

Burning and Explosion Properties of Metallic Nano Powders

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This paper describes experiences and results of experiments with several metallic dusts within the nanometer range. The nano dusts (aluminium, iron, zinc, titanium and copper) were tested in a modified experimental setup for the test apparatus 20-L sphere (also known as 20-L Siwek Chamber), that enables the test samples to be kept under inert atmospheric conditions nearly until ignition. This setup was already introduced in earlier papers by the authors. It was designed to allow the determination of safety characteristics of nano powders under most critical circumstances (e.g. minimisation of the influence of oxidation before the test itself). Furthermore the influence of passivation on explosion behaviour is investigated and additional tests with deposited dust were carried out to describe the burning behaviour of all dusts. For a better characterisation all samples were tested with a simultaneous thermal analysis (STA). To minimise the influence of oxidation all samples were handled at inert conditions until shortly before ignition or start of the test respectively.

Keywords: dust explosion, nano dust, ignition, explosion protection

Introduction

With increasing influence of nanotechnology more and more materials are being produced within the nanometer range and thus fire and explosion risks in the production, handling and transport of these materials have become an interest of research (e.g. Bouillard et al. 2010, Eckhoff 2012, Holbrow et al. 2010, Vignes et al. 2010). Burning and explosion properties of combustible dusts in general are described with so called safety characteristics. Their determination is carried out in accordance to international standards. Based on experience of dusts with particle sizes in the micrometer range it is well known that dusts are classified more critically with decreasing particle size, as their explosion severity and ignition sensitivity increase. The main questions of current and past studies arise from following specific properties of nano powders which may either promote or impede nano dust explosions:

- The increased specific surface area may lead to an increase in ignition sensitivity and reaction severity.
- Some powders may show pyrophoric behaviour when sized down to nano-scale.
- Oxygen adsorption at reactive surfaces of individual particles may result in a passivation of the powder.
- Powders may tend to form agglomerates which are of micro-scale

For example surface passivation may result in a decrease of ignition sensitivity and reactivity before the test itself. Such processes are already well known for metallic micrometer dusts. For this reason it was first of all verified whether or not current test methods are applicable for nano powders. Test methods have then been adapted regarding requirements for health protection and further been modified to determine characteristics of powders that did not get in contact with oxygen shortly before ignition. This also allows investigating the influence of oxygen exposure on nano powders.

Experimental

According to EN 14034 series and ASTM E1226-10 the 20-L sphere (Figure 1) is used for the determination of the safety characteristics maximum explosion pressure p_{max} , maximum rate of pressure rise $(dp/dt)_{max}$ or explosibility index (K_{St}) and lower explosion limit (LEL). It consists of a hollow sphere of 20 litres internal volume made of stainless steel. For testing, a dust sample is placed in the dust container, pressurised and then dispersed into the sphere via the outlet valve and the rebound nozzle. Therefore the explosion chamber must be evacuated to 0.4 bar absolute while the dust container is filled with 21 bar absolute of compressed air. The evacuation of the explosion chamber is necessary to ensure ambient pressure after the dispersion process.

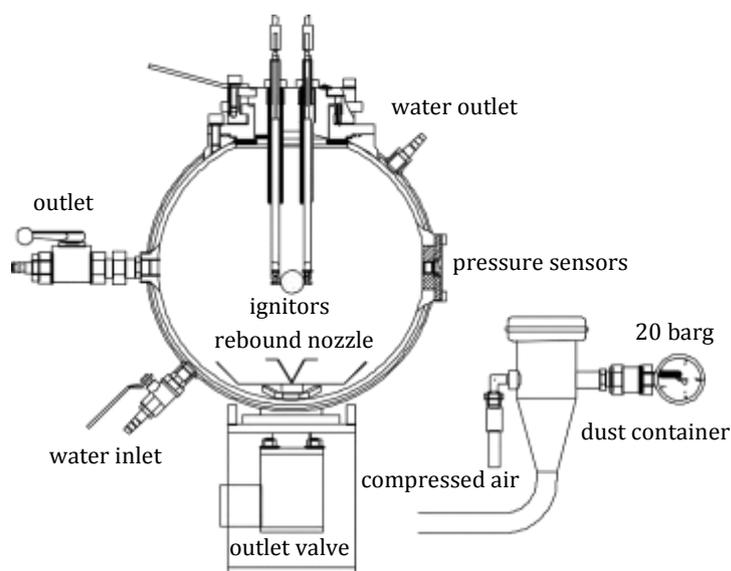


Figure 1. Schematic of standard 20-L sphere (EN 14034-1, 2004 edited).

Modified experimental setup for 20-L-sphere

Especially metallic nanopowders can ignite spontaneously during the injection process into the explosion chamber. Main reasons for that are the high ignition sensitivity of such substances and high shear forces that can occur during the dispersion process into the explosion chamber like already reported by Wu et al. (2010). This behaviour may lead to increased wear of parts of the test apparatus (e.g. outlet valve). Moreover, these uncontrolled early ignitions do not allow obtaining reliable safety characteristics of respective dusts.

