser control.

LIBS System

A typical LIBS apparatus (Figure 1) is comprised of a laser source and a spectrometer, which includes a detector, e.g. charge-coupled device (CCD) array, and a spectrograph. The laser beam is usually focused to enhance spatial resolution and to deliver maximum laser intensity irradiation on the target surface. LIBS instrumentation can include software for data acquisition and spectral processing and analysis. The spatial resolution of a LIBS system will depend on the material properties and laser parameters. At NASA LaRC, the picosecond laser system can achieve a spatial resolution of ~20 µm at 15 µJ pulse energy when a single pulse strikes a CFRP surface [7]. Therefore, understanding the laser-matter interaction is crucial to enhance the spatial resolution.

LIBS Applications to CFRP

Nanosecond laser ablation of CFRP surfaces has also been investigated for improved adhesive bonding [11]. Among several pre-bond surface inspection techniques, LIBS was used to characterize different silicone concentrations. Different surface conditions were investigated: control, surfaces contaminated with different silicone concentrations, and laser treated. Preliminary results with microjoule LIBS were reported for contaminated CFRP surfaces. Low silicone concentrations (< 0.8 μg/cm^2) were shown to interfere with the proper adhesive bonding and found to be highly detrimental to bond performance (adhesive failure mode).

Control and silicone contaminated surfaces were investigated to determine the effect of the residual contaminant on the bond performance [2]. A 355 nm, 10 ps laser system was used for LIBS and laser treatment (LT). μLIBS was used to detect silicone contamination before and after LT. Figure 2 shows the silicon-to-carbon (Si/C) ratio as a function of the silicone areal density deposited on a surface prior to LT.

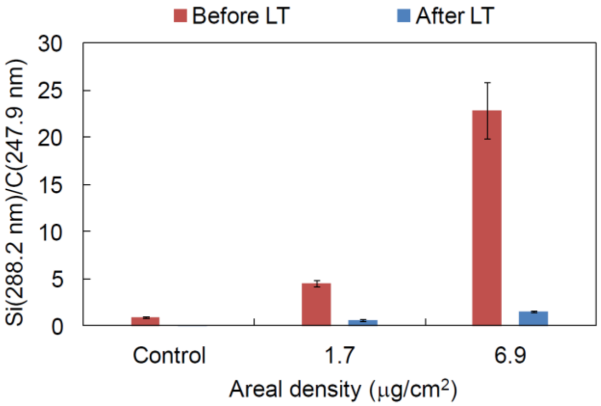

Figure 2. Si/C ratios from the μLIBS measurements before and after laser surface treatment using picosecond pulses [2].

Surface characterization using LIBS (before and after laser treatment) with 355 nm, 10 ps pulses was performed on carbon fiber reinforced epoxy panels for detection of ultra-thin silicone contamination layers from 0.15 μg/cm^2 to 2 μg/cm^2 (thickness of 1.6 nm to 20 nm) [7]. The same laser system was utilized for both treatment and LIBS characterization. LIBS was performed using 15 μJ pulses with a single shot on a fresh surface to maximize surface sensitivity. Optimization of laser parameters was studied to decrease the material ablation for LIBS inspection. Time-resolved analysis was conducted to determine plasma conditions that are optimal to detect Si. The LIBS instrument was sensitive enough to detect residual Si after laser surface treatment.

Surface sensitivity and the LIBS limit of detection (LOD) were investigated for silicone contamination on CFRP surfaces from the fabrication process [8]. XPS and LIBS analyses were performed on identical samples. XPS data were obtained from two different laboratories, BTG Labs (Cincinnati, OH) and NASA LaRC (Hampton, VA). For quantitative analysis, analytical calibration curves were constructed (Figure 3). From the calibration curves, it was possible to determine the detection limits of LIBS, which were below 0.6 at.%. The results in this work demonstrated the advantages of LIBS over XPS for rapid detection of minute quantities of silicone contaminants, with high surface sensitivity, no special atmosphere or sample preparation.

