Explosibility of Nano-Sized Metal Powders

Ashok Ghose Dastidar
Fauske and Associates LLC
16W070 83rd Street, Burr Ridge, Illinois, USA 60527
Dastidar@fauske.com

Simon Boilard
Dalhousie University, Halifax, Nova Scotia, Canada
sm416955@dal.ca
Paul R. Amyotte
Dalhousie University, Halifax, Nova Scotia, Canada
Paul.Amyotte@dal.ca

Leonid A. Turkevich
Division of Applied Research and Technology, NIOSH/CDC, Cincinnati, Ohio, USA 45226
LLT0@cdc.gov

Prepared for Presentation at
American Institute of Chemical Engineers
2013 Spring Meeting
9th Global Congress on Process Safety
San Antonio, Texas
April 28 – May 1, 2013

UNPUBLISHED

Explosibility of Nano-Sized Metal Powders

Ashok Ghose Dastidar
Fauske and Associates LLC
16W070 83rd Street, Burr Ridge, Illinois, USA 60527
Dastidar@fauske.com

Simon Boilard
Dalhousie University, Halifax, Nova Scotia, Canada
sm416955@dal.ca

Paul R. Amyotte
Dalhousie University, Halifax, Nova Scotia, Canada
Paul.Amyotte@dal.ca

Leonid Turkevich
Engineering and Physical Hazards Branch - Division of Applied Research and Technology,
NIOSH-CDC, Cincinnati, Ohio, USA
llt0@cdc.gov

Keywords: dust explosions, nano-materials, metal powders

Abstract

The explosibility of micron- and nano-titanium was determined and compared according to explosion severity and likelihood using standard dust explosion equipment. ASTM methods were followed using commercially available testing equipment. The explosibility parameters investigated for the size ranges of titanium tested include explosion severity (maximum explosion pressure (P_{max}) and size-normalized maximum rate of pressure rise (K_{St})) and explosion likelihood (minimum explosible concentration (MEC), minimum ignition energy (MIE) and minimum ignition temperature (MIT)). The results indicate a significant increase in explosion severity as the particle size decreases from <150μm with an apparent plateau being reached at <45μm and ≤20 μm. Micron-size explosion severity could not be compared with that for nano-titanium due to pre-ignition of the nano-powder in the 20-L chamber. Explosibility screening tests were also performed on other nano-sized metal powders and similar results were observed for some materials.

The likelihood of an explosion increases significantly as the particle size decreases into the nano range. Nano-titanium is very sensitive and can self-ignite under the appropriate conditions. A similar phenomenon was observed for some of the other nano-metals. Safety precautions and procedures for the nano-metal handling are also discussed.

The findings and conclusions in this paper are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health. Mention of product or company name does not constitute endorsement by the Centers for Disease Control and Prevention.

1. Introduction

Industrial accidents in the metal processing industries are not uncommon. Some of these accidents are in the form of dust explosions or flash fires. Two of the most cited incidents in North America for combustible metal dust explosions/flash-fires have been the Hayes Lemmerz accident in Huntington, Indiana in 2003 and, more recently, the Hoeganaes Corporation flash-fire in Gallatin Tennessee in 2011. It is important to note that combustible metals can be just as energetic and hazardous as organic fuels, and in some cases like aluminum, magnesium, titanium and zirconium even more energetic.

Dust explosions have been well documented for particles falling in the micron-range for different types of metals [1]. As the size is further decreased into the nano-range, new physical and chemical properties can occur changing the severity and likelihood of a dust explosion.

Interest in the production of nano-scale metal powders has developed in recent years. At the nano-scale, typically between 1 and 100 nm, properties of well-known substances change and they may exhibit unique physical and chemical changes. The bulk properties of the metal no longer hold and the surface properties of the material take precedence. As an example, bulk titanium and zinc are solid, opaque metals. However, at the nano-scale, the surface properties allow the metals to become transparent [2]. The small size of the nano-particles increases the reactive surface area within a bulk sample. This allows for the different physical and chemical properties of nano-particles. These properties are highly desirable for technological advancements but also come at a cost, with an increased explosion potential.

Dust explosion research involving nano-materials has been limited, but some research groups have performed tests with various materials to better understand the properties of nano-size powders. Holbrow et al. [3], with the UK Health and Safety Executive, performed dust explosion tests in a specially designed 2-L explosion chamber with different types of nano-materials including metals (aluminum, zinc, copper and iron). Explosions at a larger test scale using a 20-L sphere were also investigated by Vignes et al. [4] on carbon black, multi-walled carbon nanotubes and aluminum.

Using the nano-aluminum (100 nm and 200 nm) results from Vignes et al. [4], Dufaud et al. [5] compared the nano-aluminum to micron-size aluminum. The results for maximum explosion pressure, P_{max}, and maximum rate of pressure rise, $(dP/dt)_{max}$, for 100 nm samples were 8.2 barg and 1340 bar/s while the P_{max} and $(dP/dt)_{max}$ for 200 nm sample was 9.5 barg and 2480 bar/s. At the micron-scale, 3 μm and 7 μm aluminum gave a P_{max} of 9.8 barg and 9.1 barg and $(dP/dt)_{max}$ of 2090 bar/s and 1460 bar/s, respectively. Explosion severity in this case was limited by the size of the particles with the peak occurring around 1 μm [5].

Likewise, Wu et al. [6] performed nano-dust explosions with aluminum. Samples with an average particle size of 35 nm generated a P_{max} and $(dP/dt)_{max}$ value of 7.3 barg and 1286 bar/s. Samples having an average particle size of 100 nm, resulted in a P_{max} of 12.5 barg, and $(dP/dt)_{max}$ of 1090 bar/s, respectively. These results can be compared to larger micron-aluminum powder data obtained from Eckhoff [7]. For a mean particle size of 22 μm, P_{max} was 12.5 barg and $(dP/dt)_{max}$ was 1474 bar/s [7].

