Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 1-3 - Session C4
Energetic Materials and Microstructures for Nanomanufacturing

Moderators: Karsten Woll, Karlsruhe Institute of Technology (KIT), Ibrahim Gunduz, Purdue University, USA

8:00am **C4-1 Investigation of Dynamic Processes in Energetic Materials by Ultrafast Transmission Electron Microscopy at the Nanoscale**, ***Volkan Ortalan,*** Purdue University, USA **INVITED**

The ignition of exothermic chemical reaction in energetic materials has long been known to occur after locally heated regions of the material called "hot spots" are formed by various mechanical processes. Once formed, these hot spots either fail to react chemically due to thermal diffusion or react exothermically creating an ignition site. These ignition sites then grow in temperature, size, and pressure, rapidly consuming the energetic material. Despite of its significance, direct experimental evidence of such hot spots, however, is exceptionally limited; mechanisms for their generation are poorly understood and methods to control their locations remain elusive. A complete fundamental understanding of the mechanisms and dynamics of thermo-mechanical processes of energy localization at nanoscale, and the role of the microstructure in the complex energetic materials can only be obtained by directly observing their response to different stimuli at the relevant time and spatial scales. However, although the recent progresses in picosecond spectroscopy are promising, there is currently no single technique alone satisfying the required resolutions (spatial, temporal and energy) relevant to the energetic reaction events to visualize the dynamic processes occurring in energetic materials. However, recently developed ultrafast transmission electron microscopy (UTEM) opens up new possibilities for visualization of these complicated ultrafast processes.

The high time resolution of a UTEM is achieved by creating short electron pulses that are used to illuminate the specimen. A UV laser pulse stimulates photoemission of electrons from a photocathode. The resultant bunch of electrons is then accelerated and sent into the electron-optical column. It is then focused onto the specimen and magnified to produce the image. The response to be studied (chemical reactions in energetic materials, a phase transformation, shock propagation, structural change, chemical reaction, etc.) in the experiment is stimulated by a second laser pulse and the delay between the two laser pulses sets the timing of the observation. The realization of UTEM is a revolutionary step for the *in-situ* investigation of dynamic processes in materials with high spatiotemporal resolution and the capabilities of UTEM provide an ideal platform to probe dynamic phenomena through a combination of imaging, spectroscopy, and diffraction on their natural length and time scales. Here, the results of dynamic UTEM experiments performed on energetic materials, such as HMX and composite metal-organohalide materials (mixture of aluminum nanoparticles dispersed in a fluoropolymer oxidizer matrix), will be presented.

8:40am **C4-3 A Closer Look at Determining Flame Speeds w ith Imaging Diagnostics**, *R Bratton, M Pantoya,* ***Connor Woodruff,*** Texas Tech University, USA

A comparison of flame speed measurements of reacting powders utilizing various filtering and illumination techniques is presented. Reactive energetic composites are often highly luminescent and quantifying reaction propagation can often be difficult because of sensor saturation. To explore the influence of image saturation on flame speed measurements, experiments were designed using micron-sized aluminum (Al) and micron-sized molybdenum trioxide (MoO_3) mixtures and further studied with nano powders of Al +MoO_3. The micron powder mixtures were loaded into tubes at a constant bulk density of 43% of Theoretical Maximum Density (TMD), approximately an average sample mass of 1260mg. The nano powder mixture samples were loaded into tubes at a constant bulk density of 12.5% of TMD. These respective bulk densities were selected in order to maintain sample consistency and prevent density gradients. Regulating the mass and bulk density per sample is of great importance because of the significant effect of variance in bulk density in observed flame speeds. The flame speeds for each powder mixture were determined using a high speed camera and applying a series of neutral density filters to the camera's lens. This technique reduces the oversaturation effect on the camera and allows flame speed to be determined through better tracking of the reaction front. For ultimate oversaturation removal, use of a Copper Vapor Laser (CVL) and coupled 511 nm notch filter was employed to illuminate the reaction and filter the majority (i.e., >99.9%) of reaction illumination. This technique provides a perspective of the solid material and its transition from reactant to product without the interference of light emission from the reaction. The results show that the flame speeds measured through the filtering techniques were not affected by the various levels of filtration. This conclusion is evidenced by the greatest percent difference in average flame speeds in the micron powder mixtures was 15% and in the nano powder mixtures 4.2%. With this conclusion we can say that the filtration applied to the front of the camera for deflagration reactions will not impact the observed flame speed. Also with extreme filtering techniques such as a single bandwidth filter and single wavelength illumination, a more detailed view of thermite powder reaction can be observed. This advanced filtration technique can be used to analyze and characterize combustion phenomena.

9:00am **C4-4 Modeling and Experimental Study of Propagating Exothermic Reactions in Al/Pt Multilayers**, ***David Adams***, *M Abere,* Sandia National Laboratories, USA*; R Reeves,* Sandia National Laboratories, USA, US*; C Sobczak,* Sandia National Laboratories, USA

The propensity of sputter-deposited Al/Pt multilayers to undergo rapid, self-propagating formation reactions is evaluated across a broad range of stoichiometry (nAl:mPt) and layer periodicity. Experiments demonstrate self-propagating reactions in ~1.6 micron-thick Al/Pt multilayers when the molar ratio of reactants is in the range 4Al:1Pt to 1Al:4Pt. This rather large compositional range is characterized by different heats of reaction, reaction rates and reaction modes. High-speed photography shows that equimolar Al/Pt multilayers undergo the most rapid reactions with wavefront speeds as large as 80 m/s. Al- and Pt-rich multilayers react at reduced rates with speeds as low as 1 m/s. A previously developed, analytical method by Mann et al. (J. Appl. Phys. 1997) is utilized to reveal additional details of reactions in the various Al/Pt multilayers. Models that account for the reactant layer thicknesses, composition, the adiabatic temperatures, the flame temperatures, and the measured heats of reaction are used to predict wavefront speeds that closely match measured values. These results are further analyzed to extract information regarding the mass transport characteristics of reactant species.