Thus all tested samples were handled under nitrogen shortly until ignition in order to investigate the influence of oxygen and to determine the most critical behavior. For the determination of the most critical behaviour of nanopowders it is necessary to test powders which were produced and transported without or with only a minimum of oxygen. To minimize the influence of oxygen passivation during sample preparation and testing it is in addition that necessary to handle such samples under absence of oxygen until the time of ignition. A suitable experimental setup to implement that is placing test equipment and sample preparation into an enclosure with controllable gas atmosphere. Thus a special glovebox system with two separated gloveboxes (one glovebox for sample preparation and one for test equipment) operated with nitrogen has been developed in which test equipment such as the 20-L sphere and the sample preparation were integrated. Through the glovebox system it is possible to operate the 20-L sphere with two additional methods in comparison to the standard procedure. One method is comparable to the approach used by Boilard et al. (2013) for nanometer titanium or Mittal (2013) for selected experiments with nanometer magnesium. The whole setup and both additional methods are described in detail by Krietsch et al. (2013).

Burning behaviour and STA measurements

The aim of the Burning behaviour test is to determine if and to what extent a locally ignited fire started by an external source will propagate in a dust layer. The combustibility of the sample is characterised as a class number (Burning Class 1 to 6) in accordance with the course of reaction (VDI 2263-1, 1990).

The thermal decomposition and reactivity of the powders has been studied by simultaneous thermal analysis (STA). The apparatus STA 409 PC Luxx (Netzsch Germany) combines differential scanning calorimetry (DSC) and thermogravimetry (TG). Due to this the STA provides information regarding mass changes, exothermic and endothermic effects within one sample simultaneously. All measurements were done under ambient conditions and each sample was stored under nitrogen until shortly before the start of the test.

Results and discussion

For this study five different metallic nano powders (aluminium, zinc, copper, titanium and iron) were chosen. All samples were characterised using Scanning Electron Microscopy (SEM) and laser diffraction analysis. Results are presented in Table 1. Laser diffraction analysis of the tested titanium was not possible because it ignites spontaneously during the measurement process and could not be securely passivated.

It can be seen, that although being produced within the nanometer range, primary particles form agglomerates within the micron range due to inter-particle cohesion forces (e.g. van der waals interaction and electrostatic forces). Because of high particle numbers especially at concentrations that are relevant for dust explosions, nearly instant agglomeration cannot be avoided. Thus it is not necessary to modify standard test methods with the aim of avoiding agglomeration.

Table 1. Primary particle size and agglomerate size of tested samples.

Dust sample	Primary particle size ^a	Agglomerate size ^b
aluminium	90 – 110 nm	4.0 µm
zinc	90 – 150 nm	5.3 µm
copper	50 – 70 nm	6.7 µm
titanium	60 – 80 nm	n.a.
iron	50 – 70 nm	5.3 µm

^a SEM images and supplier information^b laser diffraction analysis

An analysis of the SEM images confirms these observations. Figure 2 shows two SEM images of nano aluminium. The left picture illustrates the agglomerate of a lot of smaller primary nanoparticles. On the first view there seems to be no difference to particles within the smaller micron range. But a closer look (picture on the right side of Figure 2) reveals that there are a lot of cavities and pores which increase the specific surface area.

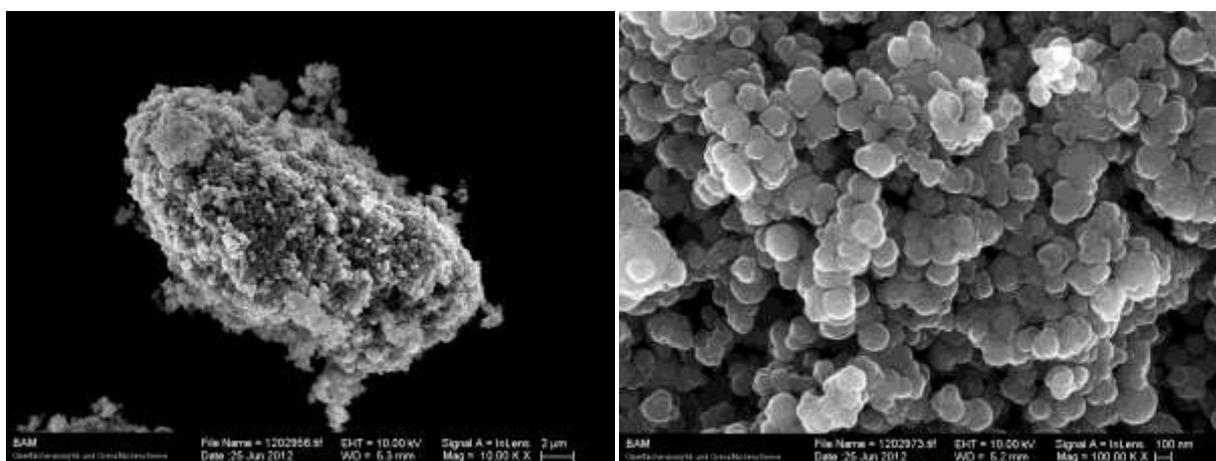


Figure 2. SEM images of nano aluminium at different resolutions.