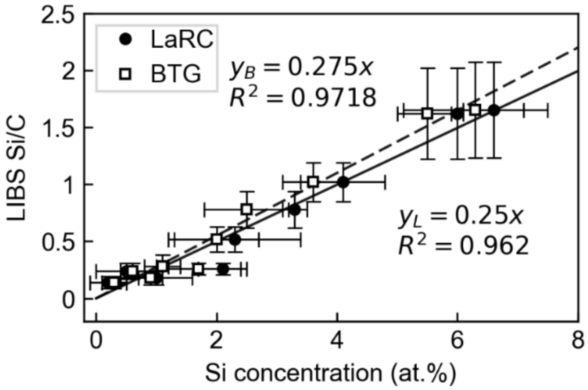

Figure 3. Analytical calibration curves with the Si/C ratio from the LIBS measurements and the Si concentration using XPS. The linear fits y_L (solid line) and y_B (dashed line) correspond to LaRC and BTG, respectively. (Reprinted from [8] with permission of SAGE Publishing)

A design of experiments (DoE) approach was used to determine optimum laser surface treatment conditions for removal of trace silicone and for improved bond performance of carbon fiber reinforced epoxy composites [12]. The Si/C ratio from LIBS was used in the study to assess silicone reduction after laser ablation. The laser ablation processing window was found to be wide, which indicated that laser treatment is a robust means of surface preparation. The DoE results indicated that average laser power was the most critical parameter influencing bond performance and the removal of silicone contamination. The optimal laser parameters were identified based on the analyzed material system [12]. The DoE statistical model was in good agreement with the full-scale validation sample prepared using optimum laser processing conditions selected by the model.

Surface Mapping

LIBS measurements are taken at specific locations and each location gives a better understanding of the surface condition in that region (Figure 4). The yellow dots represent the locations where LIBS measurements were taken. The LIBS Si/C ratio from those locations can be correlated to the surface morphology or failure modes. The numbers in parentheses represent Si/C ratios determined before (white) and after (red) laser ablation at 200 mW, 355 nm, and a pulse width of 10 ps.

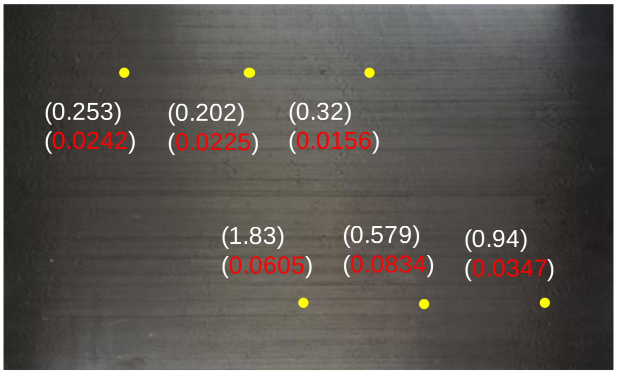

Figure 4. Surface mapping of a thermoplastic composite panel showing the LIBS Si/C before (white) and after (red) laser ablation.

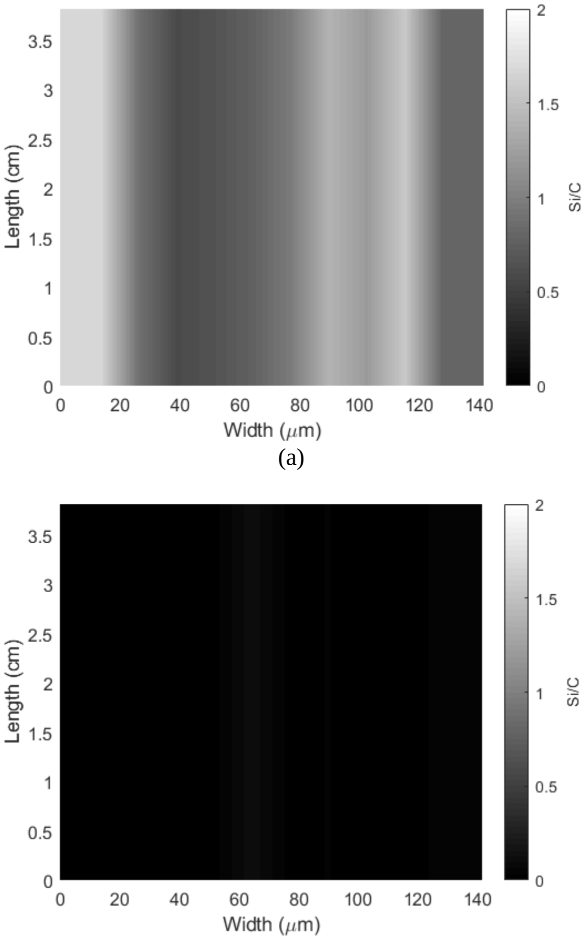

Figure 5. Surface mapping of an ablated region of 3.81 cm x 141.4 mm. After the second ablation pass (b), silicone concentration was reduced significantly, in contrast to the first pass (a).

