Insight in the burning behavior of aluminum nanopowders

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maîtriser le risque pour un développement durable

Context

1. INERIS operates since end of 2014 a Nanosafety platform dedicated to the study of physical hazards of nanopowders

2. INERIS research program dedicated to:
    1. Acquiring general knowledge on fire and exlosion hazards of ENM
    2. Adapting testing protocols to the specific behavior of ENM
    3. Establish good safety practices for handling hazardous ENM
    4. Use test results in safety studies (ATEX)

3. Collaboration with ISSeP (NANOGRA project) arround the characterization of fire and explosion hazards associated with nanomaterial (see. E. Bouhoulle's (ISSep) presentation)
    1. Intercomparison of test results for CNT, Al

Fire and explosion hazard characterization

Explosion violence (Kst, Pmax) : 20 L sphere : ISSeP and INERIS

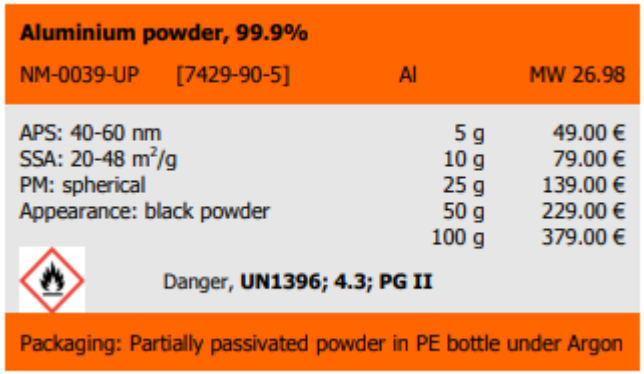
Minimum Ignition Energy : Mike 3 aparatus : INERIS

Minimum Ignition Temperature of a 5 mm Layer : Hot plate : INERIS

Fire propagation : VDI protocol : INERIS

Material tested : nanometric aluminum powder 40-60 nm

Sold as partially passivated => should not present pyrophoric behavior



Substance is identified as flammable and producing flammable gas when in contact with water (class 4.3)

Fire and explosion Nanosafety Lab

S-NANO Platform at INERIS, Verneuil-en-Halatte, France

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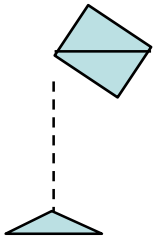
Local context at beginning of the study

During preparation of samples for ecotoxicity tests at ISSeP, the powder ignited spontaneously => Fear of pyrophoric properties

=> Need to characterize the pyrophoric behavior and adapt test protocol for safety

=> Handling in glove box under Argon (below 3% O_2) (INERIS) to prepare small size samples

=> Pyrophoric test needed to assess the risks during preparation of other tests



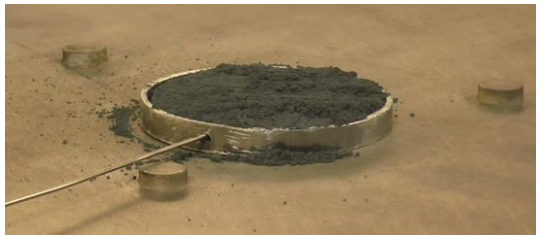
UN N2 test : drop the powder and see if it ignites within 5 minutes
=> Negative

Is this test always suitable for assessing the hazard of spontaneous ignition ?

What was the ignition mechanism involved ?

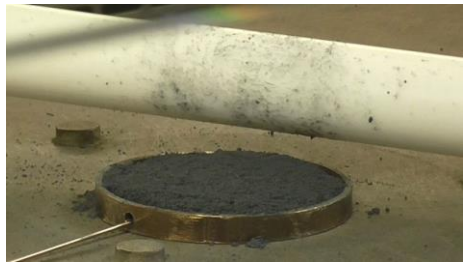
Other preliminary testing

Self heating (5 mm layer, with continuous heating ramp up to 436°C (plate)).



