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# Reactivity tuning of Al/CuO multilayered films by embedding nanoparticles

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In this work, gold and silica nanoparticles were added into reactive Al/CuO multilayers systems. Their effects on the flame front dynamics were investigated experimentally using microscopic high-speed imaging technique and theoretically via a reaction model coupling mass and heat diffusion processes. Theoretical findings contradict the experimental observations in which a net increase of the flame front velocity was observed when Au and SiO<sub>2</sub> particles are added in the multilayers. This leads to the conclusion that the faster burn rate observed cannot be fully associated with thermal effects only.

## I. INTRODUCTION

Over the past two decades, nanoenergetic materials, especially nanothermites, have received an important interest for additives in propellants, self-propagating high-temperature synthesis (SHS) or pyrotechnic chips<sup>1-9</sup>. Reactive multilayered films (RMFs) consist of stacks composed of alternating thin layers (tens to hundreds of nm) of metal/oxidizer<sup>10-12</sup>. Those thin films are usually deposited using physical vapour deposition (PVD) techniques, such as DC-magnetron sputtering. Multilayers systems offer a stable and reproducible material setting for analysing the different mechanisms involved in reaction process, under external stimulation. Moreover, sputtering deposition technique allows easily controlling the configuration of the multi-layered system, such as layer thickness, stoichiometric ratio or even layering roughness.

Among multilayers, the specific Al/CuO system arouses a lot of interest in applied research, because of its capability of releasing high energy density ( $\sim 4 \text{ kJ.g}^{-1}$ ), its low ignition temperature and more generally its good reactivity<sup>13-17</sup>. A large part of the research community is dedicated to finding ways to modulate accurately the energetic properties, such as ignition energy<sup>15,18-20</sup> and combustion wave velocity<sup>21,22</sup>. A common way consists in using additives, or dopants (metal, carbons or oxides), without changing the material itself i.e. without changing the nature of reactants, bilayer thickness or equivalence ratio. Despite numerous experimental results, the fundamental mechanisms leading to self-propagating

reaction modulation are still unclear, and the comprehension behind the observed results remains evasive.

The purpose of this study is to better understand the effect of additives on the combustion of a thermite system. To reach this goal, highly conductive (Au) and insulator (SiO<sub>2</sub>) nanoparticles were embedded in a Al/CuO multilayered systems and the combustion front (flame) is accurately monitored when reaching the Au and SiO<sub>2</sub> nanoparticle to analyse locally its effect on the self-propagating combustion. We then confronted the experimental observation with modelling thanks to a 2D combustion model. After the presentations of results, the analysis will be discussed in this paper.

## II. Multilayered system and burning experiments

### A. Al/CuO multilayered systems

The multilayers system is a well defined system consisting in 15 Al/CuO bilayers, where aluminium layer is 75 nm and copper oxide layer is 150 nm. Giving the well-known thermite reaction ( $2\text{Al} + 3\text{CuO} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Cu}$ ) this configuration corresponds to a stoichiometric stack. The multilayer were magnetron sputtered on pre-metalized glass substrate, through a physical mask (shadow mask) to pattern a line of nanothermite of 25 mm by 2 mm line (FIG. 1.a). A Ti thin pattern is used to ignite the nanothermite on the left side.

During the process, Au (between 5 and 30 nm) and SiO<sub>2</sub> ( $150 \pm 10 \text{ nm}$ ) nanoparticles were incorporated into the first CuO layer (FIG



particles, size), and calculate the thermal front (reaction front) velocity along the propagation axis. Furthermore, the thermal profile inside the reaction front in the vicinity of NPs can be analysed as further presented.

### A. Perturbation of the flame velocity around one single particle

When the reaction front crosses an Au or SiO<sub>2</sub> nanoparticle, a local perturbation of the front velocity is observed (FIG.3). Specifically, silica locally slow down the reaction front by 24 %, while gold object locally speeds up by 20 %. For both case, the combustion front regains its steady state after a pseudo-oscillating regime. Considering the length of the particle (0.13 μm), one can observe the overall perturbation extend well further the particle position.

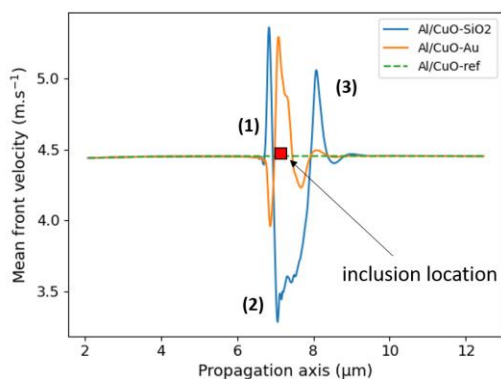


FIG. 3. Evolution of the calculated reaction front velocity along the propagation axis when the combustion front crosses an Au or SiO<sub>2</sub> nanoparticle (indicated by red square).

### B. Influence of the particle loading on the flame velocity

In order to better imitate the experiments, we performed simulations with multiple nanoparticles inside the thermite system: 1, 7, 14 and 20 NPs, which corresponds to different volume loadings (in vol. %). The global front velocity, defined as the velocity averaged along the overall propagation length is plotted in the FIG. 4 in terms of velocity changes as a function of the volume loading. The results show that the averaged flame velocity changes linearly when increasing the particle loading, but with opposite trends. Specifically, the higher thermal diffusivity of Au results in a limited flame velocity increase while the silica NPs has a more dramatic effect: flame velocity drops by 17%.

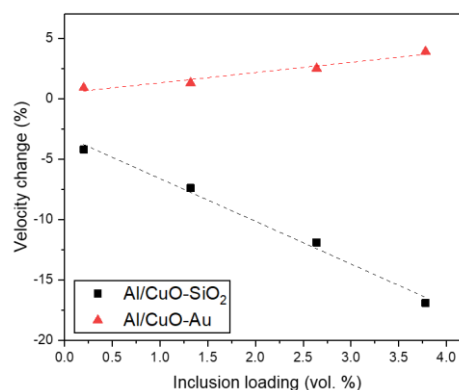


FIG. 4. Relative change (in % relatively to the reference system at 4.45 m.s<sup>-1</sup>) of the self-propagating velocity (global burn rate) for different NPs loadings (in vol. %)

## IV. CONCLUSION

This work concluded conflicting results between experimental observations and theoretical results. Combustion experiments showed an enhancement of the flame velocity in multilayers containing Au and SiO<sub>2</sub> NPs in their first bilayer. Whereas 2D propagation model predicts a slowdown of the flame especially when silica NPs. This result leads to the conclusion that the faster experimental combustion velocity observed with additives cannot be fully associated to thermal effects. Instead we propose that other chemically and/or mechanically based processes must play a role in the enhancement of the reaction rate. We suggest that locally, i.e. at the vicinity of additives, high stressed zone are created during the flame front crossing because of extreme temperature gradient associated with radically different thermal expansion coefficient differences between NPs and thermites. This assumption needs to be looked to further in a future study.

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