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

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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

To provide fundamental mechanistic studies of laser-produced particulate formation in support of the analysis of radioactive and/or toxic materials by Laser Assisted–Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS).

Research Progress and Implications

This report summarizes the second year of work in a three year project. Both WSU and PNNL have focused on particle generation. After irradiation, the particles are collected on single crystal silicon substrates, gold coated, and examined by high resolution (field ion) scanning electron microscopy at Pacific Northwest Laboratories. This work employed single crystal sodium nitrate due to the relevance of this material in the analysis of high level wastes from plutonium production.

We have shown that 1064 nm laser pulses 3.4 J/cm^2 are sufficient to fracture a stepped single crystal surface without melting, producing a multitude of small particles with sizes ranging from 100 nm to microns. We are able to characterize the morphology of the micron-sized particles in great detail and have determined that they are not due to melt spallation, but from fracture alone. The fact that they have not melted implies that their composition has not been altered by thermal processes. A second series of tests in which a stepped single crystal surface was exposed to thousands of laser pulses showed that fractured particles continued to be generated for long times, principally due to continuous undercutting and fracture at existing cleavage steps. Evidence for the generation of new cleavage steps was observed. Continuous particle generation under repeated laser irradiation provides for efficient utilization of small samples for analysis. Further, the number of sub-micron particles suitable for transport seems to grow with continued irradiation, presumably due to the development of small features along the cleavage steps.

At still higher fluences, single laser pulses produce melted spheres, typically ten µm in diameter, by spallation of melted material from the target. Although these particles are too large for efficient transport to the ICP-MS torch, the collection substrate often showed significant numbers of smaller spheres (50-200 nm in diameter) surrounding the larger ones. These “halos” were produced from material evaporated from the larger spheres and condensed on the substrate. This process is similar to the condensation of smaller particles from the vapor near the target surface. Due to the high surface area of the melted spheres, melted particulates may provide the majority of vapor under laser irradiation. Despite their thermal history, the resulting nm-scale particles are easily digested in the plasma torch. If digestion proves to be the limiting factor in LA-ICP-MS, we will optimize laser parameters for particle condensation.

We also completed a study on the characterization and mechanisms of particulate formation from a polymer, PTFE (Teflon) during laser ablation at 248 nm. Here we included measurements of electric charge which was sufficient to manipulate, sort, and select in space particles under 1 micron. These studies suggest that electrostatic forces could be very useful in controlled analysis of insulating particles.

Research efforts at PNNL have focused on laser ablation of samples that represent the range of materials that need to be analyzed as part of the DOE cleanup effort of plutonium production facilities. These include Hanford tank waste ($NaNO_3$) and vitrified waste (glasses) simulants as well as metallic and metal oxide samples that simulate the chemical and physical properties of purified plutonium. The sample parameters of interest include thermal conductivity, laser absorption depth, heat capacity, and sample form. The sample forms studied include amorphous, crystalline, metallic and conglomerate. LA-ICP-MS data for these samples were taken for a wide range of laser parameters. Wavelength was varied from 1064 to 266 nm, power densities from 1 to 50 J/cm^2 and laser pulse length from 10 ns to 20 ps. On-line particle size measurement was used to determine the particulate size distribution for correlation with the mass spectra. Ablated particles of all sample types were also collected for subsequent analysis using SEM under the range of laser parameters described above.

Three classes of particulates were observed in these studies: 1) fracture, 2)melt and 3)ultra-fine aggregates. Fracture particles dominate for material-wavelength combinations that yield low optical absorption and thus high absorption depths. Smaller absorption depths yield primarily melted particles and ultrafine aggregates. This was demonstrated by comparing particles ablated from a vitrified waste simulant (glass) at 1064 nm to those ablated at 266 nm. The low absorption coefficient at 1064 nm results in a greater absorption depth and produces large fracture particles (> 5 microns). At 266 nm, the absorption depth is much lower, and smaller melt and ultrafine aggregate particles are produced. A simple thermal model was developed based on the volume of material irradiated by the laser. Irradiating a material with lower absorption heats a larger volume of material than irradiating a material with higher absorption at the same wavelength. The temperature reached during the laser pulse will be lower for a higher irradiation volume. Lower temperatures produce thermal fracture. The higher temperatures associated with irradiating a smaller volume produce melting and vaporization. The ultrafine aggregates are due to condensation of vaporized material.

Laser pulse length studies are consistent with this model. For materials with low thermal conductivity such as glasses, the amount of material and type of particulates produced at a given wavelength are independent of laser pulse length from 10 ns to 20 ps. This is consistent with a thermal model that depends only on the amount of energy deposited and the volume irradiated.

