

Production of Energetic Nanomaterials by Spray Flash Evaporation

Martin Klaumünzer, Jakob Hübner, Denis Spitzer

Abstract—Within this paper, latest results on processing of energetic nanomaterials by means of the Spray Flash Evaporation technique are presented. This technology constitutes a highly effective and continuous way to prepare fascinating materials on the nano- and micro-scale. Within the process, a solution is set under high pressure and sprayed into an evacuated atomization chamber. Subsequent ultrafast evaporation of the solvent leads to an aerosol stream, which is separated by cyclones or filters. No drying gas is required, so the present technique should not be confused with spray drying. Resulting nanothermites, insensitive explosives or propellants and compositions are foreseen to replace toxic (according to REACH) and very sensitive matter in military and civil applications. Diverse examples are given in detail: nano-RDX (n-Cyclotrimethyltrinitramin) and nano-aluminum based systems, mixtures (n-RDX/n-TNT - trinitrotoluene) or even cocrystalline matter like n-CL-20/HMX (Hexanitrohexaazaisowurtzitane/ Cyclotetra-methyltetranitramin). These nanomaterials show reduced sensitivity by trend without losing effectiveness and performance. An analytical study for material characterization was performed by using Atomic Force Microscopy, X-Ray Diffraction, and combined techniques as well as spectroscopic methods. As a matter of course, sensitivity tests regarding electrostatic discharge, impact, and friction are provided.

Keywords—Continuous synthesis, energetic material, nanoscale, nanothermite, nanoexplosive.

I. INTRODUCTION

THIS paper presents a continuous and effective way to produce diverse energetic materials. In this domain, basic motivation is the recrystallization of material at the nanoscale in amounts compatible with industrial demands, which, in fact, constitutes an important challenge. Oftentimes, batch synthesis of energetic materials does not show good reproducibility, and diverse fractions from different batch approaches differ in particle size distribution (PSD) and particle morphology. Therefore, a continuous process, that is called the “Spray Flash Evaporation” (SFE) [1], [2], was taken and invented to optimize the production of nanoparticles regarding higher reproducibility and higher throughput combined with a higher output.

The presented SFE technique is now further foreseen to be used as an efficient and versatile approach to develop and

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realize advanced and more complex particle systems. Some details concerning the experimental set up are given within the following Section II.

Most of the material systems show an intrinsic energetic character, based on organic secondary explosives or metallic nanoparticles, especially aluminum nanoparticles, covered by an amorphous Al_2O_3 shell to passivate the highly reactive Al-core. The organic secondary explosives which are well-known and standard explosives are taken as micrometric precursors. Basic ideas, some examples, and future works are presented in more detail within Section III.

Resulting nanothermites, insensitive explosives, and combinations like nanocomposites could be used in military and civil environment, for example, secure and insensitive munitions (also for mining etc. etc.) and effective igniters for airbags and belt pretensioners.

II. EXPERIMENTAL DETAILS

TNT is 2,4,6-Trinitrotoluene, RDX is 1,3,5-Trinitro-1,3,5-triazacyclohexane, HMX is Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazo-cine, and CL-20 is 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane. Chemical formula of these molecules are depicted in Fig. 1.

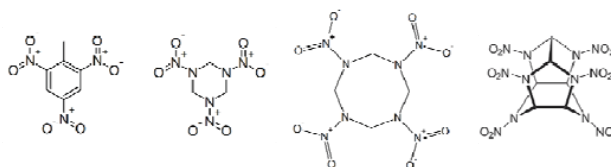


Fig. 1 Organic secondary explosives used within present study; from left to right: TNT, RDX, HMX, and finally CL-20

Acetone (HPLC grade, was used as received from Sigma Aldrich Co. LLC and without any further purification) was taken as solvent in every single experiment. The SFE process was invented at the ISL and is described in more detail elsewhere [1], [2]. A flow chart of the set-up is depicted in Fig. 2.