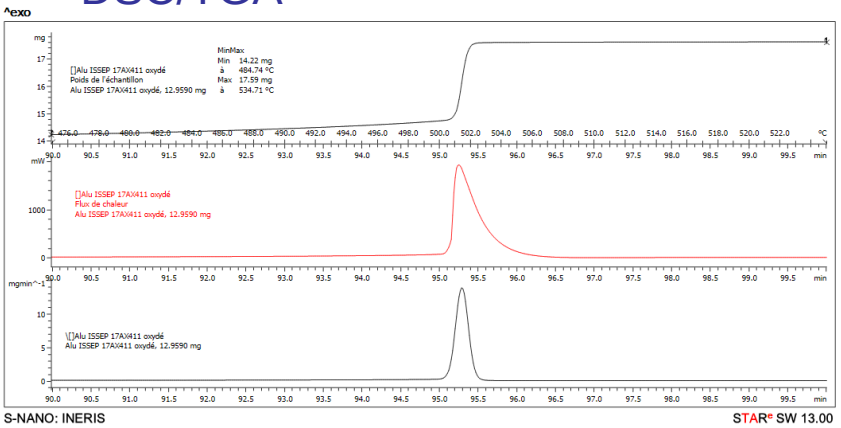
No ignition

(Low energy) Electrostatic discharge layer ignition



No ignition
But no way to measure how much energy was actually delivered

DSC/TGA

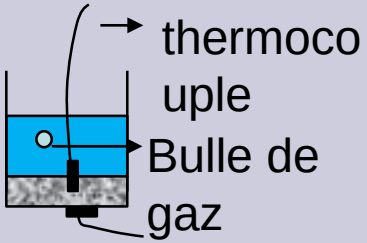
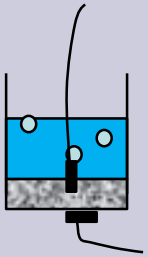
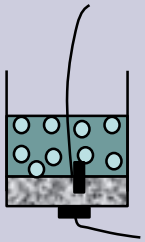


Onset 508°C (test 1)
50% of Al as Al_2O_3 (6 nm layer for a 50 nm particle)

Onset 501°C (test 2)
43% of Al as Al_2O_3 (5 nm layer for a 50 nm particle)

Based on hypothesis of 100% conversion to Al_2O_3

Reaction to water

Time	Day 1	Day 2, 12 h	Day 2, 16h
			
Temperature evolution	+ 0,3 °C	*	T_{max} = 27 °C
Gas emission	Weak	Moderate	Fast
Appearence of the water solution	clear	clear	troubled

Minimum ignition energy

Two stage ignition for high concentration

Spark

Primary ignition

Secondary ignition (air pulse)

Cause : incomplete combustion in quiet air (primary ignition) due to lack of oxygen

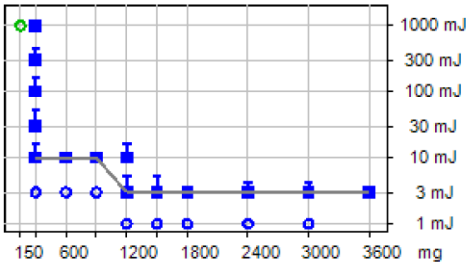
The air pulse brings the fresh oxygen to burn