Planned Activities

In the remaining twelve months of this project, we plan to test a series of $CsNO_3$-doped $NaNO_3$ crystals with a wide range of dopant levels to test the sensitivity of LA-ICP-MS in this system using the PNNL instrumentation through our collaboration. Cs is of interest as a minor (but highly radioactive) component of high level mixed wastes from plutonium production operations. $CsNO_3$ and the important thermal decomposition product, Cs_2O, are significantly more volatile than $NaNO_3$ and its principal decomposition product Na_2O. Thus this system should allow us to evaluate the role of thermal processing in the accuracy and precision of LA-ICP-MS results.

We will continue to develop models for particle fracture and condensation to improve our fundamental understanding of particle generation processes, as well as to provide guidance for optimization. An extensive effort will be focused on the ultrafine particles and aggregates in terms of determining formation mechanisms.

Studies will also be made of the ablation of conglomerate-type samples such as the saltcake found in the Hanford waste tanks. These samples are composed of particulates that range from less than one micron to hundreds of microns. Preliminary studies indicate that ablation of these samples produces large particulates for all conditions considered so far. The processes involved in ablation of these materials will be considered in more detail, including the ablation of single particles found in the original sample material.

Presentations

Invited Talks:

"The Laser Desorption of Ions from Ionic Crystals," Gordon Conference on Laser Materials Interactions, June, 1998.

"Mechanisms for and Characterization of Particulate Generation by Laser Irradiation of Inorganic Crystalline Materials," FACS National Meeting, Austin TX, October, 1998.

"Fundamental Mechanisms of Particulate Formation by Laser Ablation for Inductively Coupled Plasma Mass Spectrometry (LA/ICP-MS)," M. L. Alexander, S.C. Langford and J. T. Dickinson, presented at the SPIE East conference in Boston, MA., October, 1998.

"Topics in Surface Dynamics," Guest Lecturer, Institute of Applied Physics, University of Linz, Austria, October-November, 1998.

"New Models of Laser Desorption and Particle Formation," Physics Dept. Colloquium, University of Linz, Austria, November, 1998.

"The Use of Lasers in Chemical Analysis," University of Minho, Braga, Portugal, January, 1999.

"The Desorption of Energetic Ions from Ionic Crystals," Dept. of Physics, Washington State University, January, 1999.

"Particle Generation by Laser Ablation in Support of Chemical Analysis of High Level Mixed Waste from Plutonium Production Operations," M. L. Alexander, S.C. Langford and J. T. Dickinson, invited talk at DOE Characterization and Monitoring Sensor Technology (CMST) meeting in Gaithersburg, MD, March, 1999.

“The Use of Lasers in Chemical Analysis of Toxic Materials,” Paul Scherrer Institute, Villigen PSI, Switzerland, June, 1999

“The Laser Desorption of Ions from Ionic Crystals,” E-MRS Symposium on Laser Materials Interactions,” Strasbourg, FR, June, 1999.

“Laser Desorption and Chemical Analysis,” Departments of Physics and Chemistry, U. of Heidelberg, Germany, June, 1999.

Contributed Papers:

“Ejection of Droplets and fracture particles from Single Crystal $NaNO_3$ during Pulsed Laser Irradiation,” Gordon Research Conference on Laser Interaction with Materials, June, 1998.

“Mechanisms for and Characterization of Particulate Generation by Laser Irradiation of Inorganic Crystalline Materials,” DOE-EMSP Workshop on Waste Characterization, Chicago, August, 1998.

“The Effect of Surface Treatment on Excimer Laser Induced Positive Ion Desorption in Brushite,” American Physical Society March Meeting, Atlanta, March, 1999.

“High Energy Ions from UV Laser Irradiation of Cleaved Ionic Crystals,” American Physical Society March Meeting, Atlanta, March, 1999.

“Ultrafast and Nanosecond Laser Induced Desorption from Ionic Solids,” American Physical Society March Meeting, Atlanta, March, 1999.

“Laser Desorption of energetic ions from single crystal $NaNO_3$ at 1064 nm,” American Physical Society March Meeting, Atlanta, March, 1999.

“Investigations of Particle Formation by Laser Ablation for Elemental Analysis,” A. L. Hedges, A. Mendoza, M. L. Alexander, S.C. Langford and J. T. Dickinson, 217th ACS meeting, Anaheim, CA, March, 1999.

”Laser-induced Positive Ion and Neutral Atom/Molecule Emission from Single Crystal $CaHPO_4$ $2H_2O$: The Role of Radiation Induced Defects,” Materials Research Society, San Francisco, May, 1999.

“Studies of Particulate Formation by Laser Ablation in Support of Chemical Analysis of High Level Mixed Waste,” American Ceramics Society, Indianapolis, May, 1999.

“UV Laser Interactions with Inorganic Single Crystals with Molecular Anions,” American Chemical Society, Portland, OR, June, 1999.