Laser Trace Vaporization of Explosives

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Introduction: The low vapor pressure of many explosives presents a significant challenge for the detection of trace quantities by noncontact methods. We address this limitation by illuminating explosives including TNT, RDX, and ammonium nitrate with an infrared (IR) laser tuned to strong molecular absorption bands to efficiently heat trace amounts present on substrates. This dramatically increases the vapor concentration for immediate detection, obviating the need to manually swab surfaces to collect solid particles and transport them to a nearby detector. The instantaneously generated vapor produced by laser trace vaporization (LTV)1,2 can be identified by any number of detection or sampling techniques.

Technical Approach: Handling explosives and related materials or improvised explosive devices (IEDs) results in particulate contamination of any contacted surfaces. These particles typically offer a significant residence time and provide a detection target to monitor for IED activities. Wavelength-specific light from a miniature IR quantum cascade laser is used to efficiently couple energy into a specific molecular bond of an explosive material and rapidly heat the particle. This allows particles of explosives to be instantaneously vaporized without decomposition to form a momentary high-concentration plume suitable for various detection applications. The verification of augmented vapor signatures in this work is accomplished with a commercial ion mobility spectrometer (IMS).

Results: The ability to controllably vaporize explosive materials can be seen in Fig. 1, where 160 mW of laser power was scanned over a polycarbonate substrate densely coated with submicron particles of RDX. By careful selection of laser power, wavelength, and scanning speed, LTV is able to completely vaporize all illuminated RDX particles without damaging the substrate. Figure 2 shows that vaporization is enhanced when using a wavelength that is strongly absorbed by the explosive material. A thin, IR-transparent substrate was loaded with sufficient TNT material (~500 ng) to provide a background vapor signal detectable with the IMS and then irradiated with wavelengths that were either weakly or strongly absorbed by the TNT. When using a weakly absorbed wavelength, little to no enhancement was seen relative to the background signal. Conversely, when using a wavelength more strongly absorbed by the TNT, a significant enhancement was seen. However, when thicker substrates were used, wavelength selectivity in the TNT vapor enhancement was not observed. We believe this is due to nonspecific absorption by the substrate, causing it to heat sufficiently to contribute to the TNT vaporization, and in many cases it can mask the effect of direct vaporization of the particles due to resonant absorption.

The results discussed above were all accomplished using continuous wave lasers. To examine the effects of using short laser pulses and different particle and substrate geometries, we used a software package (COMSOL) to model these conditions. Figure 3 (left) shows the simulation results of laser heating of a strongly absorbing TNT particle (1/e absorption depth of 1 µm; 69 µm diameter) on a weakly absorbing substrate (1/e absorption depth of 100 µm). The results show that the TNT particle is heated significantly more than the underlying substrate. An infrared camera was used to empirically measure the temperature rise of laser-heated ammonium nitrate particles with diameters of ~60 microns (Fig. 3, right). The particles reach thermal equilibrium in about 50 ms, well before the end of the 200 ms laser pulse. Together these results suggest that using shorter laser pulses will allow us to heat particles on surfaces while limiting the contribution that substrate heating makes to vaporization of the particles.

Conclusion and Future Work: We have demonstrated the efficacy of LTV to vaporize ammonium nitrate, TNT, and RDX on a variety of solid substrates and in the presence of different interferents. We have found that while vaporization of selected materials can be controlled by carefully controlling the laser wavelength, nonresonant heating by the substrate can mask that specificity when continuous wave lasers are used. Our computational modeling suggests that the substrate heating can be controlled by using shorter laser pulses, which we believe, when also controlling the
laser wavelength, will allow us to selectively vaporize the materials of interest without vaporizing potentially interfering materials in the vicinity of the explosives.

The small footprint of quantum cascade lasers provides the opportunity to integrate this technology with existing detectors with only modest hardware modifications, which is especially desirable for handheld instruments. Additionally, the flexibility to manufacture quantum cascade lasers at a wide range of specific wavelengths allows LTV to be considered for use in the detection of other low vapor pressure materials such as drugs of abuse.