1g of Al requires 3 L of air for complete combustion

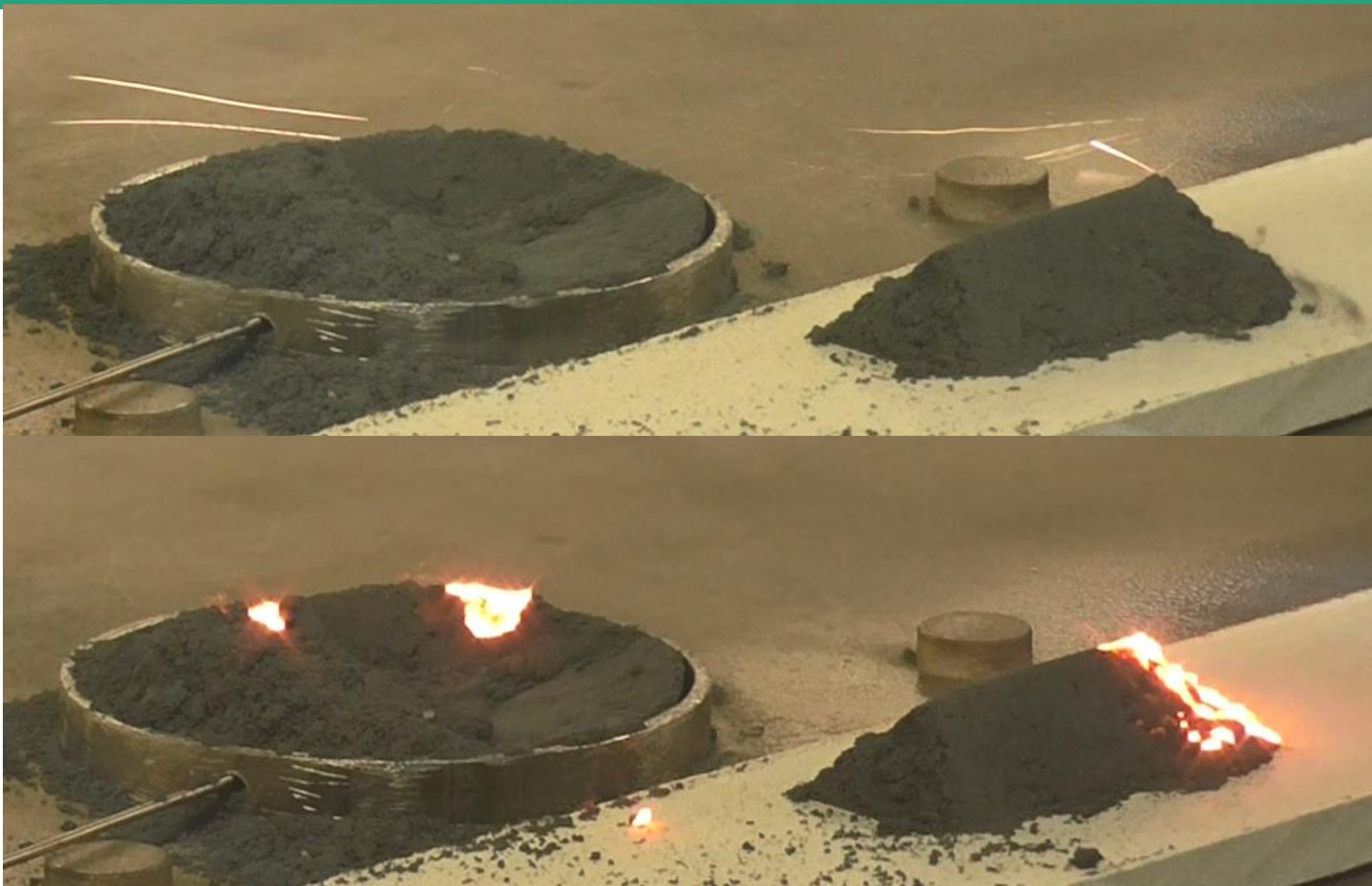
The tube has a volume of 1 L

Result with inductance L = 1 mH

1 mJ < MIE < 3 mJ / Es = 1,6 mJ

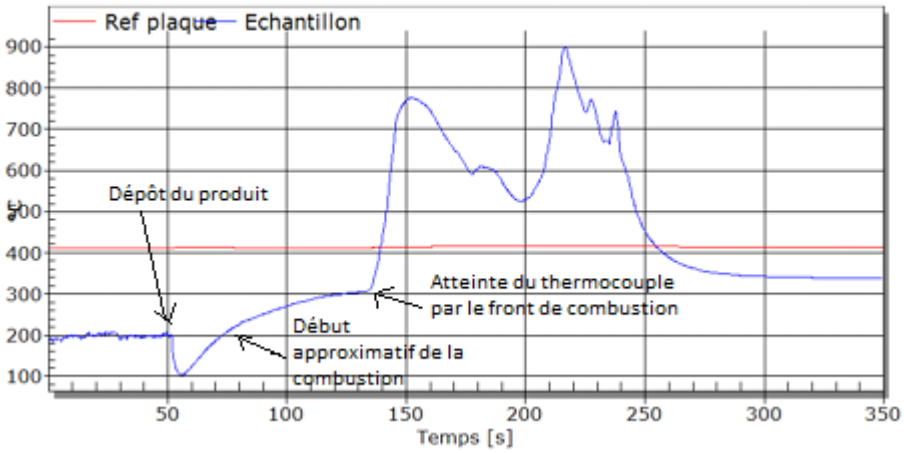


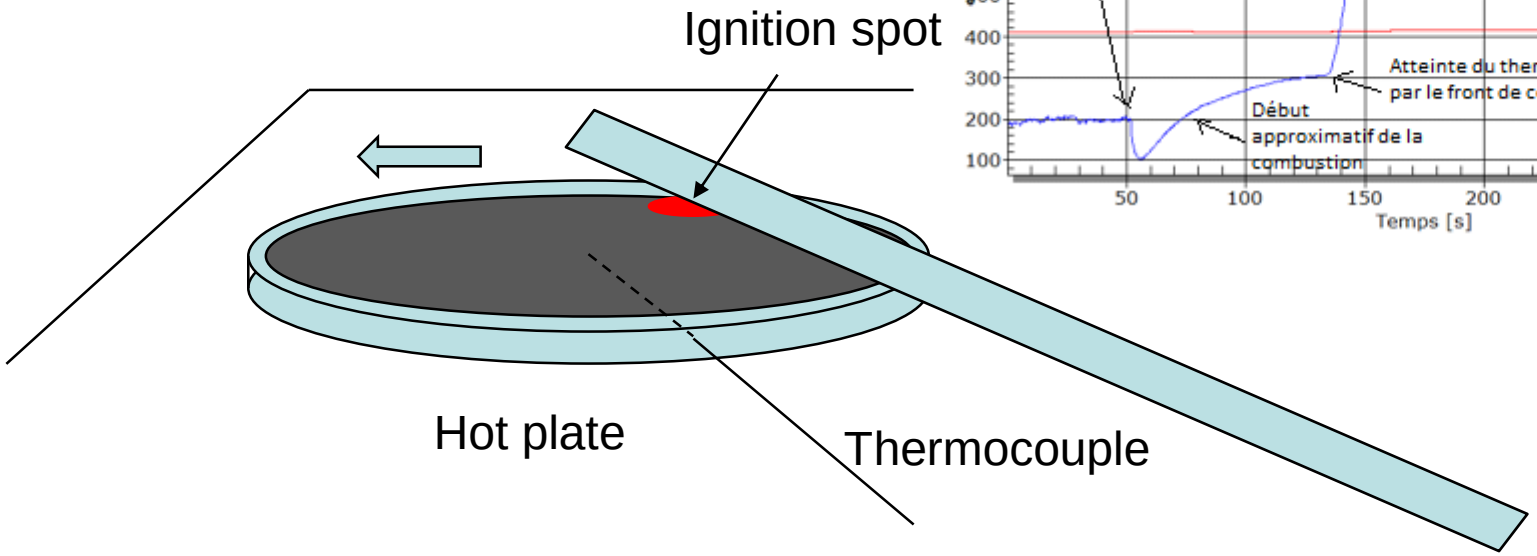
Ignition by sparks (burning particles)



Ignition by friction

Ignition occured during layering of the dust at contact point between dust and retention circle