For a better comparison BET measurements of an aluminium dust, consisting of spherical primary particles with a median diameter of about 4 µm, have been carried out. These measurements with micrometer aluminium resulted in a specific surface area of 1.9981 m²·g⁻¹. On the other hand the tested nano aluminium has an specific surface area of 18.36 m²·g⁻¹. Hence, although the nano particles formed agglomerates within in the micrometer range, these agglomerates have a much higher specific surface area than comparable micrometer particles.

Burning behaviour of tested samples

Results of burning behaviour and pyrophoricity tests are shown in Table 2. For all five tested nano powders a fire spread was observed. Even copper – within micrometer range not known to be flammable – was classified in burning class 4 which represents a glowing without sparks (smoldering) or slow decomposition without flame.

Table 2. Results of burning class and pyrophoricity tests.

Dust sample	Burning class	Description	Pyrophoricity
aluminium (90-110 nm)	5	burning with flame or spark generation	no
zinc (90-150 nm)	4	glowing without sparks (smoldering) or slow decomposition without flame	no
copper (50-70 nm)	4	glowing without sparks (smoldering) or slow decomposition without flame	no
titanium (60-80 nm)	6	very rapid combustion with flame propagation	yes
iron (50-70nm)	5	burning with flame or spark generation	yes

Again titanium has shown the highest reactivity (burning class 6) in a very rapid combustion (less than one second) with flame propagation. Figure 3 furthermore illustrates that the tested nano titanium is very friction sensitive.

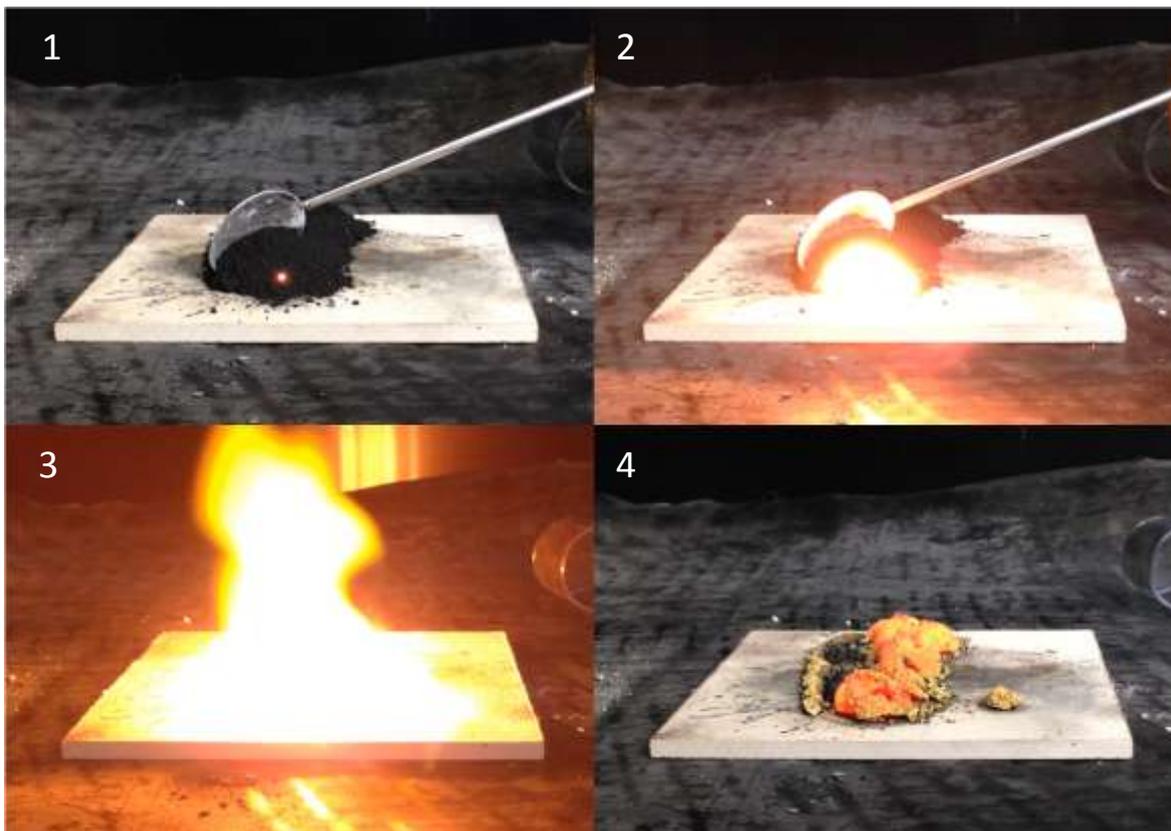


Figure 3. Burning behaviour of nano titanium.