During all experiments, the nozzle diameter was 60 μm , and the temperature of the nozzle was set to 160 $^{\circ}\text{C}$. The mass concentration of the secondary explosive was set to 1 wt.%. Exact ratios are given within the results. Pressure in front of the nozzle was 40 bar. Pressure behind the nozzle, inside the reaction chamber, was 4 through 6 mbar (during synthesis).

For surface modification of precursor particles, an example which demonstrates 2-[2-(2-Methoxyethoxy) ethoxy]-acetic

acid (TODA), received from Sigma Aldrich Co. LLC., as an effective surfactant is given.

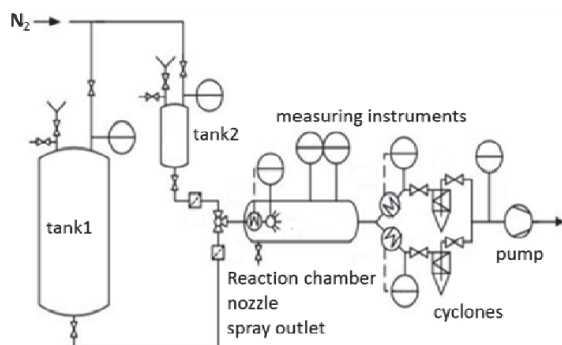


Fig. 2 Flow chart of the flash evaporation system with two tanks, an atomization chamber equipped with a hollow cone nozzle, two axial cyclones, a vacuum pump, and temperature and pressure sensors (measuring instruments). Filters in front of the nozzle system are to prevent clogging of the spray outlet (15 mm, inline type). Heaters are included to ensure fast reaction rates. Copyright Wiley and Sons 2015. Adapted with permission [2]

Atomic force microscopy (AFM) patterns were recorded by using a Multi-Mode Nanoscope IV configuration from the Bruker Metrology Group (Santa Barbara, USA) that is equipped with a Bruker 'RTESP' (Rotated Tip Etched Silicon Probe) AFM probe. This probe has a silicon cantilever with a length of 125 μm , a width of 35 μm , and a thickness of 4 μm . The tip has a curvature radius of about 10 nm.

A Transmission Electron Microscopy JEOL JEM-ARM200F that is linked to EDS (Energy-Dispersive X-ray Spectroscopy) was used for imaging the core shell particle geometries.

Fourier transform infrared spectroscopy (FTIR) records were detected by a tensor 27 from Bruker Optik GmbH (Ettlingen, Germany) equipped with a standard attenuated total reflectance unit (ATR-cell) MIRacle from Pike (Madison, USA).

A full-fledged sensitivity investigation was additionally undertaken according to the Federal Institute for Materials Research and Testing guidelines (www.bam.de; BAM; Berlin; Germany) by using classical test devices for impact (fall/drop hammer, BAM), friction (Julius Peters K.G. Berlin, Germany) and electrostatic discharge (ESD, OZM Research, ESD 2008, Czech Republic). In this context, loose and dry powders were tested.

III. RESULTS AND DISCUSSION

In this part, some new concepts for the preparation and recrystallization of energetic materials are presented. All concepts are based on the SFE process. Essentially, the fine tuning of functionalities through advanced nanostructures and interface engineering is in focus. In this context, synergistic effects from heterogeneous systems are expected.

A. Advanced Materials for Nanothermites

Physical mixtures of nanothermites, i.e. passivated aluminum nanoparticles with a metal containing oxidizer (e.g. WO_3 or $\text{Bi}_2(\text{SO}_4)_3$) and a secondary explosive (e.g. RDX), show great performances like high flame propagation velocities up to 3.5 kms^{-1} and are less hazardous than primary explosives [3]. They are able to initiate the detonation of a high (secondary) explosive, and therefore, they are promising candidates for the substitution of toxic Lead III azide ($\text{Pb}(\text{N}_3)_2$) inside of civil or military used detonators.

