Synthesis, Structural and Reactive Characterization of Miscellaneous Nanothermites

Denis Spitzer and Marc Comet
Institut franco-allemand de Saint Louis (ISL) ; Laboratoire ISL / CNRS NS3E (FRE 3026) ; 68301 Saint Louis, France

Abstract: *In this paper, we report the elaboration and the characterization of several kinds of nanothermites made at the French German Research Institute of Saint-Louis (ISL). Three types of materials are presented herein: tungsten trioxide based nanothermites obtained by physical mixing of this metallic oxide with aluminum nanoparticles; tungsten trioxide based nanothermites elaborated by coating WO_3 nanoparticles with aluminum using a chemical process; and molybdenum oxide based nanothermites composed of $Al_xMo_yO_z$ nanostructured phases and aluminum nanoparticles. In the light of these examples, we have identified general trends concerning the structural and reactive behavior of the new materials.*

Keywords: *nanothermites, tungsten oxide, molybdenum oxide, aluminum coating*

Introduction

Thermites are non-nuclear materials with a very high bulk energetic potential (10–25 kJ cm^{-3}). Thermite mixtures are composed of a metal oxide and an oxophile metal used as a strong reducer.[1] Contrary to explosive energetic compositions, thermites have a high density, and slow kinetics of combustion. Moreover, thermites have lower sensitivity than explosive energetic compositions regarding thermal and mechanical stress. Finally, they do not detonate, and generate small quantities of gaseous products. Decomposition of thermites is a redox reaction between two solid phases. The combustion kinetics are governed by the mass transfer between the oxidizer and the fuel phase. For this reason, nano-sized energetic compositions are of great interest because of the unconventional properties resulting from their high ratio of surface to volume atoms. A simplified model was used to determine the particle sizes for which the reactivity is expected to be changed.[2] From this model, we found that "nano-effects" appear when particles are smaller than some hundreds of nanometres. They are dramatically increased for particles having a diameter below twenty nanometres.

To elaborate nanothermites having energetic performances which significantly differ from classical thermites, it is necessary to use metallic oxide and metal particles having sizes in the range defined above.

As aluminum is the most efficient metal to formulate thermites, aluminum nanoparticles are commonly used to elaborate nanothermites. These particles exhibit a "cherry" structure with an aluminum core surrounded by an alumina shell. The use of aluminum nanoparticles smaller than fifty nanometres to elaborate nanothermites is not reliable because their alumina content is too high. An elegant way to solve this problem consists in coating metallic oxide nanoparticles with aluminum deposited by a chemical process.

Metallic oxide nanoparticles are easier to elaborate and to stabilize at the nano-scale. For instance, an original sol–gel process can be used to structure molybdenum oxide particles with different alumina contents. The alumina content is used to control the size and the nature of $Al_xMo_yO_z$ particles and the reactivity of nanothermites containing these phases.

Time resolved cinematography (TRC) is a method which is routinely used at ISL to study the combustion of energetic materials. From an experimental point of view, the energetic material is ignited by a laser beam (CO2; 10 W; 10.8µm) which is focused by the mean of a lens disposed on an optical bench. The ignition delay time is the duration between the laser impact on the energetic material and the beginning of its combustion. The ignition delay time can be correlated with the density of surface energy necessary to initiate the material. The combustion rate is measured by ultra fast cinematography using a Photron camera

which can capture till 125,000 frames per second.

Tungsten trioxide based nanothermites obtained by physical mixing[3]

Tungsten trioxide (WO_3) based nanothermites were elaborated by physical mixing of the oxide with aluminium nanoparticles. WO_3 and Al nanoparticles are commercially available and were purchased from Aldrich and Nanotechnologies respectively. From an experimental standpoint, the mixing was carried out by dispersing the particles in a liquid phase with ultrasonic stirring. In this case, diethyl ether was chosen as the dispersive medium because this solvent can be easily removed by evaporation. In addition, diethyl ether allows elimination of most of the adsorbed water which is trapped within the alumina shell covering the aluminum nanoparticles. Therefore, this method leads to dried nanothermite powders, which must be kept in a rigorously anhydrous atmosphere. As a general rule, adsorption water does not have a significant influence on the ageing of the aluminum nanoparticles, except if the material undergoes thermal shocks resulting in the condensation of atmospheric moisture. However, it was noticed that adsorbed water significantly desensitizes WO_3-based nanothermites towards friction stresses.