Wu et al. [8] tested the minimum ignition energy (MIE) of micron- and nano-titanium. As the particle size was decreased from 45 µm to 3 µm, the MIE dropped from 21.9 mJ to less than 1 mJ. For three nano-titanium sizes (35 nm, 75 nm and 100 nm), the MIE was lower than 1 mJ [8]. Nano-aluminum and carbon nanotubes also have similarly low MIE values.

These observations of the explosion hazard risk of micron and sub-micron sized metal powders have grave safety implications. The National Fire Protection Agency (NFPA) 484 document [9] is an occupancy standard which covers the mitigation of combustible metal dust explosion and fire hazards. While this document covers the unique hazards associated metal fine dusts and powders, it does not address the risks of metal dust combustibility at the nano-scales. Part of the reasoning for this may be due to the limited amount of experimental data in this field.

The current work is aimed at initiating an investigation into the explosion behavior of combustible metals by studying the explosion severity and likelihood of several nano-scale metal dusts and comparing the results to micron-scale combustibility data. Several metal powders including titanium, aluminum, chromium and copper were studied. The presentation here of the detailed titanium explosibility results and experimental challenges is drawn from Boilard et al. [10] and Amyotte et al. [11], with relevant excerpts.

2. MATERIALS

Various nano-metals were chosen for this study. Table 1 contains a list of the nano-metals on which dust cloud combustibility screening tests were conducted as per Section 13 of ASTM E1226 [12]. Detailed particle size analyses of the metals were not performed due to lack of sample availability. The manufacturer's specification was used for the particle size description.

Table 1 Nano-metals used for dust cloud combustibility screening tests.

Material Name	Manufacturer Reported Mean Particle Size [nm]
Tantalum Nanopowder	50-80
Chromium Nanopowder	35-45
Tungsten Nanopowder	40-60
Zinc Nanopowder	35-45
Molybdenum Nanopowder	45
Aluminum Nanoparticles 99.9% 40-60nm	40-60
Iron Nanoparticles 99.9% 40-60nm	40-60
Titanium Nanoparticles	40-60
Nickel Nanoparticles	40-60
Tin Nanoparticles	< 100
Copper Nanoparticles	25
Aluminum Nanoparticles 99.9%, 18nm	18
Cobalt Nanoparticles	25-30
Iron Nanoparticles 99.9% 25nm	60-80
Silicon Nanopowder	50-80
Iron Nanopowder – Carbon Coated	25
Nano Manganese	30-50

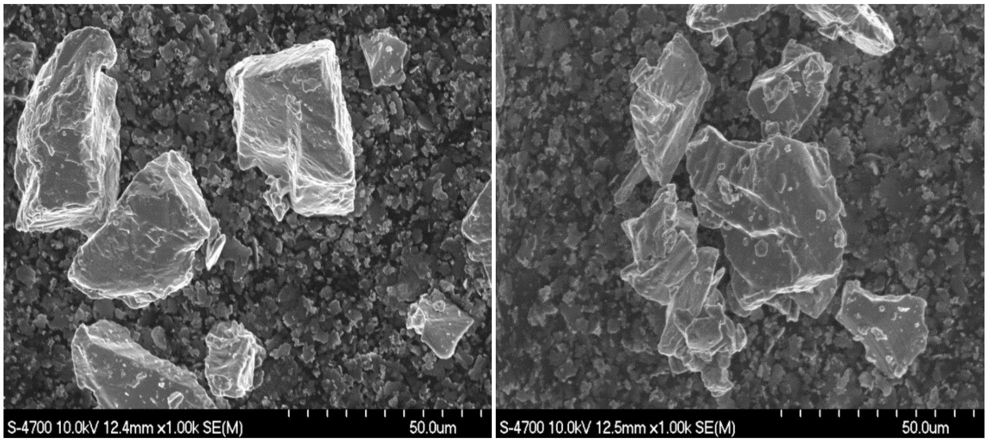
Nano-titanium was singled out for examination due to its reactivity and the availability of existing data for dust explosibility at the micron-scale. Six sample sizes were selected: <150 µm, <45 µm, ≤20 µm, 150 nm, 60-80 nm, and 40-60 nm.

Particle size distributions were determined to characterize the micron-size titanium. The powder manufacturer's literature states that the two smaller micron-titanium samples are nominally ≤20 µm and <45 µm – but are sized using different methodologies; a single-point BET surface area analysis is used to determine the size of the ≤20 µm titanium while a sieve analysis is used to analyze the <45 µm titanium. According to the manufacturer, the BET surface area analysis measures the average unagglomerated particle size. However, traditional sieve analysis measures what is essentially the particle size distribution of agglomerated particles. This can be seen in the sieve analyses performed in the current work and shown in Table 2. Particle sizes of the nano-titanium were taken to be as reported by the manufacturer and no further size analysis was performed.

Table 2 Sieve analysis of micron-size titanium powders.

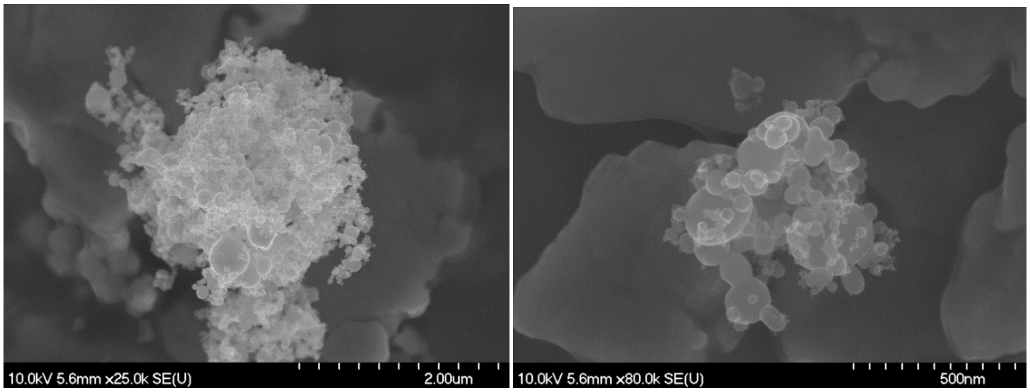
		Wt. % Retained		
Sieve Size	**Micron Size**	**≤20 µm**	**<45 µm**	**<150 µm**
+325	>45 µm	0.98	0.00	91.88
-325+400	45-38 µm	10.55	6.45	5.06
-400+450	38-32 µm	5.96	4.50	0.38
-450+500	32-25 µm	23.54	23.03	1.72
-500	<25 µm	58.98	66.02	0.96