For the burning behaviour tests an infrared camera was additionally installed (centred 1 m above the ceramic sample plate), which was used to record the surface temperatures of the samples. The camera works in a range up to 2000 °C. Highest measured temperatures of titanium and zinc nano powder are illustrated in Figure 4. Therefore combustion of deposited titanium during burning behaviour test reached temperatures of more than 2000 °C. Zinc (right side of Figure 4) on the other hand reached approximately 1150 °C on the surface of the sample. Temperatures inside the samples will be possibly higher.

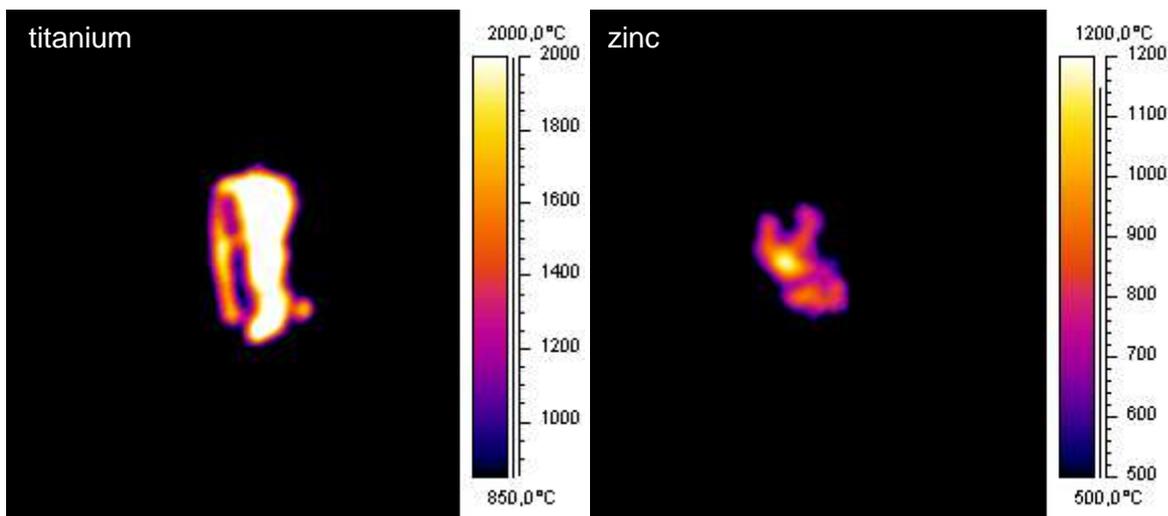


Figure 4. Infrared images of nano titanium (left) and nano zinc (right) during combustion

Also iron and titanium reacted pyrophoric. Pictures of the pyrophoricity test according to the UN test N.2 (United Nations 2009) of iron are shown in Figure 5.

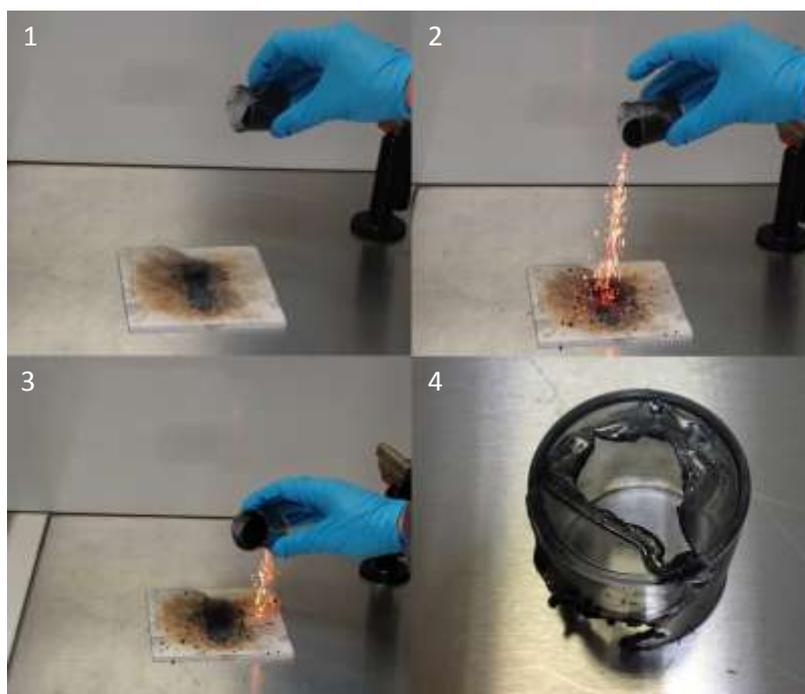


Figure 5. Pyrophoricity test (UN test N.2) of nano iron

Although burning behaviour experiments have shown high reactivity, a partially higher ignition sensitivity and even pyrophoric behaviour of tested samples, this is not only observed for nano powders. Such behaviour is also already known for very fine metallic powders within the lower micrometer range. Only nano copper has shown a for micron copper powders previously unknown behaviour.