Most of the publications dealing with the reactivity of nanothermites focus on the influence of the size of the aluminum nanoparticles. Although this approach seems attractive, it is limited by the fact that aluminum nanoparticles contain more and more alumina as they become smaller.[4] In thermite mixtures, alumina is considered as an inert compound which limits the diffusion of oxygen atoms from the metallic oxide to the aluminum. Hence, decreasing the aluminum particle size to improve the reactivity is not realistic for particles smaller than fifty nanometres. Therefore, we decided to use the same aluminum nanoparticles, having a 45.7 nm aluminum core surrounded by a 2.9 nm alumina shell, in all experiments.

Surprisingly the incidence of the size of the metallic oxide particles on the reactivity of these materials has been disregarded. However, it can be stressed that oxide tuning is the key to controlling the performances of nanothermites in the future. In order to demonstrate that the size of oxide particles plays a major role in nanothermite reactivity, three

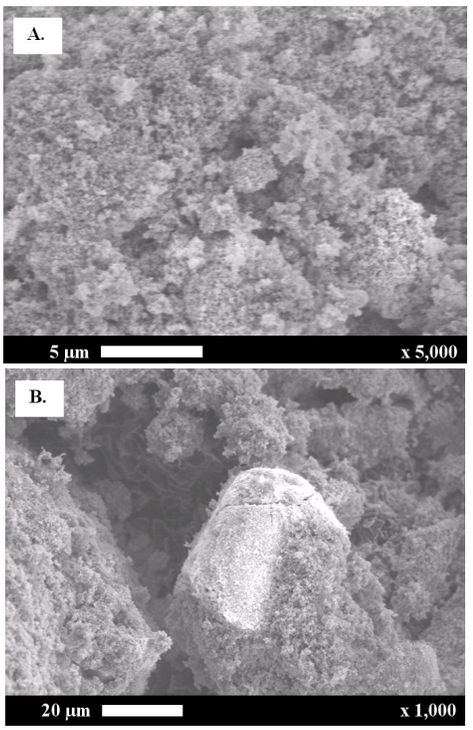

Figure 1. *Thermites obtained by physical mixing of tungsten trioxide particles having a mean diameter of 30 nm (A.) and 20000 nm (B.) with aluminium nanoparticles (diameter ≈ 50 nm).*

WO_3 grades were used. These materials, which were provided by Aldrich, had mean particle sizes of 30, 50 and 20000 nm respectively.

The microstructure of WO_3/Al nanothermites was observed by Scanning Electron Microscopy (SEM). In the mixtures containing only nanoparticles, it is difficult to discriminate particles according to their chemical nature (Figure 1A). Conversely, it appears clearly that aluminum nanoparticles homogeneously cover the surface of WO_3 micrometric particles (Figure 1B). These micrographs are a good illustration of the fact that the nanostructuring of each component is necessary to reach a satisfying contact between the reactants.

WO_3/Al nanothermites which contain only nanoparticles have an impressive reactivity. The fireball generated by the deflagration is so hot that a bang due to overpressure is heard. The combustion rate can reach 7.3 m s^{-1}. This value is extremely high compared to classical energetic materials. For example, a mixture of potassium chlorate and sugar tested in similar experimental conditions exhibits

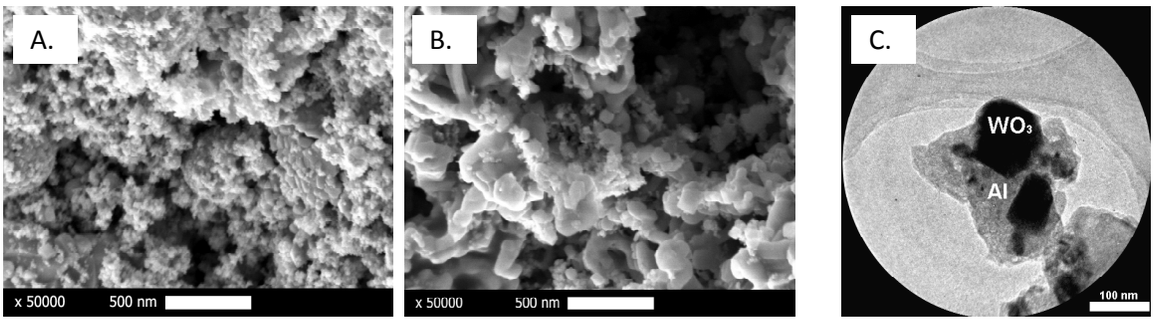

Figure 2. *Scanning electron micrographs of pure WO_3 nanoparticles (A.) and WO_3/Al nanocomposite (B.). Transmission electron micrograph illustrating the coating of WO_3 nanoparticles by chemically deposited aluminum (C.).*