A scanning electron micrograph (SEM) of the ≤20 µm titanium sample is shown in Figure 1. Individual particles of this titanium are not spherical but have a granular shape. Agglomerates occur for this sample, as illustrated in Figure 1b. Two types of agglomerates are present; larger titanium particles are covered by smaller titanium "bits", and medium-sized particles are joined to form a larger particle. Figure 2 shows the 150 nm sample. While the individual particles are of course much smaller, agglomerates are still clearly present. The nano-agglomerates varied in composition between approximately 50 particles and thousands of particles.



a **b**

Figure 1 Scanning electron micrograph of ≤20 µm titanium powder.



a b

Figure 2 Scanning electron micrograph of 150 nm titanium powder.

3. EQUIPMENT AND METHODOLOGY

The explosibility parameters investigated for the nano- and micron-size ranges of metal powders include dust cloud combustibility, maximum explosion pressure (P_{max}), size-normalized maximum rate of pressure rise (K_{St}), minimum explosible concentration (MEC), minimum ignition energy (MIE), and minimum ignition temperature (MIT). American Society for Testing and Materials International (ASTM) methods were followed using standard dust explosibility test equipment: Siwek 20-L explosion chamber, MIKE 3 apparatus and BAM oven. The applicable ASTM methods are ASTM E1226 [12], E1515 [13], E2019 [14], and E1491 [15], respectively.

Figure 3 shows a picture of the Siwek 20-L chamber with its corresponding components. The Siwek chamber was used to determine the dust cloud combustibility of the nano-metals listed in Table 1. These tests were conducted to establish a preliminary baseline on nano-metal dust explosibility from which a ranking, or prioritization, scheme could be established for further detailed study. The apparatus was operated with the standard dispersion methodology listed in the manufacturer's manual using air.

However, nitrogen was used in place of air as the dust dispersion medium for the detailed nano-titanium explosion severity testing. This was done to prevent pre-ignition of the powder in the dust storage chamber as observed by Wu et al. [6]. A lower-than-usual vacuum was therefore created in the 20-L chamber and oxygen was backfilled to create an elevated oxygen atmosphere (prior to dust dispersion). Once the dispersing nitrogen and the elevated oxygen level mixed, atmospheric conditions would be achieved with 79% nitrogen and 21% oxygen. CaRo11 (Kühner) dust was tested using this method to establish the procedural validity. The results from nitrogen dispersion and air dispersion were well-correlated. Therefore, all nano-titanium tests for explosion severity (P_{max} and $(dP/dt)_{max}$) were performed with nitrogen dispersal.

Figure 3 Siwek 20-L chamber.

4. RESULTS AND DISCUSSION

4.1 Dust Cloud Combustibility Screening Tests

Dust cloud combustibility screening tests were conducted per Section 13 of ASTM E1226 [12] for the metal nano-powders listed in Table 1. These screening tests were performed with the standard air dispersion methodology. The concentration of material tested and the subsequent explosion overpressure are reported in Table 3

Table 3 Dust Cloud Combustibility Screening Test Results

Material Name	Powder Concentration Tested [g/m^3]	Explosion Overpressure P_m [barg]
Tantalum Nanopowder	500	2.7
Chromium Nanopowder	500	Ignited on dispersion
Tungsten Nanopowder	500	0
	1000	0
Zinc Nanopowder	500	2.1
Molybdenum Nanopowder	500	0.8
	1000	4.0
Aluminum Nanoparticles 99.9% 40-60nm	500	5.1
Iron Nanoparticles 99.9% 40-60nm	500	2.1
Titanium Nanoparticles	500	Ignited on dispersion
	1000	Ignited on dispersion
Nickel Nanoparticles*	500	0.4
	1000	0.7**
Tin Nanoparticles	500	0.9
	1000	1.2
Copper Nanoparticles	Sample autoignited on removing from container	
Aluminum Nanoparticles 99.9%, 18nm	500	2.1
Cobalt Nanoparticles	500	0.0
	1000	0.0
	2500	0.8**

Table 3 Dust Cloud Combustibility Screening Test Results continued.

Material Name	Powder Concentration Tested [g/m^3]	Explosion Overpressure P_m [barg]
Iron Nanoparticles 99.9% 25nm	500	0.0
	1000	0.9
	2500	1.3
Silicon Nanopowder	500	5.5
Iron Nanopowder – Carbon Coated	500	2.5
Nano Manganese	500	0.8
	1000	1.2

* sample started to get warm on exposure to air – no fire

** may be approaching combustibility at higher concentrations.

These preliminary explosibility screening test results indicate that not all nano-metals are explosible even though the metals do form oxides. The move from micron-scale to nano-scale did not make them explosible. Other nano-metals that do explode (i.e. aluminum, tantalum, tin etc) produce explosion overpressures comparable to micron-scale metal particles. It should be noted that only limited concentrations of these metals were tested and a full comparison of overpressures between nano-scale and micron-scale can only be accomplished with detailed explosion severity testing.

Of greater importance is that some nano-scale metals have highly increased ignition sensitivities; so much so that metals reacted on dispersion (e.g. titanium and chromium) or reacted on first exposure to air (e.g. copper and nickel). Any further study into nano-metal explosibility should focus on these materials. In the next sections we discuss a more detailed study into the explosion severity and ignition sensitivity of nano-titanium.