9:20am **C4-5 Sub-critical Hotspots to Quench Reactions in Ni-Al Nanofoils**, *I Gunduz,* ***Matthew Beason,*** Purdue University, USA

Identification of intermediate reactions in reactive nickel aluminum nanofoils is challenging due to the rapid thermal front velocities up to 13 m/s and very thin reaction zones estimated to be on the order of 5-20 micrometers. We present a novel method to quench reactions at rates beyond 10^8 K/s, which are comparable to the self-heating rates in these foils. A thin aluminum wire is used to produce a microscale spark-heated spot on the surface of the foil with an energy below the self-propagation threshold. Upon the application of the spark that lasts approximately 50 ns, the reactions that are initiated are rapidly quenched due to the conductive heat losses to the rest of the foil and stop the conversion of intermediate species. SEM micrographs and TEM analysis using selected area diffraction show a transition zone of 3 micrometers, where amorphous Al solid solution, $NiAl_3$, Ni_2Al_3 and NiAl are sequentially formed at bilayer interfaces. The reactions appear to propagate faster along smoother bilayers compared to the kinked sections that form during the sputtering process, forming a fingered reaction front in the thickness direction starting from the ignited spot.

9:40am **C4-6 Laser Pulse Duration Dependence on Ignition of Al/Pt Reactive Multilayers**, ***Michael Abere***, *C Yarrington, D Adams,* Sandia National Laboratories, USA

Sputter deposited Al/Pt nano-laminates with bilayer thicknesses of 328 nm, 164 nm and 65 nm were ignited via laser irradiation resulting in rapid, self-propagating reactions. Laser ignition of these foils was characterized over eleven decades (10 ms to 150 fs) of pulse duration. For laser ignition with milli- and microsecond pulses, the go/no go threshold is equivalent to the laser intensity at which the heating time required for ignition equals the pulse duration. The heating time required for ignition at a given laser intensity was determined experimentally with high-speed photography and calculated with finite element simulations. Reducing the pulse duration to 150 fs leads to a breakdown of this Joule heating based mechanism as the ignition threshold becomes spot size invariant. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin

Corporation, for the US Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:00am **C4-7 Microstructural Evolution during Thermal Ignition of Self-Propagating Reactions in Ru/Al Multilayers***, **Karsten Woll,*** Karlsruhe Institute of Technology (KIT), (IAM-WBM), Germany*; C Pauly, F Muecklich,* Saarland University, Germany

The ignition of the self-propagating reaction represents one of the crucial processes for reactive materials. Whereas the characterization of reaction initiation often uses macroscopic parameters, such as ignition temperatures or ignition energies, the characterization lacks the knowledge about the underlying microstructural transitions, such as the phase transformations. We take this as motivation and analyze the ignition in sputter deposited Ru/Al multilayers. In greater detail, we thermally ignite free standing Ru/Al foils as well as samples on a substrate. In our experiments we use ignition temperatures and energies just below the ignition threshold. This approach enables us to arrest the reaction immediately after ignition. Eventually, we create characteristic microstructures that help us to infer the phase transformations and microstructural changes during thermal ignition. To analyze the microstructures after igntion we use the transmission electron microscope in combination with chemical analysis, such as atom probe tomography. Finally, based on the experimental observations we suggest a mechanism for thermal ignition in Ru/Al multilayers and deduce characteristics of the ignition process in reactive multilayers in general.

10:20am **C4-8 Waves of Crystallization in Amorphous Metallic Glass Films obtained by Spinning of Melts***, **Alexander Rogachev,*** National University of Science and Technology "MISIS", Russian Federation*; S Vadchenko, A Aronin,* Russian Academy of Sciences, Russian Federation*; A Mukasyan,* University of Notre Dame, USA

Metallic and semiconducting amorphous materials and films possess unique combination of properties that cannot be obtained in the crystalline materials, such as high mechanical strength, corrosion and radiative resistance, specific electrical and magnetic properties. It promotes applications of the amorphous films in contemporary industrial technologies and growing interest in scientific research of the amorphous structures formation and its transition into crystalline state. Despite of significant amount of scientific research, mechanisms and dynamics of amorphous-crystalline transition has not been studied adequately yet, especially, as related to self-propagating waves of crystallization. Propagating waves of crystallization in the vacuum-deposited films of Si, Ge, Sb and other metal or semiconductor material, have been studied for decades ("explosive crystallization") and found some prospective applications, e.g., as a new method of fine-grained polycrystalline silicon films production for solar cells. In this work, we report existence of the self-propagating waves of crystallization in the amorphous metal allows films produced by spinning of the melts. It is shown that self-propagating waves of amorphous-crystalline transformation can be initiated in the foils CuTi, $Fe_{84}B_{16}$, $Fe_{76}Si_{13}B_{11}$ and other compositions. Using thermal vision (up to 200 fps) and high-speed video (up to 20000 fps) cameras, we have measures propagating velocities, temperature-time profiles and other characteristics of the waves. Crystal structure and microstructure transformations have been studied. Characteristics of a new class of self-propagating thermal waves are compared with those of explosion crystallization in deposited films and reactive waves in multilayer bimetal nanofilms. Promising routes of utilization of this phenomenon for production sub-micron and nanocrystalline metal films are discussed.

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