a combustion speed two orders of magnitude lower. The ignition delay time of some WO_3/Al nanothermites is less than two milliseconds with a CO_2 laser source (λ = 10.6 µm) delivering a 10 W power on a surface of approximately 1 mm^2. However, dried WO_3/Al nanothermites are extremely sensitive to friction stress (<4.9 N). This sensitivity is significantly reduced when the aluminum nanoparticles contain small amounts of adsorbed water. WO_3/Al nanothermites are relatively insensitive to impact stress (42.2 J). TRC experiments showed that WO_3/Al nanothermites aged at 200 °C in air for several hours keep their reactive properties. Nevertheless, the repeatability of energetic properties is deteriorated by thermal ageing.

Tungsten trioxide based nanothermites obtained by chemical coating

Tungsten trioxide based nanothermites can be remarkably desensitized by embedding the metallic oxide nanoparticles with aluminum. This process was patented by ISL.

Scanning electron microscopy (SEM) reveals that pure WO_3 particles (Figure 2A) are significantly smaller than WO_3/Al particles (Figure 2B). The coating was proved by transmission electron microscopy (TEM) which clearly shows that aluminum is located around tungsten trioxide particles and covers them (Figure 2C).

Nitrogen adsorption corroborates this result. Indeed the experimental specific area of the WO_3/Al composite is higher than the specific area of WO_3 particles. A mathematical approach allows demonstration that the density of aluminum prevails against the increase in diameter. For instance, in the case of a WO_3 spherical particle (*diameter* ≈ 30 nm) which is covered by a homogeneous aluminum shell, the specific surface area will be smaller than that of WO_3 provided that the aluminum thickness does not exceed twenty nanometres.

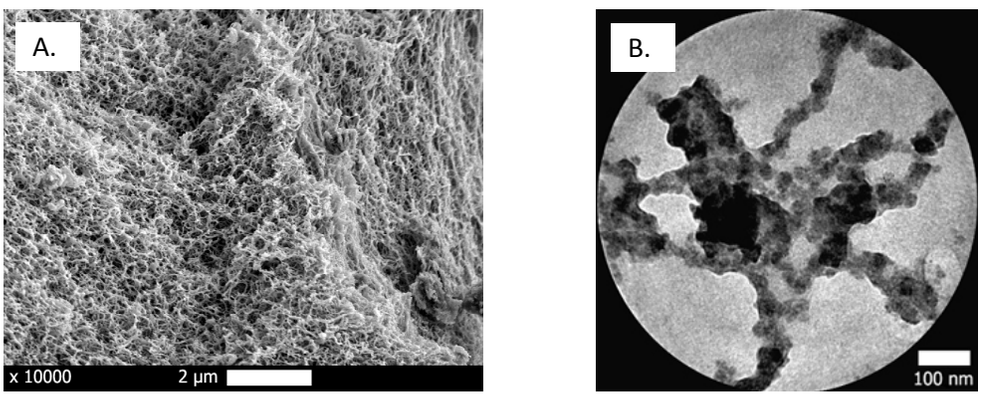

Figure 3. *SEM observation of the microstructure of an agar/APM composite gel (A.); TEM picture representing the string-like structure of elementary strands (B.).*