4.2 Explosion Severity

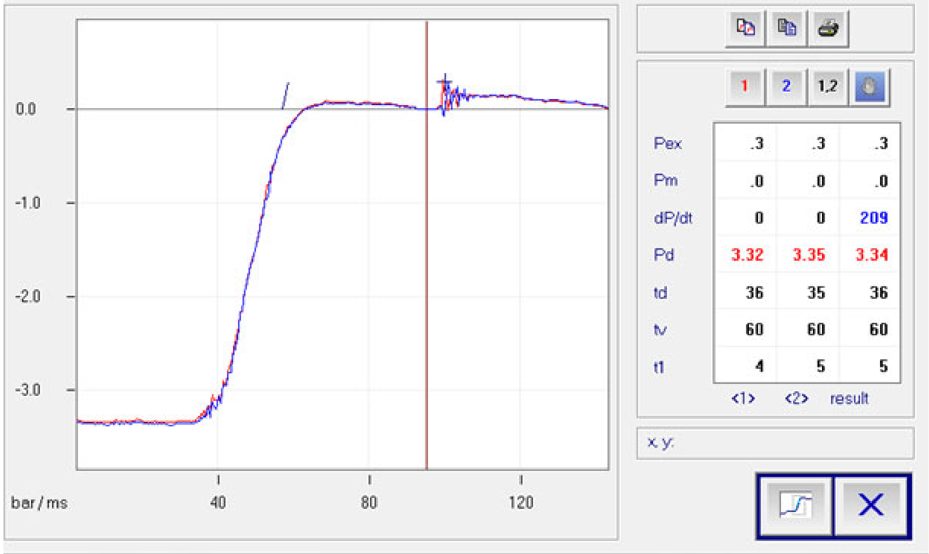
The explosion severity of the micron-size titanium samples can be seen in Table 4. P_{max} and K_{St} both increase significantly (40% and 400% increases, respectively) with decreasing size from <150 µm to <45 µm. As the particle size is further decreased to ≤20 µm, P_{max} decreases by approximately 10% and K_{St} remains essentially constant. The micron-size data therefore show the expected increase in P_{max} and K_{St} with decreasing particle size, but to a limit that may be imposed by particle agglomeration.

Table 4 Explosion severity of micron-size titanium powders.

Sample	P_{max} [bar(g)]	$(dP/dt)_{max}$ [bar/s]	K_{St} [bar·m/s]
<150 µm	5.5	84	23
<45 µm	7.7	436	118
≤20 µm	6.9	420	114

It is difficult to make a direct comparison of explosion severity between the micron- and nano-titanium due to pre-ignition of the nano-dust. Frictional or static sparking during the dispersal sequence ignited the dust before the chemical igniters were fired. (Dust ignition in the Siwek 20-L chamber is normally accomplished via one or more chemical igniters activated at a preset ignition delay time.) As previously described, nitrogen was used as the dispersing gas to prevent an explosion in the external dispersion reservoir. However, when the nano-titanium/nitrogen mixture encountered the elevated oxygen concentration in the 20-L chamber, immediate ignition occurred.

Consistent with the above discussion, Figure 4 shows a 40-60 nm titanium explosion at a dust concentration of 100 g/m^3. Here one sees an overlap of the dust dispersion and explosion steps, with the igniters firing after the dust has exploded. The pressure values in Figure 4 must be interpreted in light of the fact that the pressure transducers used are piezoelectric and hence measure only dynamic pressure changes, not static values.



	<1>	<2>	result
Pex	.3	.3	.3
Pm	.0	.0	.0
dP/dt	0	0	209
Pd	3.32	3.35	3.34
td	36	35	36
tv	60	60	60
t1	4	5	5

Figure 4 Sample pre-ignition pressure/time trace for nano-titanium.

The pre-ignition of the nano-titanium causes all the dust to be consumed and effectively prevents a typical evaluation of the maximum explosion pressure. The maximum rate of pressure rise can be estimated by a manual evaluation of the pressure/time trace. The explosion is very violent and causes complete combustion – again, even before the chemical igniters are activated.

All subsequent trials of this type involving nano-titanium were performed without igniters; results similar to those shown in Figure 4 were obtained. Because of the pre-ignition phenomenon, typical P_{max}/K_{St} testing was simply not possible with these materials. Therefore, estimates of the maximum explosion pressure and maximum rate of pressure rise were obtained from the pre-ignition phase of the pressure/time trace (the region to the left of the vertical line at 96 ms in Figure 4). It is particularly noteworthy that these explosibility parameters arise from an explosion scenario *with no external ignition source* (i.e., no chemical igniters as per typical Siwek 20-L chamber testing).

Figure 5 gives the maximum rate of pressure rise data acquired to date. For all nano-sizes, a quasi-plateau in the rate of pressure rise occurred at low concentrations. At approximately 125 g/m^3, the maximum rate of pressure rise for all three nano sizes was between 550 – 650 bar/s. It is important to note here that the rate of pressure rise data cannot be directly compared with K_{St} levels determined by international standards since the explosion is occurring in a more highly turbulent flow field as the powder jets into the test chamber from the reservoir. In the case of the

150 nm titanium, the rate of pressure rise displayed a decrease at concentrations higher than 500 g/m^3. Micron-size titanium did not reach its maximum rate of pressure rise until concentrations in the vicinity of 1500 g/m^3.

