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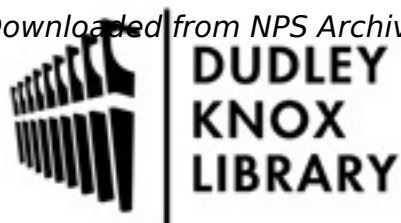
Isik, Tugba; Xu, Xiaohui; Son, Steven F.; Gunduz, I. Emre;
Ortalan, Volkan

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Investigation of Polymer Matrix Nano-Aluminum Composites with Pulsed Laser Heating by In-Situ TEM

 Tugba Isik,^[a, b] Xiaohui Xu,^[c] Steven F. Son,^[a] I. Emre Gunduz,^[d] and Volkan Ortalan^{*[b, e]}

Abstract: Nanocomposites of aluminum and fluoropolymers react rapidly due to highly exothermic aluminum fluorination because of the high specific surface area nanoscale particles. *In-situ* transmission electron microscopy (TEM) techniques are invaluable for real time monitoring of the reactions in these systems at the nanoscale. Here, we investigated the reactions in nanoscale Al (nAl) and THV (terpolymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride) and nAl-LDPE (low density polyethylene) composites, heated using a pulsed laser in a TEM.

Keywords: Nanoenergetic composites · *In situ* TEM · Fluoropolymer · Laser Heating

Results show that reactions are initiated at about 720 K, when THV starts to decompose, and proceed with the formation and growth of a hollow aluminum fluoride (AlF₃) shell. Diffraction patterns revealed that this phase is the rare η-phase AlF₃. In contrast, no reactions were observed in the inert nAl-LDPE composites. The experimental and theoretical results reveal that rapid pulsed laser heating and subsequent cooling of a nanoscale sample influences the phases that can form, and can be utilized to investigate other systems.

1 Introduction

Aluminum-fluoropolymer composites can react and release large amounts of heat due to formation of AlF₃ with one of the strongest bonds ever determined with the energy of 665 kJ/mol [1]. This product phase has applications as a catalyst material for olefin synthesis [2,3], is used as a flux for Al production in electrolytic cells [4,5], and can be fabricated into fluoride glasses for mid-infrared applications [6,7]. The common synthesis methods for AlF₃ use a wet-chemistry step involving hydrofluoric acid (HF) to produce reactants, which makes it challenging to work on these systems. Therefore, its synthesis through the combustion of solid-state reactants rather than HF chemistry [8] is highly attractive. This method can also be easily extended to other metals such as magnesium. These composite systems are of great interest for pyrotechnics such as airbag initiators because of the rapid release of heat and gas phase products [9] such as AlF₃ that sublimates at 1564 K [10] below the typical reaction temperatures in excess of 3000 K [11,12]. Although Al can react with many oxides such as Fe₂O₃ and CuO in a thermite reaction, where the oxide is reduced to form alumina and liquid/gaseous iron and copper [12,13], reactions with fluoropolymers can liberate even higher amounts of heat. For example, Al fluorination reaction to form AlF₃ can generate 56.01 kJ per gram of Al compared to Al₂O₃ which only releases 31.06 kJ [14].

These composites can be produced by ball milling of Al-PTFE (polytetrafluoroethylene) to form nanostructured particles [15,16] or by the dissolution of the fluoropolymer in a solvent mixed with the Al powders. The use of nano-aluminum (nAl) with the solvent route can greatly increase

reaction rates due to the high specific surface area of the particles compared to their microscale counterparts [17,18]. AlF₃ exhibit polymorphism with at least 5 crystal phases [19] and an amorphous form with other possible phases predicted computationally [20]. The formation of a particular phase depends both on the reaction routes and the heat treatment upon fluorolytic synthesis [8]. For example, initially formed amorphous AlF₃ crystallizes into a mixture of high temperature cubic α-AlF₃ and β-AlF₃ at an annealing temperature of 603 K, and above 703 K, entirely converts to


[a] T. Isik, S. F. Son
School of Mechanical Engineering
Purdue University
West Lafayette, IN, USA

[b] T. Isik, V. Ortalan
Institute of Materials Science
University of Connecticut
Storrs, CT, USA
*e-mail: vortalan@uconn.edu

[c] X. Xu
School of Materials Science and Engineering
Purdue University
West Lafayette, IN, USA

[d] I. E. Gunduz
Mechanical and Aerospace Engineering Department
Naval Postgraduate School
Monterey, CA, USA

[e] V. Ortalan
Materials Science and Engineering
University of Connecticut
Storrs, CT, USA

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the high temperature cubic phase [21]. However, there is no prior work on the product phases obtained from the combustion reactions of the nAl-fluoropolymer composites.