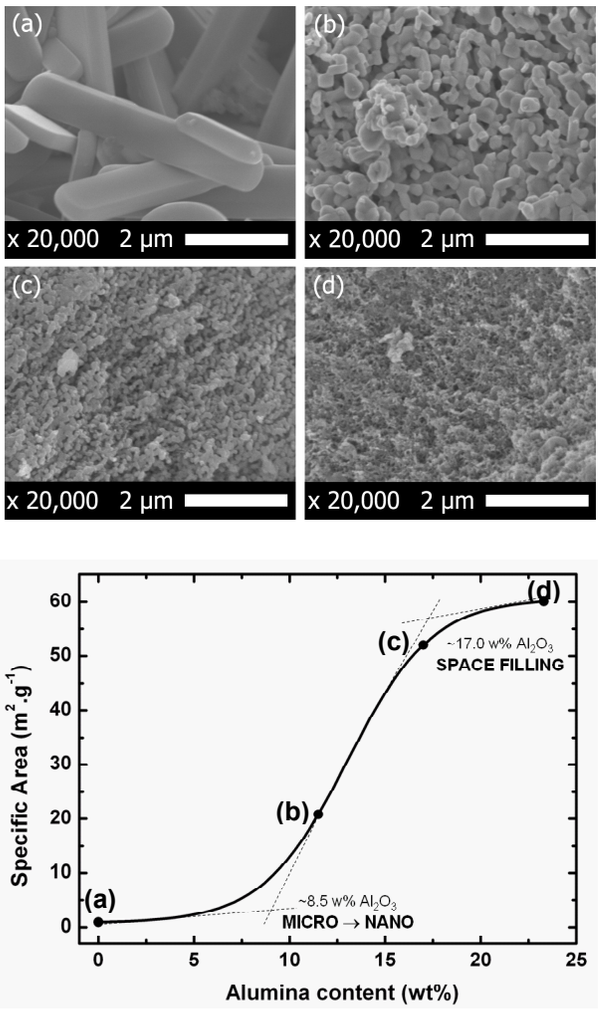

Figure 4. *Qualitative (SEM) and quantitative (BET) characterization of the microstructure of $Al_xMo_yO_z$ phases according to their alumina content: 0 wt% (a), 11.5 wt% (b), 17.0 wt% (c) and 23.3 wt% (d).*

During their thermal decomposition, these materials release the same amount of energy as the corresponding nanothermites elaborated by physical mixing. However, the sensitivity to mechanical stresses is significantly decreased. This can be explained by the fact that composite particles behave towards each other like metallic particles.

$Al_xMo_yO_z$ based nanothermites 5

Mixed oxide phases ($Al_xMo_yO_z$) were structured at the nano-scale in order to get nanothermites with tuned reactive properties. For this purpose an ammonium paramolybdate (APM) aqueous solution was gelified by using agar, a polysaccharide of botanic origin. The resulting hydrated gels were washed with acetone in order to remove water. Water extraction induced the solidification of the inorganic phase (APM) within the organic matrix (agar). These materials are highly porous crumbly monoliths called "composite gels". They have a three-dimensional porous structure formed of interlinked strands of average section equal to 45 nm (Figure 3A). APM particles are located within the agar strands, in which they define a string-like structure (Figure 3B). A mathematical approach based on specific area measurements was used to optimize the composite gel formulations. It results from these calculations that the agar content of an ideal composite gel must range between 40 and 60 wt%. For these formulations, APM does not crystallize out of the agar matrix. Moreover, APM particles have small sizes (20–34 nm) and they are sufficiently spaced in the agar strand (2.0–3.5 nm).

Composite gels underwent an oxidative treatment which allowed burning off the agar and conversion of APM into molybdenum oxide. A direct thermal oxidation of composite gels results in a structural collapse, leading to molybdenum trioxide (MoO_3) micrometric particles. A chemical treatment was developed to prevent this phenomenon. It consists in treating composite gel powders with an anhydrous aluminum trichloride ($AlCl_3$) solution in diethyl ether (Et_2O). The water adsorbed by the composite gels readily reacts with $AlCl_3$ to give an oxychloride layer at the surface of gel strands. During the thermal treatment, this layer prevents the collapse of the structure by acting as an *in situ* nano-sized crucible. Most of the chlorine atoms were removed and several chemical species were formed. The formula $Al_xMo_yO_z$ refers to these species, which mainly consist of amorphous alumina associated with crystallized molybdenum dioxide (MoO_2) and aluminum molybdate ($Al_2(MoO_4)_3$). The under-oxygenated MoO_2 phase probably forms in the reducing environment of the core of the agar strand. The aluminum molybdate most likely appears at the surface of the agar strand, where the APM particles are in contact with $AlCl_3$ and oxygen from air. The final microstructure of $Al_xMo_yO_z$ phases directly depends on the concentration of the $AlCl_3$–Et_2O solutions used to impregnate the composite gel (Figure 4). The