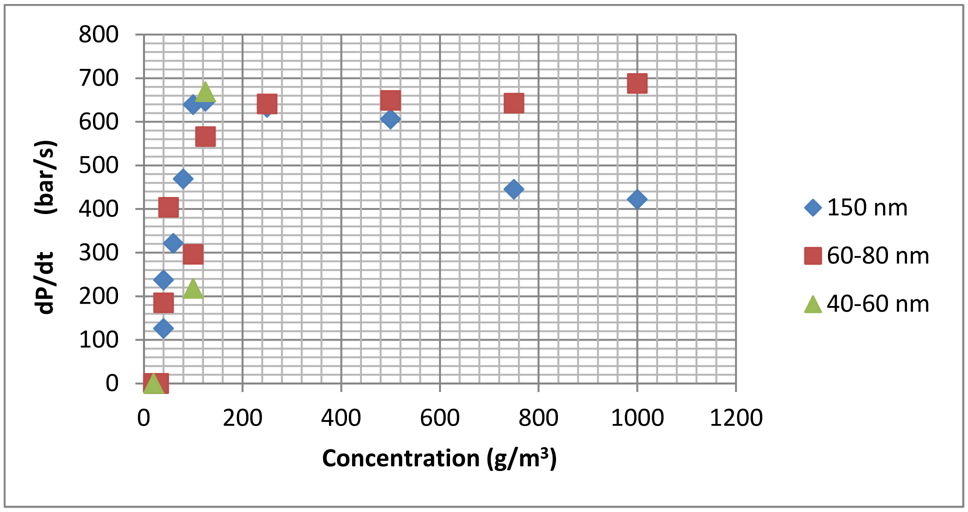


Figure 5 Maximum rate of pressure rise for nano-titanium dusts.

Surface area clearly plays a major role in the combustion of the different sizes of titanium studied in the current work. At the micron-scale, larger amounts of dust are needed to achieve the same effective surface area as with a smaller mass of nano-titanium. For complete combustion of all the oxygen in the 20-L chamber, high concentrations of micron-size titanium are needed. To react with the same amount of oxygen, much lower amounts of nano-titanium are required. There is thus a high reactivity at very low concentrations for nano-size titanium.

Maximum explosion pressure can be estimated for the nano-titanium samples via the P_d value given by the 20-L chamber control software. In the usual 20-L procedure, the chamber is partially evacuated to 0.4 bar(a) so the resulting chamber pressure upon dust dispersion and at the time of ignition (chemical igniter firing) is approximately 1 bara. The parameter P_d in the Kühner software reports the rise in pressure in the 20-L chamber due to dust dispersion. Acceptable values of P_d are in the range of 0.55 – 0.7 bar, meaning that when the value of P_d is added to the initial chamber pressure of 0.4 bar, the sum is approximately 1 bar.

Recalling that the piezoelectric pressure transducers measure only dynamic pressure changes (i.e., not static pressures), P_d values as shown in the pressure-time trace in Figure 4 are a combination of the pressure rise due to dust dispersion *and* the actual explosion itself occuring at sub-atmospheric pressures. The nano-size P_d results are therefore not directly comparable to the micon-size P_{max} results. They are, however, self-consistent as a data set as shown in Figure 6. Similar to the case for rate of pressure rise shown in Figure 5, nano-titanium reaches its highest values of "maximum explosion pressure" at lower concentrations than the micron-titanium, which again required dust concentrations around 1500 g/m^3.

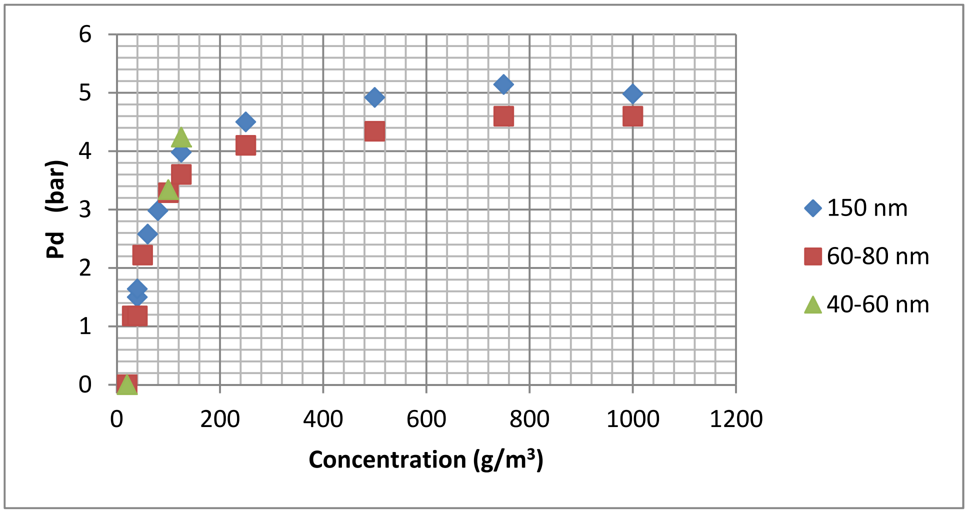


Figure 6 P_d values ("maximum explosion pressure") for nano-titanium dusts.

In these preliminary stages of studying explosion severity of nano-sized metals is appears that the explosion output is very similar between nano-sized and very small micron-sized metal powders, however the concentrations at which these maxima are reached are much lower. For the purposes of hazard mitigation where explosion protection schemes are devised for the worst-case explosion severity independent of fuel concentration, these results for nano-titanium may indicate that protection for small micron-size metals can be used for nano-sized metals as well.

4.3 Explosion Likelihood

The explosion likelihood of a dust can be assessed by measurement of three parameters: minimum ignition energy (MIE), minimum ignition temperature (MIT) and minimum explosible concentration (MEC). Results from the work reported here are given in Table 5.

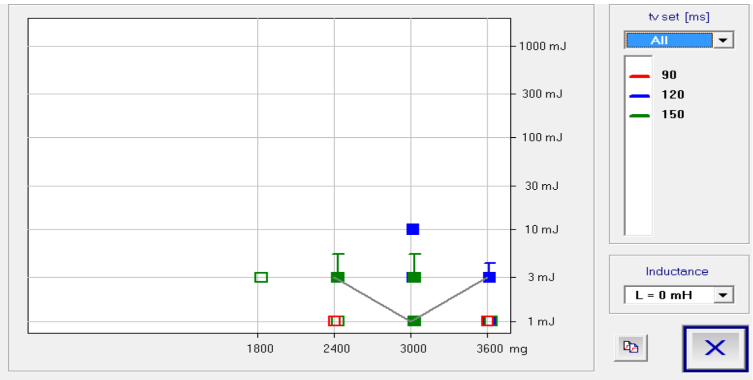
Table 5 Explosion likelihood of titanium powders.