One recent technique that can enable the observation of reactions in these nanoscale systems is transmission electron microscopy (TEM). In particular, *in-situ* TEM has an essential role in dynamic characterization of nano materials [22,23]. Additionally, the synchronized use of electron microscopy and pulsed lasers resulted in the possibility of *in situ* laser heating TEM (ILH-TEM), which has enabled spatial and temporal studies of laser induced dynamic processes at nanoscale [24–31]. In this study, ILH-TEM is utilized as a neoteric method to probe the thermal and chemical behavior of nAl-THV (terpolymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride) and nAl-LDPE (low density polyethylene). Figure 1 displays the experimental set up of the ILH-TEM, which was utilized to study the laser-induced temperature jump (T-jump) behaviour of nAl-THV and nAl-LDPE composite systems. The set-up consisted of a specialized TEM with a port of entry for the laser beam and an optical bench, wherein the laser beam was generated and processed before entry into the TEM. In regular operation of an ILH-TEM, a sample excitation laser is used to induce change in the sample. The structural changes caused by the temperature increase were monitored via high resolution TEM imaging. Diffraction patterns were collected to identify the phases before and after the pulsed laser heating. In addition, real-time movies (30 frame/s) have been captured to reveal the changes during the heating process of the composite materials (see Supporting Information for the movies).

2 Experimental Section

The powders of THV (Dyneon™ THV 221AZ) with the empirical formula $C_{2.29}F_{4.33}H_{0.25}$ and low-density polyethylene (LDPE) were mixed with methyl ethyl ketone (MEK) and xylene at 15 wt.% and 1 wt.% respectively. The mixtures were

agitated using a magnetic stirrer for 20 minutes at 600 rpm and left overnight at room temperature. Aluminum nanoparticles (NovaCentrix) with an average diameter of 80 nm and an active content of 82 wt.% were mixed with solutions at a mass fraction of 43 wt.% of the solid content and sonicated using a Branson Digital 450 Sonifier Cell Disruptor at 30% amplitude for 5 minutes. The mixtures were dried in aluminum pans. The dried solid masses were subsequently dissolved in acetone and xylene at 1 wt.% overnight and copper TEM grids were quickly immersed and retracted from the mixtures to form a thin layer approximately 200 nm thick. Samples were heated for one second via pulsed frequency doubled Nd-YAG laser beam with a wavelength of 532 nm, power of 25 mW (which was the threshold power for reactions), pulse frequency of 25 kHz, pulse duration of 1 ns and a 1/e2 spot size of 120 μ m.

Reflectance of the dried sheets of nAl-THV composites was measured using a Perkin Elmer Lambda 950 UV/VIS/NIR spectrophotometer in a wavelength interval of 320–800 nm and the amount of heat released during the exothermic reaction between nAl and THV was measured by simultaneous differential scanning calorimetry/thermal gravimetric analysis (DSC/TGA) (TA Instruments SDT Q600V20.9) at a heating rate of 20 °C/min.

The heating was simulated using a COMSOL model that incorporated the geometry of the copper TEM grid with an amorphous carbon support layer. The grid has an outer diameter of 3 mm, whereas the thickness of the copper and carbon sections are 25 μ m and 20 nm respectively. The grid had 15 × 15 square holes with an edge length of 95 μ m, separated by 35 μ m. Heat capacity and density of the composite was calculated according to the weight percentage of the compounds. Density of Al was taken as 2.7 g cm⁻³, and heat capacity value was averaged over 300–700 K and calculated as 1 J/gK [32]. Physical properties of polytetrafluoroethylene (PTFE) (1.260 J/gK and 2.2 g cm⁻³), which has similar properties with THV because of its fluorine content, was used for calculations. Thermal conductivity of Al and PTFE were taken as 205 W/mK [33] and 0.245 W/mK respectively, and thermal conductivity of the composite was calculated according to Lewis-Nielson Model, as explained elsewhere [34]. Overall, heat capacity, density and thermal conductivity of the nAl-THV composite were found as 1.15 J/gK, 2.415 g cm⁻³ and 4 W/mK, respectively.