Another example of surface mapping is when laser surface treatment and LIBS are conducted simultaneously. In this case, four collimators linearly arranged monitored the plasma emissions from a 3.81 cm ablated line. Ten lines were ablated at 200 kHz, 2 W average power (10 µJ pulse energy), and 254 cm/s scan speed, separated by 12.7 µm to produce the surface map based on the Si/C ratio (Figure 5). Figure 5a shows the Si/C surface map for the first pass and Figure 5b for the second pass, in which silicone concentration has been decreased significantly.

From the examples of surface mapping using LIBS, it shows that the silicone contamination is not uniform across a composite surface.

Discussion

Recently at NASA LaRC, LIBS has been advanced and customized for inspection of CFRP composites to detect minute quantities of silicones in real-time and in-situ, without any sample preparation or special atmosphere, and in a nearly non-destructive manner. The minute silicone quantities are at concentrations below those empirically known to be a threat to adhesive bonding. Since adhesive bonding occurs within the top 10-20 molecular layers of a surface, the characterization and quality control tools must have the appropriate resolution to interrogate at this length scale.

Recommendations

Shorter wavelengths deliver higher energy photons which most likely induce photochemical ablation in polymers [13]. Shorter pulse widths enable higher peak powers which can produce direct ionization of the irradiated polymer material [14]. Therefore, a laser source that can enable photochemical ablation is recommended to reduce heat affected zones and thermal stresses on CFRP surfaces.

The laser fluence for a LIBS process should be set above the ablation fluence threshold of the matrix resin and below that of the fiber. Considering the LIBS apparatus at LaRC, the deposited fluence by LIBS used for CFRP characterization is much lower than that by laser surface treatment since only a single shot on a fresh surface is used.

Common LIBS detectors are based on CCD technology. One main consideration is the sensitivity of the detector, which depends on the dynamic range. A larger dynamic range will enable the detection of dim light above the read noise level. The advancement of CCD technology has allowed the implementation of enhancements to detect low-intensity emissions, improving the detection of minute analyte concentrations.

The wavelength range depends on the grating installed in the spectrograph. Depending on the type of contaminants, the grating should be optimized and provide high quantum efficiency for that spectral region. The groove density in the grating should be chosen such that the spectral resolution is optimal. When surfaces are inspected for a wide variety of elements, an echelle grating should be used to have a wide wavelength range and high spectral resolution.

In order to reduce the footprint of the LIBS hardware, there are currently microchip laser units. Microchip lasers can achieve high peak powers (in the kW order) and at least microjoule pulse energies. The pulse frequencies are in the kHz range in this type of laser.

Technique Maturity

Extensive research has been performed at LaRC to demonstrate the versatility of LIBS to characterize CFRP laminates with both thermoset and thermoplastic matrices [15]. LIBS has been shown to have a LOD well below the threshold of contaminants empirically known to be a threat to adhesive bonding [2,7,8,12]. Currently, work is underway to automate and integrate the LIBS instrument into a laser surface treatment process to enable simultaneous detection of minute quantities of contaminants while the target surface is being treated [16]. Real-time, closed loop control of automated surface treatment methods is also possible using an integrated LIBS inspection system [16].

Summary

Laser surface treatment has been investigated by NASA LaRC to remove ultralow levels of contamination on aerospace composite surfaces and to activate the surface chemistry and increase surface area prior to adhesive bonding and coating processes. Silicones are ubiquitous in the fabrication process of CFRP substrates and, even at low concentrations, can significantly diminish adhesive bond performance. LIBS has been utilized as a surface quality control tool for the detection of silicone contaminants and was demonstrated to be an adequate and robust technique that can be integrated for in-line control of a bonding process, which may include laser surface treatment.

The LIBS instrument developed at LaRC was shown to obtain surface sensitivity comparable to XPS. Extensive research has been conducted at LaRC to prove the reliability of LIBS for the detection of ultralow levels of silicone species on CFRP surfaces prior to adhesive bonding.

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