Sample	MIE [mJ] (no inductance)	MIT [°C]	MEC [g/m^3]
<150 µm	1 – 3	>590	60
<45 µm	1 – 3	460	60
≤20 µm	<1	460	50
150 nm	<1	250	30 –40
60-80 nm	<1	240	Not determined yet
40-60 nm	<1	250	Not determined yet

Micron-size titanium has been previously shown to be ignitable at very low spark energies. Randeberg and Eckhoff [16] demonstrated that 3 µm and 9 µm titanium can ignite at energies as low as 0.012 mJ and 0.36 mJ, respectively. Low MIE values for titanium were also measured in the current work as shown in Table 5 (1 mJ being the lowest spark energy attainable with the MIKE 3 apparatus).

There is, however, a fundamental difference between the MIEs of the micron- and nano-size samples. As shown in Figure 7 for the ≤20 µm sample, ignition at 1 mJ occurred only at a high dust loading of 3000 mg. Figure 8, a MIKE 3 ignition graph for the 150 nm titanium, illustrates the significantly lower dust loadings are ignitable at 1 mJ (as low as 100 mg). Note that in Figures 7 and 8, dust quantity appears on the abscissa and spark energy on the ordinate; the open boxes indicate no ignition at the particular delay time and the solid boxes indicate ignition.

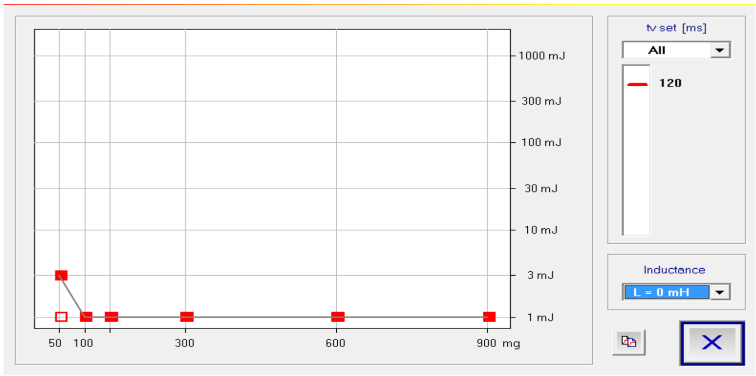
MIE tests with dust loadings greater than 900 mg were not attempted for the nano-titanium samples due to the risk of damage to glass components of the MIKE 3 apparatus and operator safety concerns.



tv set [ms] All

Inductance L = 0 mH

Figure 7 MIE data (no inductance) for ≤20 µm titanium.



tv set [ms] All

Inductance L = 0 mH

Figure 8 MIE data (no inductance) for 150 nm titanium.

A significant increase in explosion likelihood occurs as MIT decreases with decreasing particle size (Table 5). Large <150 µm particles could not be ignited in the BAM oven at 590 ºC (which is the highest temperature attainable with our apparatus). Smaller micron-size particles at <45 µm and ≤20 µm ignited at a lower oven temperature of 460 ºC. The minimum ignition temperature of the nano-titanium (all sizes) was in the range of 240 – 250 ºC. These temperatures are obviously much lower than those required to ignite the micron-titanium, thus clearly demonstrating the enhanced potential for nano-titanium ignition by hot surfaces. This observed trend is also indicated from tests reported in Table 2, some nano-metals become pyrophoric and autoignite at room temperature once exposed to air (see copper and nickel).

It was in fact difficult to determine the minimum ignition temperature of the nano-sizes due to the nature of the powder. Titanium ignition produces flames that are very bright and fast, and test temperatures exceeding 350 ºC would cause the nano-titanium to flash-off rapidly. In these tests, a ‘hissing’ sound could be heard as the powder entered the BAM oven upon dispersal. Visual observation of flames exiting the oven was more readily accomplished at temperatures below 300 ºC.

While MEC determination for the micron-size samples in the Siwek 20-L chamber was relatively straightforward, the nano-size samples again posed an experimental challenge – this time due to the previously described pre-ignition of the powder during the dispersion sequence. With the 150 nm titanium, pre-ignition did not occur at low concentrations of 20 and 30 g/m^3; these concentrations could therefore be tested with nitrogen dispersion and the chemical igniter (5 kJ) in place. No explosions in the 20-L chamber were recorded at these conditions, meaning that the MEC of the 150 nm sample is greater than 30 g/m^3.

With a dust concentration of 40 g/m^3, and again nitrogen dispersion and a 5-kJ igniter in place, pre-ignition occured as evidenced by a P_d value of 1.64 bar. Given that approximately 0.6 bar of the P_d value would normally be associated with dust dispersal, and a 1 bar overpressure is the accepted explosion criterion for MEC testing, it can be argued that a P_d value greater than 1.6 bar indicates that an explosion occurred. The main difference from this procedure and usual MEC testing is that the nano-dust ‘MEC explosions’ occur with no external ignition source.