3 Results and Discussion

Figure 2 shows the TEM images of the deposited thin layers of the composite materials, where the insets (Figure 2b and 2d) are the selected area diffraction (SAED) patterns acquired from the center of the images. The nAl particles that are nominally 80 nm, are relatively well dispersed within the approximately 200 nm thick polymer layer and both systems appear similar with a weak contrast from the polymer layer. The pulsed laser beam excitation did not trigger

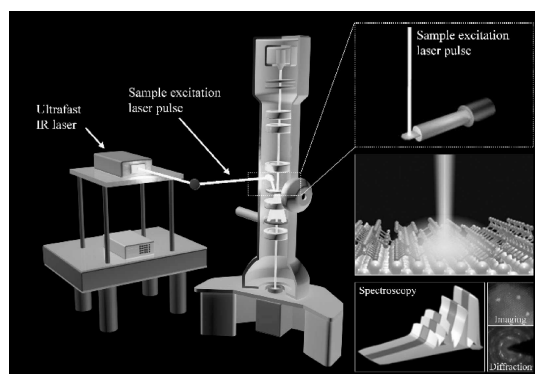


Figure 1. The schematic of the modified 200 kV TEM with ultrafast laser system utilized to perform *in-situ* laser heating experiments.

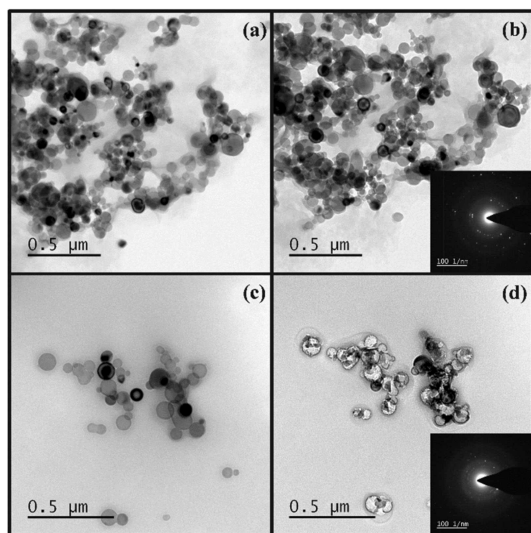


Figure 2. TEM images of the two samples heated with laser pulses. (a, c) Images of nAl-LDPE and nAl-THV samples before the laser stimulation, respectively. (b, d) Images, with inset diffraction patterns, of nAl-LDPE and nAl-THV samples after the laser heating, respectively.

a reaction or any changes in the nAl-LDPE as shown in Figures 2a and 2b. On the other hand, temperature increase initiated a chemical reaction in the nAl-THV sample, where changes in the morphology of the sample after the laser excitation can be clearly seen in Figure 2c and 2d. The reacted particles appear porous and show lower contrast.

SAED patterns were used to identify the reaction products, using four diffraction spots with identifiable intensity to calculate the interplanar spacings (d-spacings) of corresponding crystal planes as shown in Figure 3(a). This analysis showed the presence of η phase AlF_3 ($\eta\text{-AlF}_3$), which is a metastable phase with cubic pyrochlore structure, same as formulae FeF_3 [35]. This was also verified with diffraction pattern simulation (Figure 3b) of the three dimensional mo-

lecular geometry shown in Figure 3c using CrysTBox software [36]. It was found that the measured d-spacings agree very well with the d-spacings of four planes, namely, (0 2 2), (2 2 2), (0 4 4) and (1 5 5), in the simulated pattern.

