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Particle Generation by Laser Ablation in Support of Chemical Analysis of High Level Mixed Waste from Plutonium Production Operations

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Research Objective

Our goal is to provide fundamental mechanistic studies of laser produced particulate formation in support of the use of Laser Assisted-Inductively Coupled Plasma-Mass Spectroscopy (LA-ICP-MS) to be used for analysis of radioactive/toxic materials.

Research Progress and Implications

The work reported here represents the first nine months of this 3-year project. The major focus of these studies is determining the detailed mechanisms and character of the particulates generated by laser ablation of solid targets relevant to sampling materials for chemical analysis using inductively coupled mass spectroscopy, ICP-MS. In this application, particles generated by laser ablation must be transported to the plasma "torch" of the ICP-MS, often through a hollow tube with an interior diameter of a few µm. Proper digestion and ionization of particles in the plasma limits particle sizes to under a micron. Thus the production of submicron particles which truly represent the stoichiometry of the specimen is of critical importance.

We have initiated fundamental studies of the mechanisms and resulting characteristics of particulate formation by laser ablation of single crystal materials. One material under study at WSU is a wide bandgap ionic material with relatively low melting point to easily trigger the numerous electronic, thermal, and mechanical processes contributing to particulate formation. This material, $NaNO_3$, has a reasonably high sensitivity to defect formation via exposure to ionizing radiation and by mechanical deformation. This allows us to vary the laser fluence thresholds for a number of these processes.

Pulsed UV laser radiation (248 nm KrF excimer) at high fluences (> 10 J/cm^2, 30 ns pulses) of $NaNO_3$ produces large numbers of particles. Irradiation in air or vacuum produces large spherical particles (> 10 µm in diameter) due to shock-induced spallation of melted surface material. The majority of the particulates are under < 1 µm in diameter and are produced by "hydrodynamic sputtering," where repeated melting and solidification, with the associated thermal expansion and cooling, induce asperity growth and tip ejection over the course of many laser pulses. We have developed a one-dimensional numerical model of the formation and propagation of laser induced shock waves, which verifies that the tensile stresses in the melt layer are sufficient for liquid spallation. In addition, the numerical model provided estimates of the peak surface velocity, which we input into models of hydrodynamic sputtering to predict the minimum particle sizes produced by this means. To date the hydrodynamic sputtering model is consistent with the experimentally observed production of small particles.

Although hydrodynamic sputtering produces large numbers of particles in the size range desired for laser-ablation ICP-MS, there is considerable concern that the repeated melting and solidification required for asperity growth and will alter the stoichiometry of the sampled vs. original material. At PNNL we are using Raman spectroscopy and Secondary Ion Mass Spectroscopy of collected particles to test for this fractionation using $NaNO_3$ grown with 0.01 to 10 % Cs doping. Similar spectroscopy and dissolution ICP-MS of the original samples is being performed on the as-grown material for comparison.

A promising approach to the production of stoichiometric particles that we are pursuing is optimizing laser-induced fracture. Fracture has negligible effect on the composition of micron and sub-micron-sized particles relative to the original sample. The chief concern is the ability of fracture to produce sufficiently small particles. Initial tests of $NaNO_3$ single crystals with 8 ns 1064-nm laser pulses (Nd:YAG fundamental) show that melting is hindered significantly relative to 248 nm pulses. Hydrodynamic sputtering is avoided by using single laser pulses to generate the fracture. Although sodium nitrate is quite transparent at 1064 nm, sufficient absorption is obtained at fluences below 10 J/cm^2 (7 ns pulses) to produce the required particles. This unconventional particle generation mechanism is associated with a departure from conventional wisdom, where UV lasers have been reported to produce more stoichiometric emission products due to the relatively high absorption of most materials at UV wavelengths. Target surface morphology and ejected particulate characterization are showing that over a range of fluences, fracture is indeed producing particles of the desired size for ICP-MS.

Studies at PNNL as part of this program have focused on the use of optical particle size measurements in conjunction with LA/ICP-MS to determine the laser pulse energies, pulse lengths and focal areas that produce particle size distributions that maximize performance of LA/ICP-MS. The samples studied have included simulants of vitrified waste and tank waste simulants as well as more idealized samples such as calcium carbonate, copper and aluminum. These samples span a large range of optical and physical properties relevant to the laser ablation process, representative of the properties. This is similar to the range of properties expected in Pu wasteforms including tank waste, contaminated equipment as well as pure Pu metal and oxide samples. Analytical performance was measured in terms of sensitivity, precision, and accuracy. The focal offset (distance from the laser focus to the surface) was varied to cover a wide range of fluence and pulse energies.

The first studies were performed using a 10 ns ablation pulse length at 355 nm. Pulse energies from 50 uJ/pulse to 3 mJ were used, corresponding to energy densities of < .1 J/cm^2 to 20 J/cm^2 over the range of focal offsets employed. The relative degree of laser-induced plasma and particulate formation was tested by comparing the relative population of particulates, ions and neutral species as a function of focal offset. These quantities were measured by a combination of light scattering and optical absorption spectroscopy with a CW dye laser. Results were markedly different for samples with low thermal conductivity (glasses, simulants, chalk) than for the metal samples. Particulate production from laser ablation of the poor thermal conductors exhibits maxima on either side of the focal point. This corresponds to energy densities below or at the threshold for generation of a laser-induced plasma. The metal samples showed a much weaker dependence on the focal offset, with a slight maximum at the focal point. The maximum in the particle size distribution from ablation of the poor conductors is from .2, 1 micron while ablation of the metals primarily produces particles < .2 microns.

Picosecond (15-20 ps) ablation studies of the poor thermal conductors showed that the dependence of the particulate production on focal offset depends on the total pulse energy, or the number of photons striking the surface, rather than the fluence. These results suggest that the production of particulates is not strongly coupled to the formation of a laser-induced plasma. When the metal samples were ablated with picosecond pulses, the focal offset behavior displayed slight maxima away from the focal point, suggesting that thermal conductivity may constrain/define the laser parameters for optimum production of particulates suitable for analysis by ICP-MS. Also being studied with WSU is what role fracture vs. melting is playing in the particulate production for low thermal conductivity materials.

Planned Activities

In the next 15 months we plan to continue the Nd:YAG induced fracture studies on “transparent” materials in both air and vacuum to better understand the particle size determining mechanisms and to work jointly on measurement and minimization of fractionation. We also will examine more closely the trajectories of the various types of particles to determine possible separation schemes to improve selection of the “best” particles. Electric charge on the fracture induced ejecta has been demonstrated and will be examined as a possible means of separation. Further studies using shorter (fs) pulses will be investigated to determine what role pulse width has on tye types of particles produced. Finally, additional modeling and simulations of the thermal-mechanical processes will be carried out to clarify mechanisms. These efforts will be coordinated and performed on the same materials to maximize their impact on chemical analysis technology.