Dust explosion experiments

In a next step dust explosion experiments were conducted. Results of experiments with the modified setup of the 20-L sphere are presented in Table 3. Tests with aluminium resulted in a maximum overpressure of 9.7 bar and a K_{St} -value of 490 $\text{bar}\cdot\text{m}\cdot\text{s}^{-1}$. According to the test procedures copper was also determined as being dust explosible. However, obtained values are very small. This might indicate a slow combustion process and thus a pressure rise due to the generated heat.

Table 3. Explosion characteristics of tested dust samples.

Dust sample	p_{\max} [bar]	dp/dt_{\max} [$\text{bar}\cdot\text{s}^{-1}$]	K_{St} [$\text{bar}\cdot\text{m}\cdot\text{s}^{-1}$]	LEL [$\text{g}\cdot\text{m}^{-3}$]
aluminium (90-110 nm)	9.7	1806	490	30
zinc (90-150 nm)	4.3	652	177	125
copper (50-70 nm)	0.3	18	5	250
titanium (60-80 nm)	n.a.	n.a.	n.a.	30
iron (50-70 nm)	n.a.	n.a.	n.a.	60
p_{\max}	maximum explosion overpressure			
dp/dt_{\max}	maximum pressure rise			
K_{St}	dust explosion constant			
LEL	lower explosion limit			

Unfortunately it was not able to determine reliable dust explosion severity characteristics with the tested nano titanium and nano iron. Both dusts ignited spontaneously during injection process into the explosion chamber before ignition itself (both standard test and modified procedures). Therefore results are not listed in the Table. This behaviour and results are already reported by the studies of Boilard et al. (2013) and Mittal (2013) for titanium and magnesium. It is difficult to assess the validity of determined values for iron and titanium because preignition takes place under completely different conditions (lower ambient pressure, for modified methods local oxygen concentrations can be much higher or lower than under ambient conditions, different turbulence level etc.). A pressure time curve of one test with nano iron is shown in Figure 6.

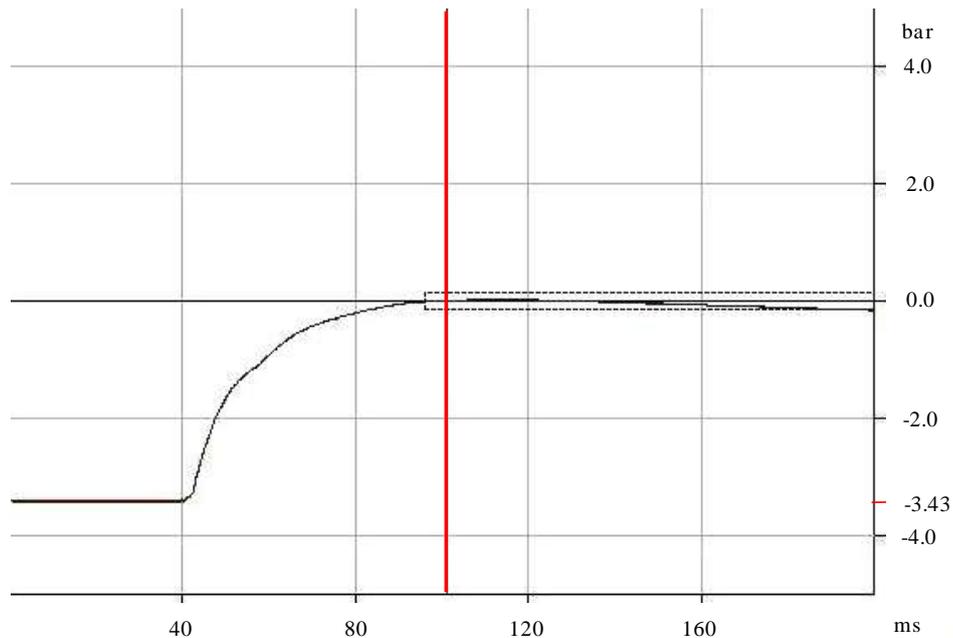


Figure 6. Pressure-time curve of an dust explosion test (preignition) with nano iron

The software of the 20-L sphere automatically assumes ambient pressure conditions (0.0 barg) at trigger time (100 ms), when ignition of the chemical ignitors is triggered by the software (symbolised by the red vertical line). Since the pressure sensors measure the pressure before the software ignition trigger, one can determine the pressure difference which is equal to the overpressure caused by the self ignited explosion. At least such results allow an estimation of the explosion behaviour of a dust to be tested. These results were furthermore used to determine the influence of passivation or exposure to air respectively.