Under ordinary combustion reactions in nAl-fluoropolymer systems, the temperatures are extremely high in excess of 2500 K [37], where the more stable $\alpha\text{-AlF}_3$ can be expected to form from the condensation of the gaseous AlF_3 as typically utilized in thermal vapor-condensate production route of $\alpha\text{-AlF}_3$ [19]. However, the rapid heating and cooling cycles of a nanoscale composite appears to allow the unusual formation of the metastable η -phase. Thermal analysis using simultaneous differential scanning calorimetry/thermal gravimetric analysis (DSC/TGA) suggests that THV starts to decompose around 720 K. The possible products such as HF can react with the nAl exothermically (Figure 4), rapidly releasing heat as seen in DSC and form the

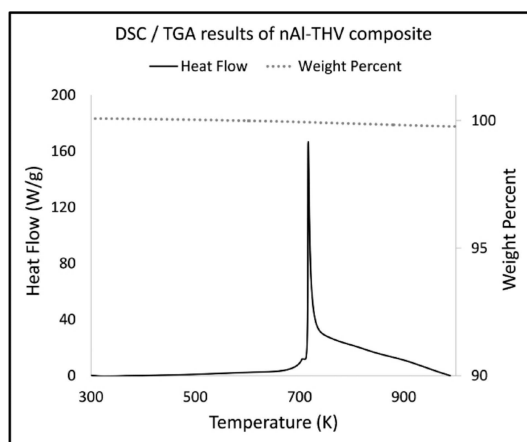


Figure 4. Differential scanning calorimetry measurement of nAl-THV.

AlF_3 as imaged with TEM. However, it is possible that the heat losses are sufficient to keep the temperature at moder-

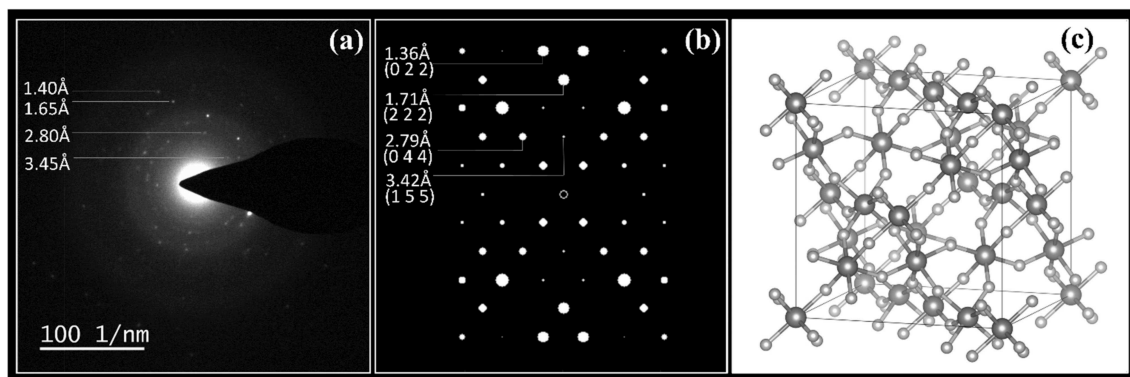


Figure 3. (a) Experimental diffraction pattern obtained by TEM and $\eta\text{-AlF}_3$ peaks (Al peaks were not shown for clarity). (b) Simulated diffraction pattern of $\eta\text{-AlF}_3$ under zone axis $[0 \bar{1} 1]$ with d-spacings of four crystal planes. (c) Simulated crystal structure of $\eta\text{-AlF}_3$.

ate levels in nanoscale TEM samples and much lower compared to what would be observed in a larger scale combusting system.

For a better understanding of the heat transfer mechanism and temperature change of the sample over time, experimental conditions were simulated in COMSOL Multiphysics. The TEM grid and the sample geometry used in the experiment were fully modeled in 3D (Figure 5), along with the thermal properties of the sample and sample holder. The modeled TEM grid, schematic illustration of the pulsed laser beam and heated zone temperature values at the end of one second long heating time can be seen in Figure 5. Since the beam has a Gaussian profile, it develops a radial temperature gradient, forming a heat affected zone in the form of a spot (Figure 5b). It is highly plausible that the temperature within this zone is higher than the decomposition temperature of THV (~720 K). The absorbed laser flux was estimated based on the measured absorbance ($A = 0.85$) of a thick layer of the nAl-THV composite at the same laser wavelength ($\lambda = 532$ nm) using a spectrophotometer. However, since the thin layer contains a lower amount of nAl due to the way the solution is diluted and deposited on the TEM grid, this was corrected using the volume fraction of the nAl in the thin layer compared to the thick layer. For this purpose, a binary version of the image in Figure 5b was created to determine the area ratio of nAl and THV in the region, which was 0.074 as opposed to 0.381 for the thick foil case (43 wt.% nAl), which yields a TEM sample absorptivity of 0.165. This approach assumes uniform absorption across the heat affected zone. Although the areas around nAl particles can be expected to absorb the laser nearly completely, the thermal diffusion is fast enough to quickly equalize the temperatures. For example, the thermal dif-

