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TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

PRESIDENT'S LETTER

Friends :

The gravest problem facing the tantalum and niobium community is still the ongoing worldwide economic chaos; however, our commodities' difficulties will not be resolved until the overall crisis is resolved.

One phenomenon worth noting, however, is that the U.S. strategic stockpile is being more or less gradually sold by continuous auctions; the accent is on massive disposals with hardly any acquisitions being made. Very few items in stock are being upgraded and practically none are being bought. Among the "rarities" that are under government purchase contracts are tantalum and niobium metal and the general belief is that more acquisitions of these metals are planned after the existing contracts are fulfilled — say a year and a half from now. This underlines the (high-tech) importance of our materials.

The host committee has reported positively on the site for the up-coming General Assembly — the only reservation being doubt as to the authenticity of the food in the Hotel's French Restaurant (small wonder in the northern part of Honshu). If we want to eat western food, we shall have to make do with simple fare. For a better cuisine, we will eat nippon style which, after all, Japanese gourmets do regularly.

The trip to the site is quite long, however, direct busses from Narita will be arranged for those who register in time.Transport by rail also exists for those rugged individualists who are not averse to changing trains.

As you all (should) know, we are having an Executive Committee meeting in Brussels on Monday, April 18th. All of you are cordially invited to join us for a few hours on the 19th when we will report to the membership. A special trip to Brussels for this purpose alone makes little sense but quite a few manage to work this small event into a more comprehensive schedule.I would like to urge you — whether you attend or not — to let us have your suggestions, preferably by short informal memo, as to the points you would wish us to discuss and possibly act on. Remember that the Committee, writer automatically excepted, consists of people who are accustomed to getting things done and consequently your thoughts will not only get careful consideration but also stand a good chance of being implemented.

One of the topics under discussion will be plans for the location of the 1996 General Assembly : we would be grateful for your ideas. Although 1996 sounds far away, long-range planning is a must.

By the time you read this it will be spring which brings a festive occasion for everyone. Therefore, all appropriate good wishes to all of you and a special good luck to my fellow Americans in their yearly wrestling match with our tax authorities.

Sincerely,

Hubert Hutton
for the T.I.C.

SUMMARY

T.I.C. ACTIVITIES

INFORMAL MEETING

On the morning of Tuesday April 19th 1994 there will be an informal meeting at 40 rue Washington, 1050 Brussels, followed by lunch. The Executive Committee will report on the meeting it will hold on April 18th, and there will be an opportunity for general discussion.

Invitations will be sent to the nominated delegates of member companies, anyone else interested in attending should apply to the Secretary General for details of registration.

GENERAL ASSEMBLY

This year's annual conference of the T.I.C. will take place in Japan in October. The technical and social programme will be based at the Urabandai Nekoma Hotel, where delegates will also stay, and a tour of the Showa Cabot Supermetals plant at Higashinagahara is offered.

The Thirty-fifth General Assembly will be held on the morning of Tuesday October 25th 1994, followed by the technical presentations. The day will close with a gala dinner : all participants will be the guests of Showa Cabot Supermetals and Cabot. The plant tour will take place on Wednesday October 26th, and after lunch the delegates will return to Tokyo City Air Terminal by bus. Registration will be carried out on October 24th, and in the evening delegates are invited to a welcome reception to open the conference. A sightseeing tour for accompanying persons will be arranged.

Urabandai Nekoma Hotel is splendidly situated on the shore of Lake Hibara, near Aizu-Wakamatsu in Fukushima Prefecture. The city of Aizu-Wakamatsu is more than a thousand years old, it prospered in the Edo period when Japan was ruled by a Shogun. During the Boshin War, a civil war between clans, the

Tsurugajo Castle in the centre of the city was the site of a tragic siege in 1868. The area is know for production of saké and of lacquer ware, and the region has many hot springs.

Special T.I.C. buses will run on October 23rd and 24th to the Hotel from Tokyo city or from Narita airport. It is also possible to travel independently by taking the Tohoku Shinkansen (bullet train) from Tokyo station to Koriyama, and transferring there to the Ban-etsu Saisen Line (local train) to Aizu-Wakamatsu.

Pre-registration for the meeting is essential (not to mention reservation of places on the bus services !) : invitations, forms and full details will be sent to the voting delegates of member companies; others interested in attending should contact the T.I.C., 40 rue Washington, 1050 Brussels, for information.

Offers of technical presentations for consideration will be most welcome.

INTERNATIONAL SYMPOSIUM

In September 1995 an International Symposium on Tantalum and Niobium will be held in Goslar, Germany, a major event for this industry, building on the success of the International Symposium in Orlando, Florida, in 1988 and the Tantalum Symposium in Germany in 1978. The conference will be held in conjunction with the Seventy-fifth Anniversary celebrations of H.C. Starck, a long-standing member of this association.

STATISTICS

The Tantalum-Niobium International Study Center has decided that the quarterly statistics collected by the association will no longer be published in the Bulletin. The statistics will be circulated to members by mail, as before.