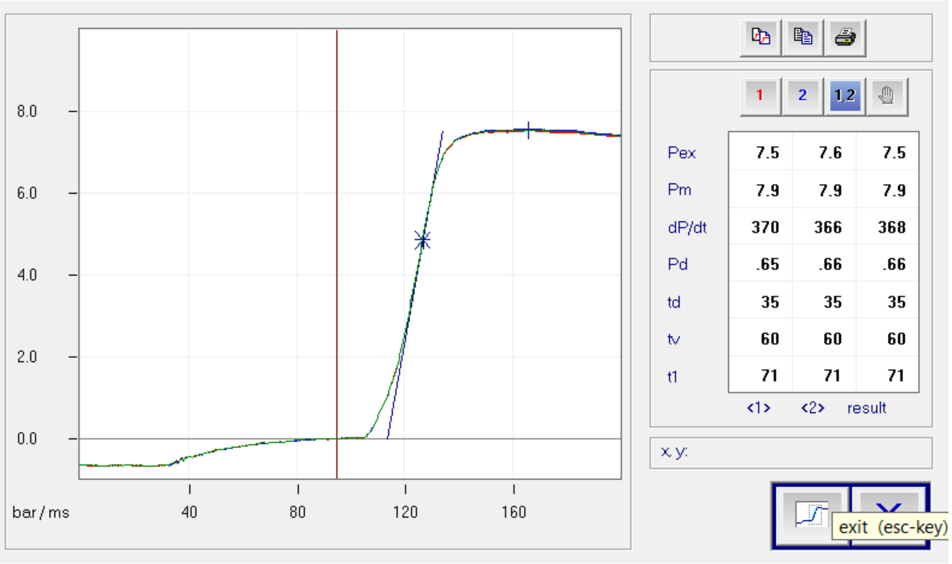
5. EXPERIMENTAL CHALLENGES

There are many experimental challenges that arise when performing dust explosion research with micron- and nano-titanium. These include challenges related to the experimental methods, material handling, waste disposal and laboratory safety. These challenges were especially apparent with the nano-materials.

5.1 Experimental Methods

Issues with titanium powder were first noticed during the 20-L P_{max}/K_{St} testing of the <45 μm and ≤20 μm samples. Ignition at high concentrations would cause explosion residue to be lodged beneath the dispersion valve of the Siwek chamber and disrupt subsequent trials. The dense titanium could not be completely dispersed, leaving a few grams beneath the dispersion valve. It seems that this remaining powder would then be ignited by the intense heat of the explosion occurring in the 20-L chamber and transferred through the valve assembly.

Figure 9 shows a ‘normal’ pressure/time trace for a test in the Siwek 20-L chamber. In this routine trace for one of the micron-size samples, one can see the pressure rise due to dust dispersion into the 20-L chamber followed by the igniters firing and then the dust itself exploding. This may be compared with the pre-ignition behavior displayed in Figure 4.



	<1>	<2>	result
Pex	7.5	7.6	7.5
Pm	7.9	7.9	7.9
dP/dt	370	366	368
Pd	.65	.66	.66
td	35	35	35
tv	60	60	60
t1	71	71	71

Figure 9 Sample pressure/time trace for micron-titanium.

Table 6 illustrates that no suitable combination of experimental conditions could be identified so as to disperse the nano-titanium into the 20-L chamber and achieve a pressure/time trace of the type shown in Figure 9. Numerous attempts were made by varying: (i) dust concentration, (ii) dispersion gas (nitrogen or air), (iii) dispersion gas pressure and ignition delay time (both of which affect dust cloud turbulence intensity), (iv) location of the dust prior to dispersion (placed in either the external dust storage container or the 20-L chamber itself), and (v) expected oxygen concentration in the 20-L chamber once dispersion was complete. Although no external ignition source (i.e., chemical igniters) was used in these tests, the result was an explosion similar to that shown in Figure 4 in every case.

Table 6 Trials with various experimental conditions for 150 nm titanium (no igniters).

Dust Concentration [g/m^3]	Dispersion Gas	Dispersion Pressure [barg]	Ignition Delay Time [ms]	Dust Placement	Final O_2 % in 20-L Chamber	Explosion During Dispersion?
125	N_2	20	60	Dispersion Reservoir	21.0	YES
125	N_2	20	60		19.5	YES
125	N_2	20	60		17.6	YES
125	N_2	20	60		15.0	YES
125	N_2	20	60		9.0	YES
500	Air	20	60	Under Rebound Nozzle	21.0	YES
500	Air	20	60	On Rebound Nozzle	21.0	YES
500	Air	10	60		21.0	YES
500	Air	10	120		21.0	YES
500	Air	5	120		21.0	YES
500	N_2	20	60		9.0	YES
250	N_2	10	60		9.0	YES

5.2 Material Handling

Titanium has been shown to react with water at elevated temperatures around 700 ºC. The metal has a high affinity for oxygen, stripping the oxygen from water to form titanium dioxide and hydrogen gas [17]. Hydrogen explosions have occurred in the past when cooling water unintentionally comes in contact with molten titanium [18]. At ambient temperatures, micron-size titanium does not pose a hazard in this regard. Nano-size titanium, however, can have the same effect as molten titanium; it reacts with moisture to create hydrogen gas but this occurs at ambient temperatures. Hydrogen co-existing with easily ignitable nano-dust causes many concerns for handling the nano-titanium. Therefore, nano-titanium should have limited exposure to air or moisture and should be kept under dry nitrogen or argon. A nitrogen-filled glove bag was an essential feature of the safety precautions taken for the handling of nano-titanium in the current work. This reduced the potential nano-titanium contact with moisture and air. These precautions are also warranted for other nano-metals presented in Table 1 that autoignited and may be necessary for the other nano-metals so as to minimize self-oxidation prior to experimentation.

5.3 Waste Disposal

Disposal of unused nano-titanium powder was important to minimize storage of the material for extended periods of inactivity. The nano-titanium should be deactivated and stored in a fume hood. Nano-titanium was carefully mixed in small quantities with water or dilute nitric acid. Mixing the titanium with water creates stable titanium dioxide while forming hydrogen gas within a vented and controlled environment. Adding nitric acid to the mixture promotes deactivation of the nano-titanium.

5.4 Laboratory Safety

Before any experimentation began, the laboratory was assessed for proper ventilation equipment and personal protective equipment (PPE). An improved ventilation extraction arm was installed and the vacuum exhaust sent through the ventilation system. Appropriate PPE included: a filtered mask, safety glasses, face shield (when working with chemical igniters), lab coat, and double nitrile gloves.