One aim of the study was to investigate the influence of oxidation on explosion behaviour and whether or not short time exposure to air before the test itself leads to lower values. If this were the case, current test procedures would not be applicable to nano powders in general. Results of experiments with nano zinc are illustrated in Figure 7. For the first two test series zinc was handled under nitrogen until shortly before ignition. For series 3 (red squares) and series 4 (blue squares) the samples were exposed to air for 15 min and 30 min respectively. After 15 min exposure to air values do not decrease significantly. Moreover values seem to be even a touch higher after being exposed to air. Values of series 4 confirm this tendency.

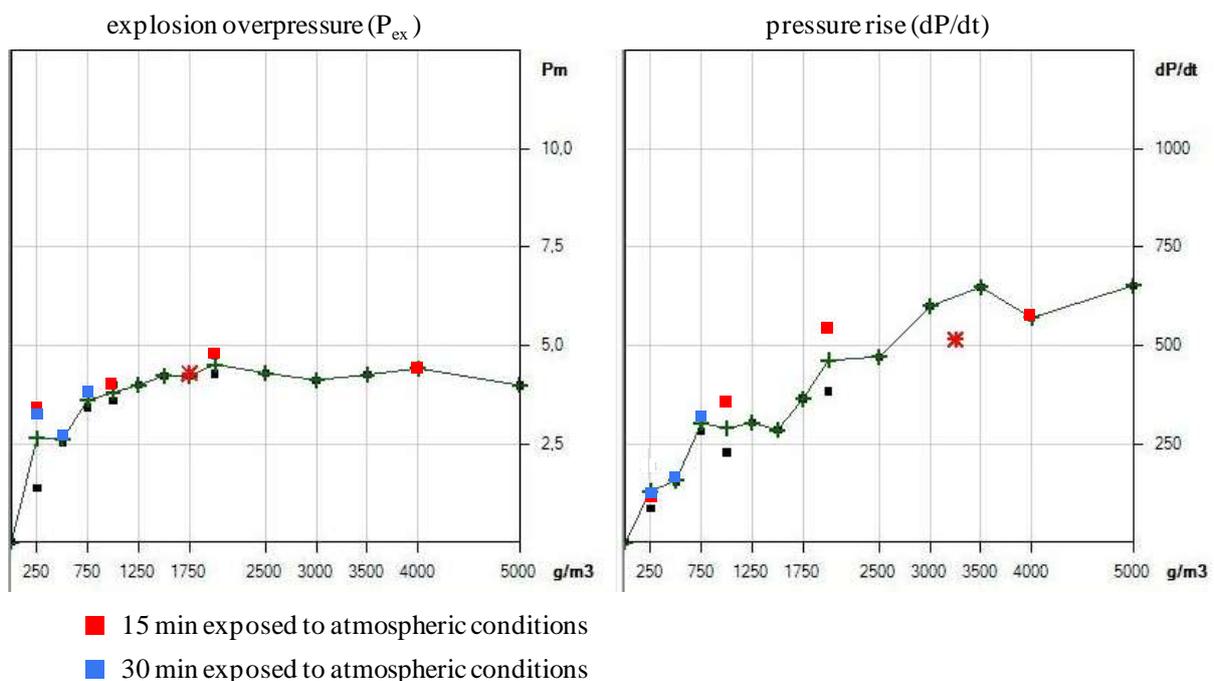


Figure 7. Explosion pressure and pressure rise of nano zinc depending on exposure to air

All efforts have been taken to determine the most critical behaviour of nano powders to be tested. However, dust explosion experiments also did not reveal a significantly higher explosion severity in comparison to most critical dusts within the micron range. On the other hand ignition sensitivity increases with decreasing particle size.

STA-measurements

In addition to dust explosion testing STA measurements were conducted in order to determine the thermal decomposition and the reactivity behaviour of the tested powders. Figure 8 illustrates STA tests (TG on the left and DSC on the right side) with varying initial weight from 13.07 mg (yellow) up to 123.05 mg (black). Based on the TG results on the left side of Figure 8 it can be seen that the mass increase of all experiments are relatively similar. At temperatures above 800 °C tests with much higher initial weight (test 1 and test 4) seem to scatter less. The evaluation of the DSC data (right side of Figure 8) shows that reactivity behaviour changes with increasing initial weight.

