Nano-scale energetic films by superfluid helium droplet assembly

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Abstract. The helium droplet technique has been utilized to study a wide range of topics in chemical physics such as atomic scale manifestations of superfluidity, chemistry at ultra-low temperatures, and the assembly of exotic Van der Waals complexes. Our efforts have transitioned the helium droplet methodology from a cryogenic nano-scale matrix to a film deposition technique capable of creating nano-structured films of composite metal-based energetic materials (EM). Such materials are ideal candidates to study propagation of reactions at small scale, and could be alternatives to organic based EM due to their higher energy densities. The helium droplet methodology may also provide a solution overcoming issues of reaction-limiting effects such as the formation of oxide layers by exploiting ‘magic-number’ cluster sizes and core-shell cluster mechanisms. This proceeding describes our previously reported efforts to model and characterize the deposition of magnesium clusters by superfluid helium droplet assembly, our efforts to produce magnesium-Fomblin core-shell EM cluster-based films, and our early attempts at making intermetallic cluster-based films.

1. Introduction

It has been postulated that reaction rates of metastable intermolecular composites (MICs) could be dramatically increased by reducing the domain sizes of the composite material to overcome mass diffusion limitations [1]. However, native oxide layers on MIC fuel particles comprise a majority of the material surface thus limiting thermal and mass diffusion [2]. Surface coated nanoparticles have been explored as a means of protecting metal fuels from oxidation, but achieving reaction speeds exceeding 2 km/s has been challenging [3-5]. Processing MICs in inert, non-oxidative, atmospheres has also shown promise; for example, combustion wave speeds up to 2400 m/s and peak pressures of up to 5.7 MPa were observed for Al/CuO [6]. The predominant approach for producing MICs has largely followed a top-down methodology, where bulk material is mechanically converted to the nanoscale by milling, swaging, or grinding. However, bottom-up approaches where energetic
composites are assembled at the atomic and molecular level offer exciting options such as forming oxidation resistant superatoms of metal fuels [7].

Superatoms and clusters hold tremendous promise to military and industrial applications due to their unique magneto-optical-electric properties [8, 9], their medical applications [10], and catalytic properties [10]. In order to exploit these properties the deposition impact energy must be kept below the cluster cohesive energy (typically ~0.1 eV per atom) to insure that the structural integrity of the cluster is preserved [11, 12]. Several cluster-formation methods such as gas aggregation and laser vaporization are capable of providing low-energy impacts, however drawbacks exist (e.g. small yields, poor control of cluster sizes, etc.) [9, 13, 14]. Recently, the Air Force Research Laboratory Munitions Directorate (AFRL/RWME) transitioned a bottom-up approach, based upon an academic matrix isolation tool, for synthesizing atomic clusters by helium droplet cluster assembly, into a film deposition tool [15, 16]. The helium droplet mediated deposition technique assembles clusters with a narrow size distribution and subsequently provides them a gentle landing comparable to rare gas solid deposition methods [17]. Several groups have made contributions to this technique by producing, and depositing sub-monolayer clusters of Ag [18-22], Au [18, 21], and Ni [21], as well as mixed species of Ag/Ni [21] and Au/Ag [18, 21]. Recently at AFRL/RWME we demonstrated an optimized helium droplet instrument with cluster deposition rates exceeding 1 µg/cm²/hr with well characterized hydrodynamics [15]. Following this work we presented a model for helium droplet mediated deposition and yield, and validated this framework with Mg clusters by measuring Mg deposition yields as a function of stagnation pressure and nozzle temperature [16]. In this same report we demonstrated that the deposition behavior is highly dependent upon the hydrodynamics of the helium droplet beam.

To date, most groups have only explored sub-monolayer deposition of mixed or core-shell clusters that are non-reactive. In principle, this deposition method can be applied to the formation and deposition of nanoscale reactive materials. In 2006, Kupper, et al. demonstrated the capture of highly reactive pyrolant free radicals by helium droplets, finding that they form pre-reactive complexes inside the droplets [23]. In 2009, Mauracher, et al. captured trinitrotoluene (TNT) in helium droplets demonstrating the suppression of decomposition after electron attachment; a strong contrast to the behavior of gas phase TNT [24]. Similarly, in a 2013 report, Bartl, et al. used helium droplets to capture and stabilize large perfluoroethers and their short-lived decomposition intermediaries after ionization [25]. This evidence strongly supports the ability for helium droplets to ‘freeze-out’ reactions and deposit metastable materials, enabling the production of, pre-reactive, nanocomposites.

In this proceeding we report on our preliminary efforts to produce energetic nanocluster films. This includes our efforts to generate core-shell cluster structures of the pyrolant Mg/Fomblin (perfluoropolyether) and intermetallic Mg/Cu cluster matter films.

2. Experimental Details

The design and layout of the helium droplet assembly technique is described in detail elsewhere [15, 16]. In short, droplets were produced by expanding chromatographic grade helium gas through a 6.4 µm diameter platinum aperture into ultra-high vacuum, where it adiabatically cools thus forming a jet of liquid helium droplets. The jet was shaped by a 0.05 cm skimmer positioned 1.7 cm downstream from the aperture to yield a diverging beam with a 0.68 mrad solid angle. The beam of liquid helium droplets was defined relative to the position of the skimmer and the entrance to a quadrupole mass spectrometer aperture located 85 cm downstream. Beam alignment was conducted by translating the nozzle assembly to maximize the 8 amu He²⁺ signal.