They will also be available outside the association on subscription : those interested in subscribing should apply to the T.I.C. secretariat for terms and conditions. The data published in 1994 onwards may not be copied or re-printed without the express permission of the T.I.C.

THE SAFE HANDLING OF FINE TANTALUM POWDER

by W.W. Albrecht, T. Pontillo, R.W. Simon & M.K. Shetty (presented by Dr Albrecht at the Vienna meeting of the T.I.C., October 1993)

1. INTRODUCTION

One of the driving forces in the manufacture of tantalum capacitors is to store more and more electrical energy in smaller and smaller capacitor sizes. Reducing capacitor size is made possible by the development of tantalum powder with high surface area or, in other words, finer powders.

One of the measures used for characterizing fine powder is the Fisher Average Particle Diameter (FAPD). Fig. 1 illustrates the general trend of the average particle diameter of tantalum powder during the past three decades.

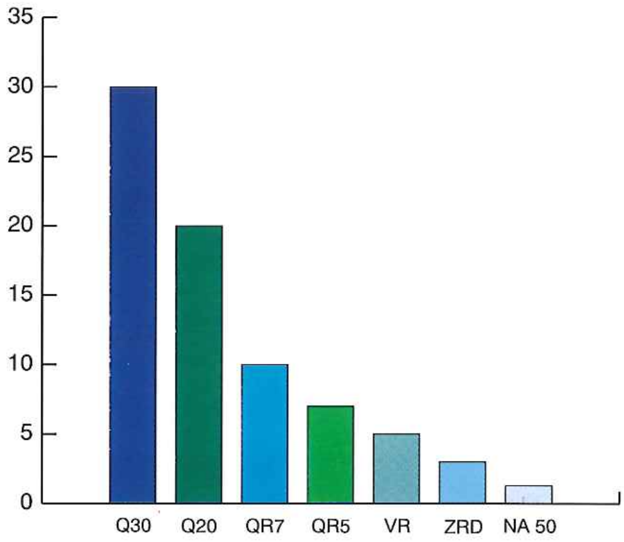

Figure 1
General trend of FAPD of tantalum powder from 1960-1993 (H.C. Starck Inc./NRC)

A closer look at the modern day tantalum powder using a scanning electron microscope shows that each particle is made up of even finer particles (below 1 μm), which together form an agglomerate.

The above examples illustrate that the industries producing tantalum powders are moving towards manufacturing finer and finer metal powders. But fine powders, sometimes called dusts, have their own set of reaction patterns, regardless of the type of dust, be it food, wood or metals. They can be hazardous if proper precautionary measures are not taken.

This presentation focuses on the issues of combustion and explosion reaction mechanisms and ways of preventing and mitigating hazards involved in handling of fine powders. It has to be noted that fine tantalum powder used as an example in this presentation is not a specifically hazardous material compared to other metals, it just follows the reaction pattern of other fine materials.

Dust is defined[1] as a dispersed solid of any form, structure and density with a particle size in the range of 300 microns and below. Dust fires have been in evidence since the changeover from mechanical production to the industrialized manufacture of powder. Accidents due to explosion have caused considerable damage to human life and property.

The earliest incident of a serious dust explosion was reported by Count Morozzo in 1795 in Turin : his report contained a detailed analysis of an explosion in a flour warehouse. The United States National Fire Protection Association published detailed information on all reported dust explosions which occurred in the U.S. from 1900 to 1957. The selection covers a wide range of dust from all categories : wood, food, metals, plastic, coal, etc. Fig. 2 illustrates the number of explosions due to different materials during the period 1900-1989[2].

In 1989 Jeske and Beck made a detailed analysis of dust explosions in West Germany from 1965 to 1985. Their statistics showed that in explosions involving plant equipment 62 % occurred in dust collecting systems, and 71 % were ignited by mechanical sparks[2].

2. PHENOMENON

Let us focus for a while on the physical phenomenon of these reactions.

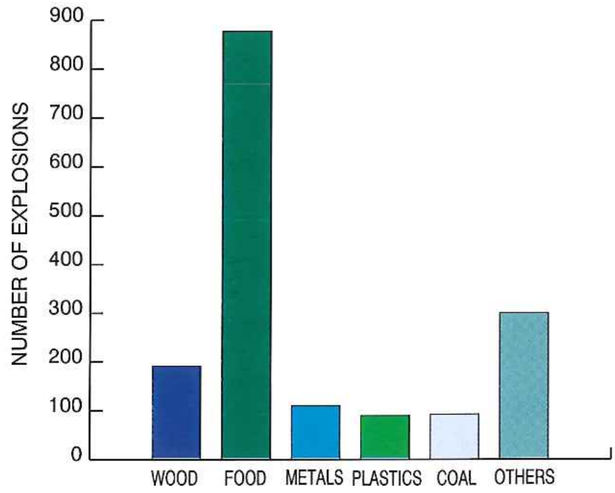

Figure 2
Estimated number of explosions in different materials, U.S., 1900-1989 (compiled from NFPA US)

Dust combustion or even explosion is a rapid exothermic oxidation reaction in the gaseous phase.It occurs when small particles of sizes of the order of 10 microns or less react in a sufficiently large volume of air to give each particle enough space for its unrestricted burning.