The ongoing project is strictly aiming for a further development of the approach from above - to replace the physically mixed system by a chemically mixed system: by means of the SFE process, heterogeneous energetic nanocomposites on the basis of an $\text{Al}/\text{Al}_2\text{O}_3$ core-shell nanoparticle suspension in acetone are to be formed in the presence of RDX, and, if applicable, further metallic oxidizing agents or precursors for the same would be added. A chemical transformation of a metal oxide precursor into metal oxide nanoparticles inside the SFE was already effectually shown in [2]. Therefore, stable dispersions are a basic requirement for spraying aluminum nanoparticle precursors. Consequently, the stability of the particles against sedimentation and agglomeration should be tuned by surface modification with energetic or inert organic molecules. A changed sensitivity of diverse aluminum nanoparticles by surface modification is investigated in detail [4]. In this context, first results show the effective binding of diverse organic molecules to the particles surface. This successful surface functionalization of passivated aluminum nanoparticles directly leads to much more stable particle dispersions. This means that surface modified particles are suspended stably over a few days whereas the unmodified particles start to settle down within minutes. Dynamic light scattering exhibits a much narrower PSD that is shifted from $x_{\text{mean}} = 90 \text{ nm}$ (TODA modified) to $x_{\text{mean}} = 190 \text{ nm}$ for blank Al-particles with 0.03 wt.% (blank) vs. 0.05 wt.% saturation concentration for modified particles. In Fig. 3, a selective FTIR pattern from 950 to 1900 cm^{-1} provides possible reason for stabilization of the suspension. TODA, known as an effective stabilizer [5], binds via a condensation reaction with its acid group to the OH-terminated surface of the passivated Al-nanoparticles. The C=O stretching vibration is shifted significantly which gives a strong hint for the successful formation of a chemical bond between TODA and OH-Al.

An example for recrystallizing RDX at the nanoscale by SFE for thermite application is given in Fig. 4. Here, the comparison of both AFM images clearly show the submicron-/nanometer structure in (b) whereas the precursor particles in (a) offer a much larger structure. Changed sensitivity values, derived from recrystallization, can be taken from Table I in the following section.

A scheme of a sample particle geometry which combines all of the physically mixed components ($\text{Al}/\text{Al}_2\text{O}_3$ - metal oxide - RDX) in one particle is presented in Fig. 4. These possible material geometries, like core shell multilayer, given in Fig. 5, or hierarchical geometries (e.g. smaller particles attached to

the surface of bigger particles) and, of course, diverse material inner structures like amorphous vs. crystalline and “semi” structures (e.g. crystalline domains vs. amorphous domains)

are thinkable, and methods to produce them will be presented in future.

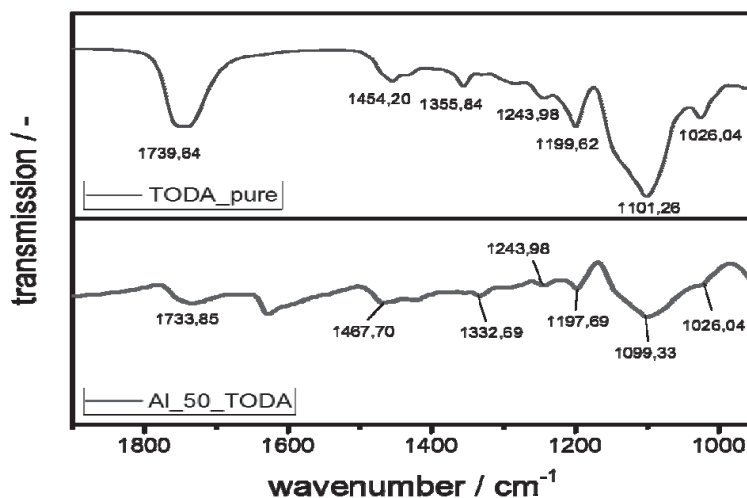


Fig. 3 FTIR spectra (fingerprint region) of pure TODA and TODA that was bound to the surface of Al-nanoparticles with an diameter of 50 nm on average. C=O stretching vibration is significantly shifted from 1739.6 to 1733.9 cm⁻¹ ($\Delta = 5.7$ cm⁻¹), which gives a strong hint for the successful formation of a chemical bond between the OH terminated Al-Al₂O₃ surface and the TODA