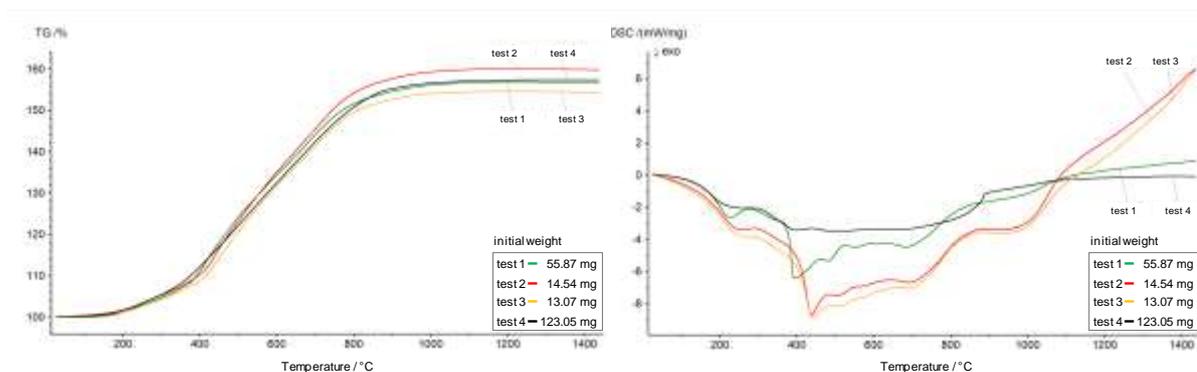


Figure 8. STA measurements of nano titanium with varying initial weight

The comparison of a fresh sample (test 2) and a sample that has been exposed to air for several days (test 5) is illustrated in Figure 9. It is apparent from the TG curves (left side) that the mass increase for test 5 at temperatures below 200 °C is different and mass is nearly constant. This indicates that the sample has already reacted with oxygen at ambient conditions. But this does not seem to greatly affect the reactivity of the tested titanium, because both DSC curves (right side) are rather comparable.

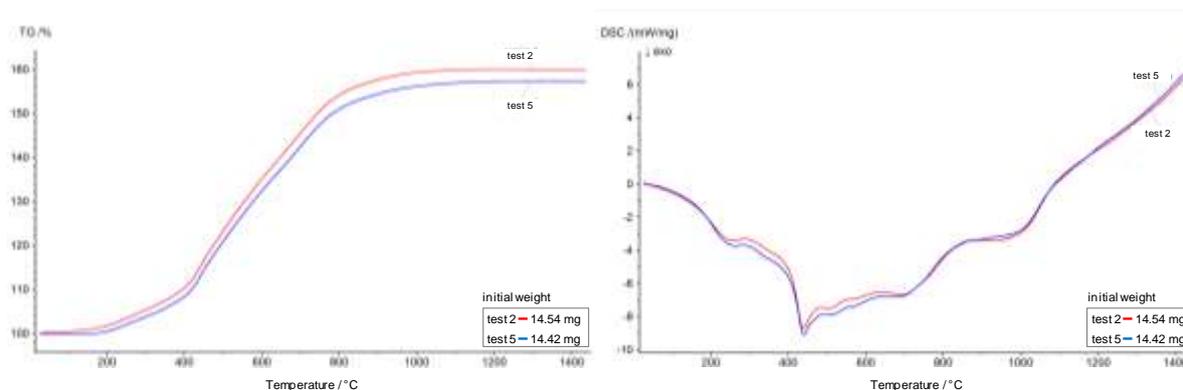


Figure 9. STA measurements of "fresh" nano titanium and a sample exposed to air

Thus the results of the STA measurements with nano titanium confirm the results of burning behaviour and explosion tests. Observations made with titanium cannot be applied to all investigated nano powders. DSC curves of STA measurements with nano iron are illustrated in Figure 10. For tests 1 and 2 fresh samples have been taken. For test 3 the nano iron sample was exposed to air for 30 min and for test 4 even several days. It can be seen that with increasing time being exposed to air, reactivity of the sample decreases. Both at higher temperatures and lower temperatures (zoom on right side of Figure 10).

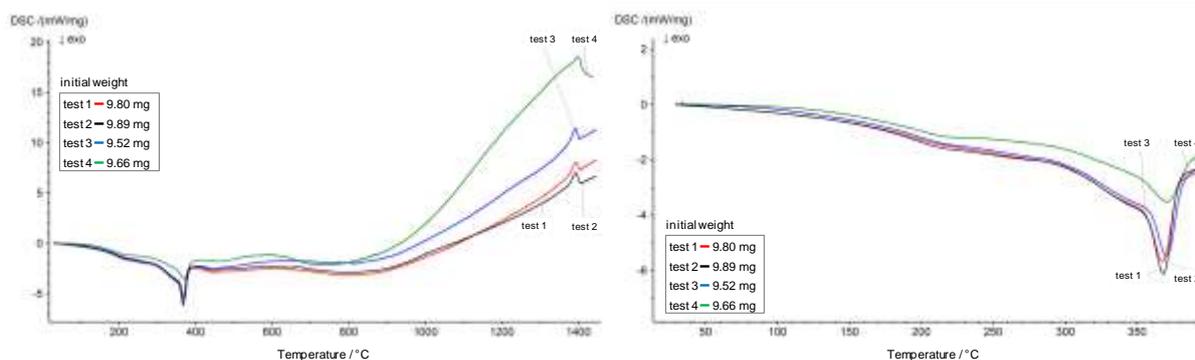


Figure 10. DSC-records of STA tests with nano iron

Conclusions

Aim of this study was to determine most critical burning and explosion behaviour of nano powders to be tested. Therefore all measures have been taken to avoid oxygen contact before ignition and the test itself. Results have shown that nano powders do not generally react completely different and do not possess a more critical burning behaviour or explosion severity than dusts in the lower micron range. But copper for instance becomes flammable with nanometer particle sizes.