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References


Heat Sensitization Effects in Aluminum Ship Structure Alloys

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Background: Aluminum-magnesium alloys with 3 to 6 percent magnesium are important ship structure alloys because they exhibit excellent resistance to
general corrosion and high as-welded strength. However, Al-Mg alloys can become highly susceptible to intergranular corrosion and stress corrosion cracking if exposed to temperatures above 50 °C for extended periods of time. This phenomenon is known as sensitization and is a consequence of the precipitation of β-Al3Mg2 on the grain boundaries. β is anodic relative to Al, and corrodes and dissolves very quickly upon exposure to seawater. Key research issues concerning sensitization include how the microstructure evolution relates to bulk measurable properties, how critical fatigue properties degrade with sensitization, and strategies for structural health assessment. The NRL core program investigating sensitization is a multidisciplinary collaboration of the Multifunctional Materials Branch and the Center for Corrosion Science and Engineering. The main research thrusts are detailed microstructure analysis, corrosion fatigue, and stress corrosion cracking experimental investigations.1

Evolution of Sensitized Microstructure: Figure 4 shows the general microstructure evolution trends of a 5083 alloy aged for various times and temperatures, as observed by transmission electron microscopy. At a given temperature, as a function of time, the β phase initially forms as isolated particles and eventually becomes a continuous coating on the grain boundaries as shown in Fig. 4(a). For intermediate times, the β phase forms a complex, partially continuous pattern. Aging temperature affects the time required to form the continuous network and the final thickness of the grain boundary phase, as shown in Fig. 4(b). The standard method of assessing the susceptibility to stress corrosion cracking is the ASTM G67 test, which measures the mass loss of a sample following immersion in nitric acid for 24 hours. Comparing our transmission electron microscopy studies with ASTM G67 measurements, we have established that the transition from isolated β particles to continuous β coverage of the grain boundaries corresponds to ASTM G67 values centered around 30 mg/cm². For reference, ASTM G67 values of 15 mg/cm² or less are currently considered acceptable for new ship construction, while values of 50 to 60 mg/cm² are often found for cracked plates in service.

Corrosion-Fatigue Behavior: Figure 5 shows the fatigue crack growth rates (da/dN) as a function of stress intensity amplitude (ΔK), for an Al-Mg alloy in the as-received (unsensitized) condition, and fully sensitized condition (grain boundary β phase is continuous). The data shown are for a high load ratio, R = 0.85, which corresponds to a high average load with small cyclic amplitude superimposed. At high R, in air, sensitization has no discernible effect on the fatigue crack growth rates or thresholds. However, in salt water, sensitization has a huge effect on threshold,

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**FIGURE 4**
Evolution of sensitized microstructure in a 5083 aluminum alloy (Al-4.5% Mg). (a) For fixed temperature aging, the development with time is initially isolated β particles, followed by a transition to continuous coverage of the grain boundaries by β. The intermediate condition exhibits complex morphology that may be partially continuous. (b) The time required to form the continuous β network increases with lower aging temperatures. The β phase is much thinner for lower aging temperatures, as well.
as indicated in Fig. 5. This finding led us to systematically investigate the high R behavior in salt water as a function of degree of sensitization for various aging temperatures and times. The high load ratio corrosion-fatigue threshold values for series of specimens aged at 70, 100, and 175 °C are shown in Fig. 6(a), plotted as a function of the ASTM G67 mass loss. Two things are remarkable about these data: (1) The data for all three aging temperatures fall on the same curve, and (2) there is a transition in the behavior at a particular mass loss value of 30 mg/cm². For degree of sensitization less than 30 mg/cm², the corrosion-fatigue threshold is not degraded, but above 30 mg/cm², the threshold degrades rapidly. A similar, though even more abrupt, transition behavior is seen in the stress corrosion cracking threshold, which is the cracking threshold for static loading (essentially R = 1), in Fig. 6(b). The transition at 30 mg/cm² corresponds quite nicely with the transition in the microstructure described in the preceding section. Thus, as long as the β phase is discontinuous, the material retains essentially its full fatigue and stress corrosion thresholds, but when the β phase becomes continuous, the material fails readily if exposed to salt water.

**Significance:** The commonality of the dependence of corrosion-fatigue and stress corrosion cracking thresholds upon the degree of sensitization regardless of aging temperature has several important implications. It means that the structural health of the material does not depend on the details of the time-temperature aging history; it depends only upon the degree of sensitization at any given time. This behavior also can be the basis for accelerated sensitization rate testing for manufacture quality control because rapid aging at high temperatures produces the same effects on the material as the very long aging at low temperatures that occurs in service. The existence of a critical degree of sensitization above which degradation of the corrosion-fatigue and stress corrosion cracking thresholds occurs provides a rational, quantitative basis for structural health assessment.