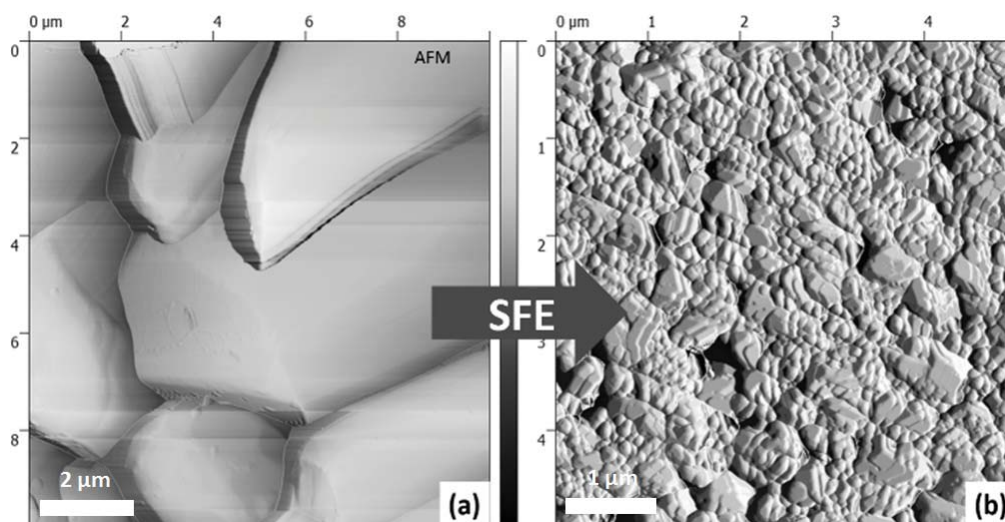


Fig. 4 Comparison from AFM images clearly show the submicron-/nanometer structure in (b), whereas in (a) the particles offer a much larger structure. Please note the magnification bars which offer same length represents different scales: 2 μm in (a) and 1 μm in (b) [8]

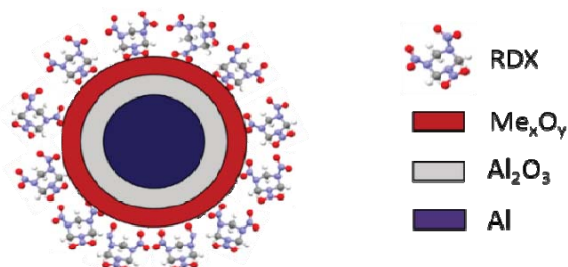


Fig. 5 Scheme of a possible particle geometry with dimensions less than 100 nm. RDX, a metal oxide (e.g. Fe₂O₃), amorphous Al₂O₃ and an aluminum core multilayer single “all-in-one”-nanothermite particle