fusion length is approximately $1.2 \mu\text{m}$ in $1 \mu\text{s}$ ($\alpha = 1.44 \text{ mm}^2/\text{s}$), much larger than the spacing between the particles and clusters. The validity of the assumptions can also be verified by the fact that nAl particles do not melt at either laser fluxes below the critical flux or in nAl-LDPE composites at the same flux. The calculated maximum temperature rapidly rises within 1 ms and continues to rise slowly reaching a temperature of 797.4 K within 1 s (Figure 5c). The radius of the calculated heat affected zone with a cutoff value of 720 K also matches well with the observed spot size, which were both close to $25 \mu\text{m}$.

4 Conclusion

Overall, this work demonstrates that ILH-TEM design constitutes a successful experimental tool for the *in-situ* laser heating and laser-matter interactions experiments. In the experiments performed, it is shown that the sample temperature can be increased in a very short time via the sample excitation laser in the ILH-TEM system. The specimen is excited by a Gaussian laser beam with 532 nm wavelength to observe the interaction of THV and LDPE with nanosized aluminum particles. While LDPE did not show any significant change, the fluorine in THV reacted with the Al particles. Structural change was inspected by high resolution TEM images and reaction temperature was calculated. Differential scanning calorimetry measurement shows that exothermic reaction between aluminum and fluorine occurs near 716 K, and the heat transfer simulations prove that the temperature of nAl-THV sample reached more than 797 K. Diffraction pattern analyses revealed the effect of pulsed laser heating on the reaction products of nAl-THV sample. In this particular case, η - AlF_3 , which is one of the known phases (α -, β -, η -, τ -, κ - AlF_3) [35] of aluminum fluoride, was formed rather than the well-known α phase. The formation of metastable η phase instead of the thermodynamically stable α - AlF_3 , was most likely caused by the nonlinear heating of the laser pulses. The production of η - AlF_3 generally requires complex chemical processes including ACF, $[\text{AlF}_2\text{Py}_4]^+\text{Cl}^-$ [19], HAlF_4 [38] or HF [35]. In that respect, nanosecond pulsed laser heating offers a viable alternative to obtain η - AlF_3 by pulsed laser heating of nAl-THV composite rather than other complicated chemical methods. Although more research and experimentation is needed to understand applicability of this method in bulk materials, we still think formation of η - AlF_3 by laser heating in two-dimensional surface applications could be applicable.

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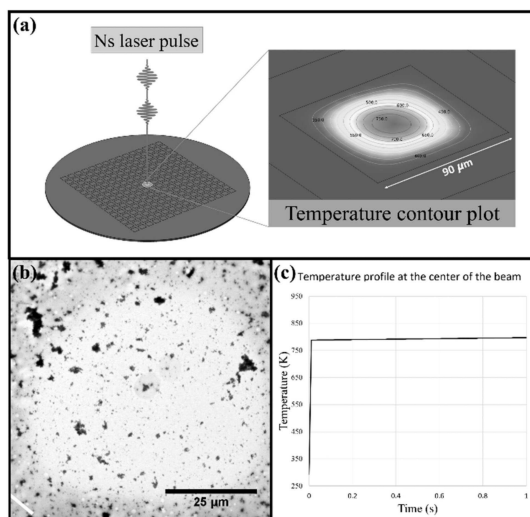


Figure 5. (a) 3D model of the sample and temperature calculation for 1 s laser heating. (b) TEM image showing the laser beam affected area of the sample. (c) Maximum temperature evolution at the center of the beam.

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