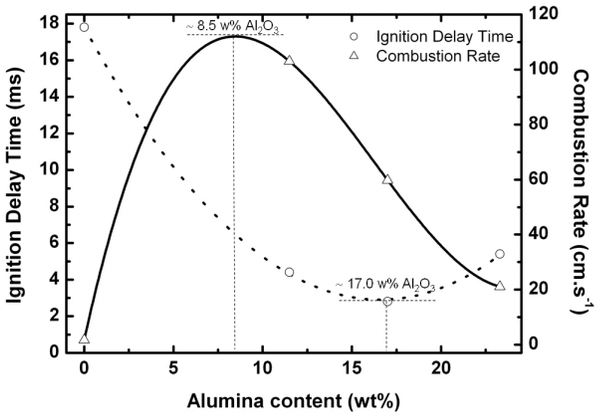

Figure 5. *Evolution of the ignition delay time (δ) and of the combustion rate (V_r) of $Al_xMo_yO_z$ nanothermites depending on the alumina content of the $Al_xMo_yO_z$ phase.*

transition from micro- to nano-scale occurs for alumina weight contents higher than 8.5%. An alumina content of more than 17.0% results in the densification of the material.

Nanothermites were elaborated by physical mixing of the $Al_xMo_yO_z$ nano-sized phases with aluminum nanoparticles. From an experimental standpoint, the dispersion was performed by ultrasonic stirring in hexane. The powdery materials were pelletized and characterized by time resolved cinematography (Figure 5). Their ignition delay times (2.8–17.8 ms) and their combustion rate (1.7–103 cm s^{-1}) can be adjusted through the formulation of $Al_xMo_yO_z$ phases. It can be noticed that the reactivity of these nanothermites is correlated to the structure of the $Al_xMo_yO_z$ phases. Indeed, the higher combustion rate corresponds to the micro to nano transition while the smaller ignition delay time is observed just before the $Al_xMo_yO_z$ densification.

Although they have better energetic performances, $Al_xMo_yO_z$ nanothermites are more insensitive to thermal and friction stresses than a thermite elaborated with pure micron-sized molybdenum trioxide. This insensitivity is probably due to the presence of alumina, which limits the contact between the reactive species.

Conclusions

The energetic performances of nanothermites strongly depend on the elementary microstructure of the metallic oxide (WO_3, $Al_xMo_yO_z$) and the reducing metal (Al) they are made of.

Concerning aluminum, the main obstacle is the "cherry" structure of the particles which limits the amount of useful matter and prevents contact with the metallic oxide. To solve this problem, the unique solution is to coat metallic oxide nanoparticles by chemically deposited aluminum.

Concerning metallic oxides, a decrease of the WO_3 particle size dramatically shortens the ignition delay time and significantly accelerates the combustion rate of WO_3/Al nanothermites. Alumina can be used to tune the structure of molybdenum oxides in the form of $Al_xMo_yO_z$ phases. These nanostructured materials allow elaboration of highly insensitive $Al_xMo_yO_z$/Al nanothermites and control of their reactivity.

References

1 S. H. Fischer and M. C. Grubelich, Theoritical Energy Release of Thermites, Intermetallics, and Combustible Metals, *Proceedings of the 24th International Pyrotechnics Seminar*, Monterey, California, USA, 27–31 July, 1998.

2 M. Comet and D. Spitzer, Des thermites classiques aux composites interstitiels métastables, *Actualité Chimique*, Vol. 299, 2006, pp. 20–25.

3 D. Spitzer, M. Comet, J.-P. Moeglin, E. Stechele, U. Werner and Y. Suma, Synthesis and investigation of the reactivity of nano thermite mixture, *37th International Annual Conference of ICT*, Karlsruhe, BRD, June 27–30, 2006, pp. 117-1 to 117-10.

4 M. Comet and D. Spitzer, Elaboration and characterization of nano-sized $Al_xMo_yO_z$/Al thermites, *33rd International Pyrotechnics Seminar*, Fort Collins, Colorado, USA, July 16–21, 2006, pp. 93–102.