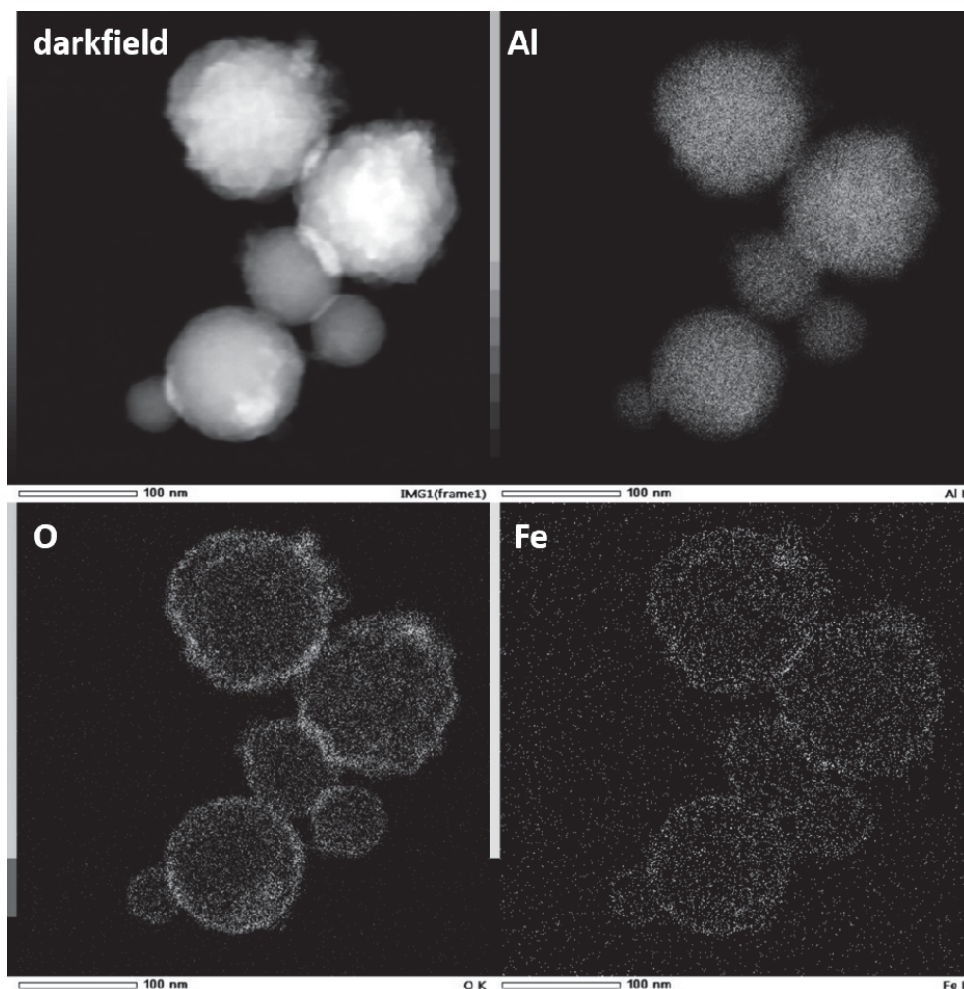


Fig. 6 Dark-field TEM images combined with EDS. The chemical mapping offers an insight into the chemistry and the elemental distribution at the surface/ interface of the Al-particles. In this case, a Fe-O layer is detected

A chemical mapping of an Al-Fe-system was done by using TEM/EDS (CENTURIO, see exp. part) and is shown in Fig. 6. A ratio of $\sim 2\text{Fe}:3\text{O}$ was measured by the evaluation of the single signals (pixels). A reference image from blank particles only reveals some few and statistically distributed signals for Fe and O (not shown). Finally, as-prepared material will undergo a consequent comparison with physical mixes. In this context, a further optimization is expected regarding secure processing of igniter materials and energetic performances. Mixtures of n-RDX and n-TNT were synthesized just by mixing RDX: TNT precursor particles in a certain ratio (for Hexolite, see Table I, Section B). In contrast to cocrystals, the mixtures form a nanocomposite with separated phases and no new crystal lattice.

B. Cocrystals via SFE

Cocrystals are defined as “Solids that are crystalline single phase materials composed of two or more different molecular and/or ionic compounds generally in a stoichiometric ratio which are neither solvates nor simple salts” [6]. State of the art

binary approaches show the great and promising potential of organic energetic and organic inert cocrystals [7]. The latter is predominantly found in the fabrication and study of pharmaceuticals. In fact, the cocrystallization of an active pharmaceutical ingredient (API) - coformer couple indicates a highly promising tool for tailoring and optimizing drug properties like dissolution kinetics, degree of bioavailability (optimized drug up-take), and stability concerning pH and temperature. Within this context, a caffeine based model cocrystal (caffeine/oxalic acid 2:1) system was chosen to demonstrate effective cocrystallization of active pharmaceutical materials by means of the SFE process [7]. Regarding energetic compounds, higher performances and lower sensitivities are the basic motivation of further work within the scope of present topic.