Two combustion regimes

Explosion violence

	Essai à 10 kJ
P_{max} (bar)	7,9
dP/dt (bar/s)	701
k_{max} (m.bar/s)	190

Explosion violence seems low if compared to available data on micrometric aluminum powder

But in good agreement with (Bouillard and Vignes, 2010) and subsequent more recent works

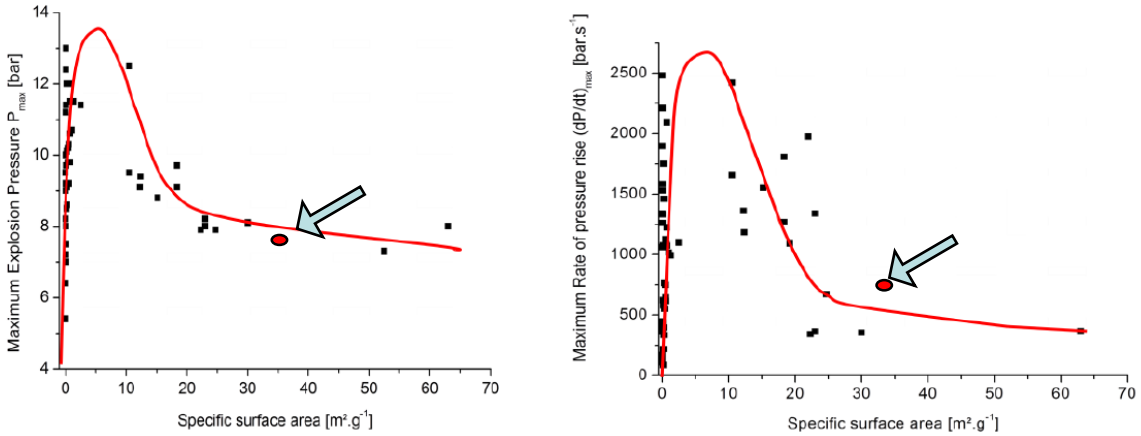
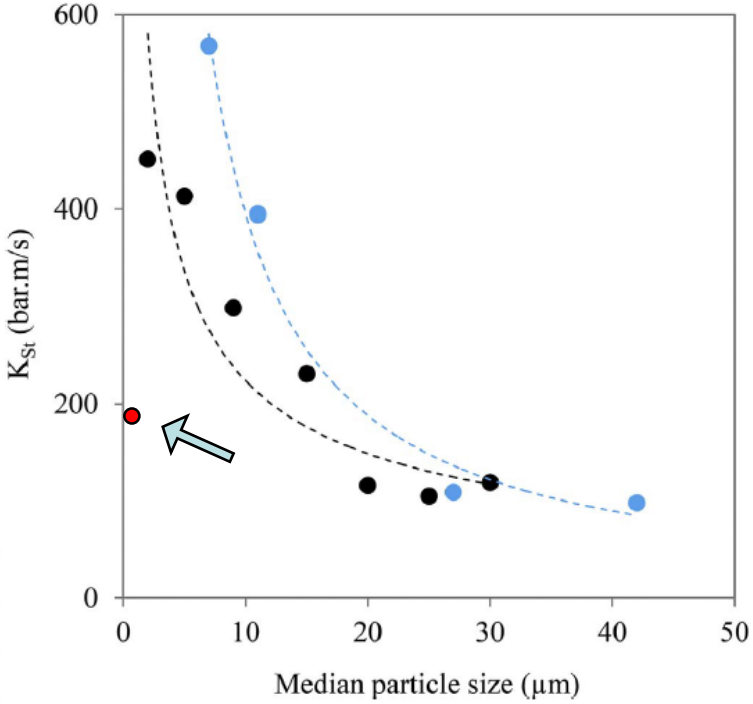