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**Reference**

Biosensor Triage for Traumatic Brain Injury

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**Traumatic Brain Injury:** Traumatic brain injury (TBI) has been labeled the signature injury of the modern battlefield, occurring most commonly in association with exposure to blasts from improvised explosive devices. While improvements in battlefield medical response and widespread use of body armor have decreased mortality rates in Operations Iraqi Freedom, New Dawn, and Enduring Freedom well below those of previous conflicts, an ever larger number of military personnel are returning home with significant neurological damage. TBI impairs many aspects of brain function, including mood, reactions, memory, perceptions, and motor coordination. To date, researchers and clinicians rely primarily on neuroimaging and behavioral measures for limited diagnosis, prognosis, and treatment of brain injuries. TBI, and especially mild TBI, is difficult to accurately diagnose because symptoms are heterogeneous in both their nature and in the timing of their resolution or appearance. The semiquantitative nature of neuroimaging techniques and the subjectivity of evidence-based tests often leave in-theater medical personnel struggling to determine whether and when warfighters are well enough to return to duty. A rapid method to quantify any compromise to brain function is, therefore, vital to protect both the injured personnel and their brothers-in-arms.

**Immunoarray Technology:** There is a significant drive toward identification of physiological molecules — or “biomarkers” that can be used as quantitative predictors of the severity and type of TBI. However, as TBI involves many interrelated processes, many of which are shared by other neurodegenerative syndromes, it is unlikely that a single biomarker will be able to provide the sensitivity and specificity needed for the diagnosis of TBI. For this reason, we have taken the approach of assessing time-associated changes for a suite of biomarkers as a whole as an indicator of TBI.

Immunoarray-based sensors offer the capability of rapid, sensitive, and simultaneous detection in a variety of different sample matrices, and are well suited to operational environments and point-of-care settings. We are using NRL Array Biosensor technology to develop and evaluate TBI biomarker tests for deployment to forward laboratories and aid stations. Antibodies immobilized on a glass slide at spatially discrete locations are used to capture the target biomarker molecules from solution (Fig. 7, top), which in turn react with a second detection antibody that is also specific for the antigen. A specially tagged tracer antibody is added, and binds to the detecting antibody to provide a fluorescent signal (Fig. 7, bottom). Carefully optimized antibody pairs guarantee specificity of the reaction and achieve detection into the picomolar range.

**FIGURE 7**
Schematic of the capture antibody array (top) used to detect multiple TBI biomarkers in a single multiplex test (bottom). For each target, a “sandwich” immunoassay format is used (detail).
Biomarker Tests for TBI Diagnosis: Our approach has been to develop array-based tests for biomarkers involved in different physiological processes in TBI. After identifying eight promising TBI biomarkers and screening over 100 different pairs of antibodies for their sensitivity and affinity, we have downselected a core panel of three biomarkers: glial fibrillary acidic protein (GFAP), ubiquitin hydrolase L1 (UCH-L1), and S100β. Each of these biomarkers has been demonstrated to indicate a different aspect of TBI pathophysiology (Fig. 8). As an added benefit, NRL Array Biosensor technology accommodates additional biomarkers as they are validated in clinical studies and the recognition reagents are developed.

Figure 9 shows a representative example of a fully multiplexed assay for our three TBI biomarkers. Using an array of “capture” antibodies specific to each target and immobilized at discrete locations, the sample is analyzed and binding of each biomarker to its appropriate capture antibody is determined after sequential addition of detection antibodies and tagged tracer antibodies. Results clearly demonstrate detection of UCH-L1, GFAP, and S100β in the appropriate spots, with no significant signals observed in negative controls. We have optimized the system to minimize cross-reactivity and to improve sensitivity. By the addition of an enzymatic signal amplification step, we can obtain a 100-fold improvement in sensitivity, overcoming one of the disadvantages of many rapid tests. We are currently validating these tests in spiked serum. After integration into a commercial off-the-shelf (COTS) system, these assays will be tested with commercial sample from TBI patients. We anticipate that these multiplexed assays, once optimized in the COTS system, will be a valuable tool for clinicians and forward-deployed personnel.

These tests will provide both the critical capability to determine the severity of and formulate a prognosis for TBI, and the opportunity for early intervention and improved clinical outcome.

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