First promising results on nanoscaled energetic cocrystals from binary precursor mixtures were done by the SFE process and successfully show the formation of diverse cocrystals (e.g. CL-20/HMX, 2:1) [7]. Moreover, first steps on a ternary approach dealing with the energetic organic compounds

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 2-Methyl-1,3,5-trinitrobenzene (TNT) were performed and are under intensive research at the moment. In this context, differential scanning calorimetry (DSC) and X-Ray Diffraction (XRD) suggest the formation of a mono- or biphasic crystalline structure, which is independent of their individual precursor compounds. Furthermore, sensitivity to friction of single compounds like the very sensitive CL-20 is strictly decreased by the new ternary cocrystalline matter (Table I). However, to confirm results from ternary mixtures, more investigations must be done.

- [4] Klaumünzer, M.; Hübner, J.; Krysch, C.; Spitzer, D.; Tunig the stabilization of Al-nanoparticles by surface modification with organic molecules, 2016, in preparation.
- [5] Klaumünzer, M., Kahnt, A., Burger, A., Mačković, M., Münzel, C., Srikantharajah, R., Spiecker, E., Hirsch, A., Peukert, W., Guldi, D.M.; Surface functionalization and electronic interactions of ZnO nanorods with a porphyrin derivative; (2014) ACS Applied Materials and Interfaces, 6 (9), pp. 6724-6730.
- [6] Aitipamula et al., Cryst. Growth Des., 2012, 12, 2147–2152
- [7] Spitzer, D., Risse, B., Schnell, F., Pichot, V., Klaumünzer, M., Schaefer, M.R.; Continuous engineering of nano-cocrystals for medical and energetic applications; (2014) Scientific Reports, 4
- [8] Klaumünzer, M., Pessina, F., Spitzer, D.; The Puzzle of Desensitizing RDX through Recrystallization at the Nanoscale; (2016), adapted, Journal of Energetic Materials, accepted

TABLE I
SENSITIVITY VALUES FROM PRECURSOR MATERIALS AND RECRYSTALLIZED MATERIALS AT THE NANOSCALE

System	ESD [mJ]	Impact [J]	Friction [N]
CL-20: HMX: TNT 1/1/1	n/a	5.0	80
CL-20: HMX (n-Co) 2/1	225.8	1.5	94
n-CL-20	186.6	n/a	28
n-HMX	280.6	1.6	168
μ-HMX	n/a	6.5	120
n-TNT	60	49.6	20
μ-TNT	n/a	12.8	40
n-RDX	268.7	1.6	360
μ-RDX M5	120	3.0	160
μ-RDX: TNT (60/40)	353.6	n/a	54
n-RDX: TNT (60/40)	755.2	10.3	72

IV. SUMMARY

In this proceeding, past and present works regarding the production of energetic nanomaterials by the SFE process are presented. Within the main part, some examples and future works are defined and reveal the extraordinary potential of the SFE process. The further development of new approaches and novel material designs and -structures at the nanoscale are in focus. These new and advanced materials on the nanoscale are foreseen to fulfill extraordinary and high requirements and claims-realized through tailor made and fine-tuned particle structures (e.g. core-shell structures). Two main application domains are outlined: multifunctional particle systems on the basis of aluminum nanoparticles for energetic uses, and cocrystals for energetic or even pharmaceutical / medical application. Basic experimental set up is the SFE process, established at the French-German Research Institute of Saint-Louis.

REFERENCES

- [1] Risse, B.; Hassler, D.; Spitzer, D.; Preparation of Nanoparticles by Flash Evaporation, 2013, WO 2013/117671 A1
- [2] Klaumünzer, M., Schlur, L., Schnell, F., Spitzer, D.; Continuous Crystallization of ZnO Nanoparticles by Spray Flash Evaporation vs. Batch Synthesis (2015) Chemical Engineering & Technology, Volume 38, Issue 8, 1, pp. 1477-1484.
- [3] Comet, M., Martin, C., Klaumünzer, M., Schnell, F., Spitzer, D.; Energetic nanocomposites for detonation initiation in high explosives without primary explosives; (2015) Applied Physics Letters, 107, 243108