Figure 8 Evolution of safety parameters for explosion as a function of specific surface area (aluminium)

Source : A. Vignes, Final report of Eu Project MARINA



Source : Taveau et al., Explosion hazards of aluminum finishing operations, *Journal of Loss Prevention in the Process Industries 51 (2018) 84–93*

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On pyrophoric behavior

Two interpretation of the pyrophoric behavior :

A. **Single particle pyrophoricity**.

The heat balance at particle level governs its reactivity.

$$\begin{cases} \dfrac{dE_{ox}}{dt} = \dfrac{d(m_{ox}Cp_{ox}T_{ox})}{dt} = Q_{prod} - Q_{ext} - Q_{metal} \\ \dfrac{dE_{metal}}{dt} = \dfrac{d(m_{metal}Cp_{metal}T_{metal})}{dt} = Q_{metal} \end{cases}$$

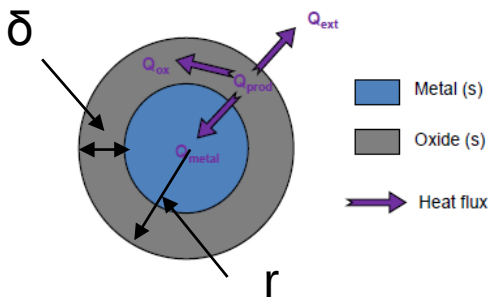


Figure 35 : Heat balance performed on a pyrophoric particle

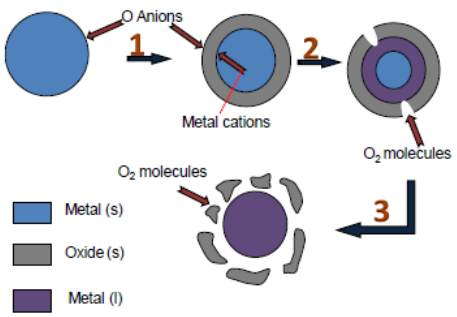


Figure 36 : Sketch describing the steps in pyrophoricity phenomenon

Based on the Glassmann theory a limit oxyde/radius ratio was assessed by for Aluminum beyond which it could become pyrophoric

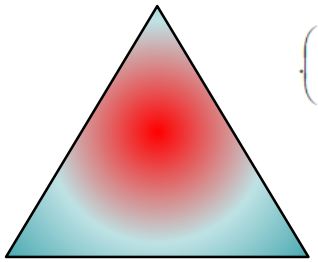
δ/r=0,18

To be compared with the **0,2** and **0,24 δ/r ratio** measured by DSC/TGA

Source : A. Vignes, Final report of Eu Project MARINA

B. **Low volume/temperature self heating**

The heat balance in the pile governs the heat rise and global kinetics of the reaction as described by the Franck-Kamenetskii model.



$$\left(\frac{d^2T}{d^2x} + \frac{j}{x}.\frac{dT}{dx}\right) = -\frac{Q.\rho.A.e^{\left(\frac{-E}{RT}\right)}}{\lambda}$$

Still needs to be fully explored for this nanometric Al Although layer self ignition temperature have shown no specific self-heating behavior

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Conclusion

Experiments carried out in partnership with ISSep on nanometric Aluminum.

Good agreement with previous experimental studies for :

- Minimal ignition energy
- Explosion violence

Cause of spontaneous ignition still not clear

- Pyrophoricity due to insufficient Al_2O_3 layer thickness ?
- Self-heating behavior ?
- Sensitivity to friction : still needs to be confirmed by dedicated tests ?

Different combustion behaviors depending on the fate of the oxyde layer ?

Adequate characterization of the ignition mechanism and efficiency of the passivation is an issue for industrial safety when handling such powders

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