The droplets were first loaded with magnesium by passing the helium beam above a Knudsen style effusion cell filled with 99.99% pure magnesium pellets held at 848 K. In the Mg/Fomblin configuration, after the magnesium pick-up cell the beam is passed through a region of Fomblin Y 140/13 (6500 amu average molecular weight, obtained from Sigma-Aldrich and used as-delivered) vapor generated from a 480 K copper Knudsen oven. The design of the magnesium and Fomblin cells is described in detail elsewhere [26]. In the Mg/Cu configuration a second high-temperature effusion
cell replaced the Fomblin cell and was filled with $\geq 99.8\%$ pure copper granules from Aldrich. The copper cell was operated in a temperature range of 1640 K to 1670 K.

After pick-up, the composite clusters are deposited onto a substrate surface. For the Mg/Fomblin experiments, the cluster beam was directed to a tantalum foil substrate held at 115 K where temperature programmed desorption (TPD) could be performed. The details of the TPD setup are discussed elsewhere [26]. In short, a tantalum substrate with a tantalum heater wire, cooled by liquid nitrogen electrical feedthroughs was utilized with a Type-K thermocouple. A residual gas analyzer (RGA) was utilized to measure the partial pressures of the desorbed species. For the Mg/Cu experiments, the doped beam impinged upon a glass substrate, and Mg/Cu cluster matter was deposited. After Mg/Cu clusters deposition, the cluster matter films were removed from vacuum and transitioned to an FEI Quanta 200 FEG SEM for the collection of micrographs.

3. Discussion and Results

3.1. Magnesium/Fomblin

Magnesium, a common element in pyrotechnics, was the material selected during the development of helium droplet cluster assembly technique due to its high vapor pressure at modest temperatures. Concurrent with the development of the helium droplet instrumentation, magnesium was utilized by our group in the production of thin multi-layer films via physical vapor deposition (PVD) of magnesium and Fomblin (perfluoropolyether) [26]. This work studied the effect of layered structures of Mg/Fomblin with temperature programmed desorption (TPD) finding that MgF$_2$ formed at the Mg/Fomblin interfaces. However, co-deposits of Mg and Fomblin via PVD react during deposition, and no magnesium desorption was detected.

Presented in figure 1 is the TPD spectrum of deposited Mg/Fomblin cluster matter by helium droplet cluster assembly. Here we see a strong release of CO (open squares) at low temperatures, an indication of the formation of an MgF$_2$ shell. This implies that during cluster assembly, and later deposition onto a cold surface (115 K), the Mg/Fomblin cluster matter had not reacted. Further heating reveals that the Fomblin begins to decompose into CF$_3$ (open circles) beginning at 580 K. At 720 K magnesium (closed circles) migration begins, as unreacted magnesium begins to desorb. At 780 K, a strong magnesium desorption peak forms (indicated by the rupture) representing the rupture of the MgF$_2$ shell [26]. From 850 K and ending at 920 K (Mg boiling point) only neat magnesium evaporation occurs. The helium droplet methodology provided a dramatically different result from that of the PVD co-deposition where reaction occurred immediately.

**Figure 1.** TPD spectrum of Mg/Fomblin cluster deposits. Arrow indicates release point of trapped magnesium.
3.2. Magnesium/Copper

For our first MIC system, the intermetallic Mg/Cu system was selected due to its energetic properties as well as its promise as a hydrogen storage candidate material [27]. Further, the Mg/Cu system served as a safe-to-handle, proof-of-concept material for the purposes of establishing a methodology for handling more energetic systems with the helium droplet technique. The Mg/Cu system has two intermetallic reactions depending on its stoichiometry: Cu+2Mg which yields a heat of reaction 195 cal/cm³ with an adiabatic reaction temperature of 665 K and 2Cu+Mg which yields a heat of reaction 285 cal/cm³ with an adiabatic reaction temperature of 721 K [28].

In figure 2 the mass spectrum of the helium beam doped with Mg/Cu clusters is presented. Here magnesium and copper atom fragments are found for mass 24 amu (and its less abundant isotopes at 25 and 26 amu) and mass 63 amu (and its less abundant isotope at 65 amu) respectively. Most importantly the MgCu fragments were found at mass of 87 amu (and their isotope mass combinations) indicating the presence of the Mg/Cu mixed cluster species. Higher order fragments such as Mg₂Cu were also observed.

![Figure 2](image)

**Figure 2.** Mass spectrum of Mg/Cu doped helium beam.

Presented in figure 3 is a SEM micrograph image of an Mg/Cu cluster matter film grown by helium droplet mediated deposition utilizing helium droplets containing an average of 22,000 helium atoms. Observed are very small, high island density cluster agglomerates consistent with low-energy ballistic deposition of clusters (i.e. soft-landing). The cluster agglomerates have a nominal diameter of 50 nm, and feature numerous dark areas (i.e. pores or voids) caused by self-shadowing. Additional energy dispersive X-ray spectroscopy measurements indicate that the elemental content and stoichiometric ratios of Mg/Cu is highly dependent on the gas density and pick-up order of the effusion cells. TPD measurements of this system are being planned.
4. Conclusions
We have reported on the preliminary efforts at AFRL/RWME to produce highly controlled energetic cluster matter films via helium droplet mediated deposition. Our initial experiments with this technique demonstrated that pre-reactive species can be combined into clusters, deposited, and later reacted through thermal heating. In addition, a demonstration of the formation of intermetallics in the helium droplet beam was shown, and the resulting cluster matter was found to both have a narrow size distribution and be porous in nature. The critical conditions for initiation may largely be determined by the observed porosity (sub-micron) and the amount of surface area provided by the nanoscale cluster agglomerates [29]. Future studies on the initiation of these thin cluster films are underway.

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