Air quality measurements for airborne nano-particles were performed during normal operation of the 20-L chamber. Two types of particle counters were used: a FLUKE 983 particle counter for particles in the range of 300 nm to 10 µm, and a KANOMAX handheld CPC model 3800 for particles in the range of 15 nm to 1 µm. It was determined that no excess particles become airborne as a result of the use of nano-materials.

6. CONCLUSION

Preliminary results seem to indicate that explosion severity is not significantly different in the nano-scale than in the micron-scale however, the likelihood of an explosion increases significantly as the particle size decreases into the nano range. These nano-scale materials are very sensitive and can self-ignite under the appropriate conditions during laboratory testing and handling. As a result, safety precautions and procedures for the nano-scale metal dust combustibility testing should include laboratory personnel wearing appropriate PPE which should include, but not limited to, full face protection (face-shield or full-face respirator), breathing protection (half-face or full-face respirator), anti-static clothing, and fire-retardant clothing. Additionally, precautions should be taken to maintain an inert gas blanketing over unused samples.

The results obtained in the current detailed work on nano-titanium illustrate that it is much more sensitive to ignition than micron-titanium. Relatively low quantities and very low spark energies can cause nano-titanium to ignite yielding severe explosions. Nano-titanium is so reactive that traditional explosion test procedures using the Siwek 20-L chamber were not possible. Modifications to these procedures were attempted with limited success at preventing pre-ignition of the powder.

Based on this preliminary study, implications to explosion hazard mitigation are mixed. Given that the explosion overpressure of the various nano-metals, and the explosion severity data of the more detailed study of nano-titanium, are not that different than explosion severity of small micron-size metal powders; mitigation methods based upon overpressure containment, deflagration venting or suppression of micron-size nano-metals may be applicable to nano-sized metals as well.

The same is not true for mitigation methodologies involving ignition sensitivity. Here a new strategy must be developed factoring in lower autoignition temperatures, lower minimum ignition energies and lower concentrations of material at which combustion is possible. Such a discussion is beyond the scope of the current work.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council (NSERC) of Canada in the form of a strategic grant. Additionally, the authors would like to acknowledge partial financial support from the Nanotechnology Research Center (NTRC); part of the National Institute for Occupational Safety and Health (NIOSH) of the Centers for Disease Control and Prevention (CDC).

7. REFERENCES

[1] Cashdollar, K. L. and Zlochower I. A. (2007). Explosion Temperatures and Pressures of Metals and Other Elemental Dust Clouds. Journal of Loss Prevention in the Process Industries 20: 337–348.

[2] Pritchard, D.K. (2004): Literature Review – Explosion Hazards Associated with Nanopowders, UK Health and Safety Executive. EC/04/03.

[3] Holbrow, P., Wall, M., Sanderson, E., Bennett, D., Rattigan, W., Bettis, R. and Gregory, D. (2010): Fire and Explosion Properties of Nanopowders. UK Health and Safety Executive. RR782.

[4] Vignes, A., Traoré, M., Dufaud, O., Perrin, L., Bouillard, J. and Thomas, D. (2009): Assessing Explosion Severity of Nanopowders with the 20 L Sphere, 8th World Congress of Chemical Engineering, Montréal, Canada, 23-27 August, 2009.

[5] Dufaud, O., Vignes, A., Henry, F., Perrin, L. and Bouillard, J. (2011): Ignition and Explosion of Nanopowders: Something New Under the Dust. Journal of Physics: Conference Series 304: 012076.

[6] Wu, H.-C., Kuo, Y.-C., Wang, Y.-H., Wu, C.-W. and Hsiao, H.-C. (2010): Study on Safe Air Transporting Velocity of Nanograde Aluminum, Iron, and Titanium. Journal of Loss Prevention in the Process Industries 23: 308-311.

[7] Eckhoff, R.K. (2003): Dust Explosions in the Process Industries, 3rd edition, Gulf Professional Publishing/Elsevier: Boston, MA.

[8] Wu, H.-C., Chang, R.C. and Hsiao, H.-C. (2009): Research of Minimum Ignition Energy for Nano Titanium Powders and Nano Iron Powder. Journal of Loss Prevention in the Process Industries 22: 21-24.

[9] NFPA 484, Standard for Combustible Metals (National Fire Protection Association 2012).

[10] Boilard, S.P., Amyotte, P.R., Khan, F.I., Dastidar, A.G. and Eckhoff, R.K., “Explosibility of Micron- and Nano-Size Titanium Powders”, Paper No. 009, Proceedings of Ninth International Symposium on Hazards, Prevention, and Mitigation of Industrial Explosions, Krakow, Poland (July 22-27, 2012).

[11] Amyotte, P., Khan, F., Boilard, S., Iarossi, I., Cloney, C., Dastidar, A., Eckhoff, R., Marmo, L. and Ripley, R., Explosibility of Nontraditional Dusts: Experimental and Modeling Challenges”, Hazards XXIII, IChemE Symposium Series No. 158, Southport, UK (November 12-15, 2012), pp. 83-90.

[12] ASTM (2010): Standard Test Method for Explosibility of Dust Clouds, E1226. West Conshohocken, PA: ASTM International.

[13] ASTM (2007): Standard Test Method for Minimum Explosible Concentration of Combustible Dusts, E1515. West Conshohocken, PA: ASTM International.

[14] ASTM (2003): Standard Test Method for Minimum Ignition Energy of a Dust Cloud in Air, E2019. West Conshohocken, PA: ASTM International.

[15] ASTM (2006): Standard Test Method for Minimum Autoignition Temperature of Dust Clouds, E1491. West Conshohocken, PA: ASTM International.

[16] Randeberg, E. and Eckhoff, R.K. (2007): Measurement of Minimum Ignition Energies of Dust Clouds in the <1 mJ Region. Journal of Hazardous Materials 140: 237-244.

[17] Patnaik, P. (2003): Handbook of Inorganic Chemicals, McGraw-Hill: New York, NY.

[18] Poulsen, E. (2000): Safety-Related Problems in the Titanium Industry in the Last 50 Years. JOM 52: 13-17.