Moreover, experiments have highlighted the influence of passivation on the burning and explosion behaviour of metallic nano powders. Contact with oxygen for several minutes does not decrease explosion severity and ignition sensitivity significantly. This means that the standard test methods for the determination of reliable safety characteristics of nano powders appear suitable at least down to the particle sizes that were tested. A longer exposure to air may though in accordance to the material to be tested decrease the reactivity of the sample, especially for even smaller particle sizes. Therefore it is highly recommended to handle nano powders under inert conditions until shortly before the test.

With decreasing particle size especially unpassivated nano powders can react very ignition sensitive. For even smaller particle sizes far below 50 nm further materials may possibly react pyrophoric. The determination of explosion severity of pyrophoric dusts according to the standardised methods is not possible yet. Current modified methods if at all only allow an estimation of the explosion behaviour of pyrophoric powders.

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References

- ASTM E1226 - 10, (2010). Standard Test Method for Explosibility of Dust Clouds. ASTM International.
- Boilard, P.S., Amyotte P.R., Khan, F.I., Dastidar, A.G. and Eckhoff, R.K. (2013). Explosibility of micron and nano-size titanium powders. *Journal of Loss Prevention in the Process Industries*.
- Bouillard, J., A. Vignes, O. Dufaud, L. Perrin and D. Thomas, (2010). Ignition and explosion risks of nanopowders. *Journal of Hazardous Materials* 181 2010: 873 - 880.
- Eckhoff, R. K. (2012). Does the dust explosion risk increase when moving from μm -particle powders to powders of nm-particles? *Journal of Loss Prevention in the Process Industries* 25 (2012): 448-459.
- EN 14034-1, (2004+A1:2011). Determination of explosion characteristics of dust clouds - Part 1: Determination of the maximum explosion pressure p_{max} of dust clouds. European Committee for Standardisation (CEN).
- EN 14034-2, (2006+A1:2011). Determination of explosion characteristics of dust clouds - Part 2: Determination of the maximum rate of explosion pressure rise $(dp/dt)_{\text{max}}$ of dust clouds. European Committee for Standardisation (CEN).
- EN 14034-3, (2006+A1:2011). Determination of explosion characteristics of dust clouds - Part 3: Determination of the lower explosion limit LEL of dust clouds. European Committee for Standardisation (CEN).
- EN 14034-4, (2004+A1:2011). Determination of explosion characteristics of dust clouds - Part 4: Determination of the limiting oxygen concentration LOC of dust clouds. European Committee for Standardisation (CEN).
- Holbrow, P., M. Wall, E. Sanderson, D. Bennett, W. Rattigan, R. Bettis and D. Gregory, 2010, Fire and explosion properties of nanopowders. prepared by the Health and Safety Laboratory for the Health and Safety Executive (HSE) 2010.
- Krietsch, A., Gothe, C., Scheid, M., Krause, U. (2013). Determination of explosion behaviour of nano powders with modified 20-L sphere test. *Proceedings of 7th International seminar on fire & explosion hazards (ISFEH7)*
- Mittal, M., (2013). Explosion characteristics of micron and nano-size magnesium powders. *Journal of Loss Prevention in the Process Industries* (2013), doi:10.1016/j.jlp.2013.11.001.

United Nations (2009). Recommendations on the transport of dangerous goods - Manual of test and criteria (fifth revised edition). United Nations New York and Geneva, 2009

VDI 2263-1, 1990, Dust Fires and Dust Explosions; Hazards - Assessment - Protective Measures; test methods for the Determination of the Safety Characteristics of Dusts. VDI - Verein Deutscher Ingenieure.

Vignes, A., F. Munoz, J. Bouillard, O. Dufaud, L. Perrin, A. Laurent and D. Thomas (2010). Risk assessment of the ignitability and explosivity of aluminum nanopowders. 13th International Symposium on Loss Prevention 2010. Bruges.

Wu, H.-C., Y.-C. Kuo, Y.-H. Wang, C.-W. Wu and H.-C. Hsiao (2010). Study on safe air transporting velocity of nanograde aluminum, iron and titanium. Journal of Loss Prevention in the Process Industries 23 (2010): 308-311.