A combustion reaction or an explosion requires

Combustible dust (fuel)
Oxygen
Ignition source

as shown in the hazard triangle.

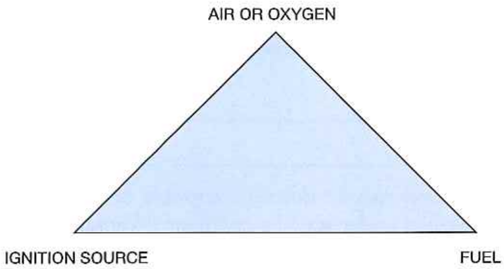

Figure 3
Hazard Triangle

If any one of the three conditions is missing there can be no combustion or dust explosion.

2.1.1 Dust Characteristics

When a piece of wood is ignited it burns slowly, releasing heat over a long period of time. When the wood is cut into smaller pieces, the rate of combustion increases and also the ignition of the wood becomes easier, indicating that as the surface area increases, it is easier for a combustible material to ignite and burn more intensely. In general, we deal with two different kinds of reactions : combustion and/or explosion, depending upon how the dust is dispersed and the concentration of the dust dispersed in air.

2.1.2 Influence of Particle Shape on Combustion

Shape of a particle has considerable effect on the surface area of the particle. Consider a spherical particle of diameter 10 microns. It is compressed and deformed to form a flat shaped particle of diameter 30 microns and thickness of 0.1 micron. It was found that the surface area of the flat shaped particle was about 18 times greater than the original material, indicating that a flat shaped particle is easier to ignite compared to a spherical particle of the same mass. Therefore flake shaped powder has a tendency to ignite faster than spherical shaped powder.

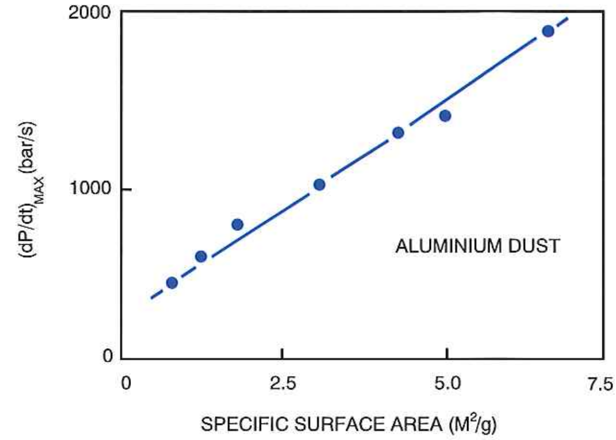

Figure 4
Illustrates influence of specific area of aluminium dust vs. pressure rise.[1]

2.2 Effects of Oxygen Content in Dust/air mixture

Oxygen is an essential parameter of the combustion process. Depending on the oxygen content in a dust cloud, ignition sensitivity of dust can vary as shown below.

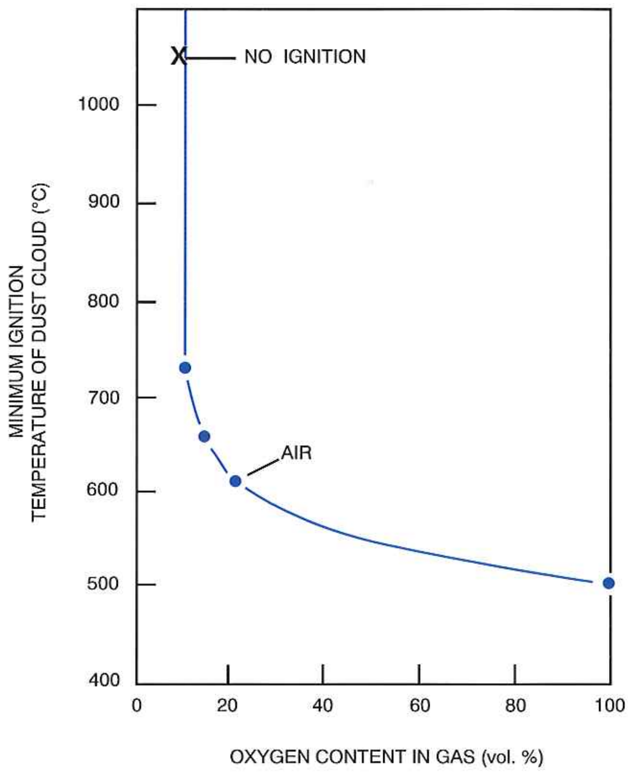

Figure 5
Influence of oxygen content on minimum ignition temperature for coal dust.[2]

Various parameters that are related to oxygen content :

Particle size distribution has to be considered rather than the most populous size because fine particles can form a tail to large particles. These tails require less oxygen and ignite faster than large particles. Reducing the oxygen content increases the minimum ignition energy and decreases pressure rise. In general no dust ignition can occur when the oxygen concentration is under 8 % volume for organic dust and under 4 % volume for metal dust.

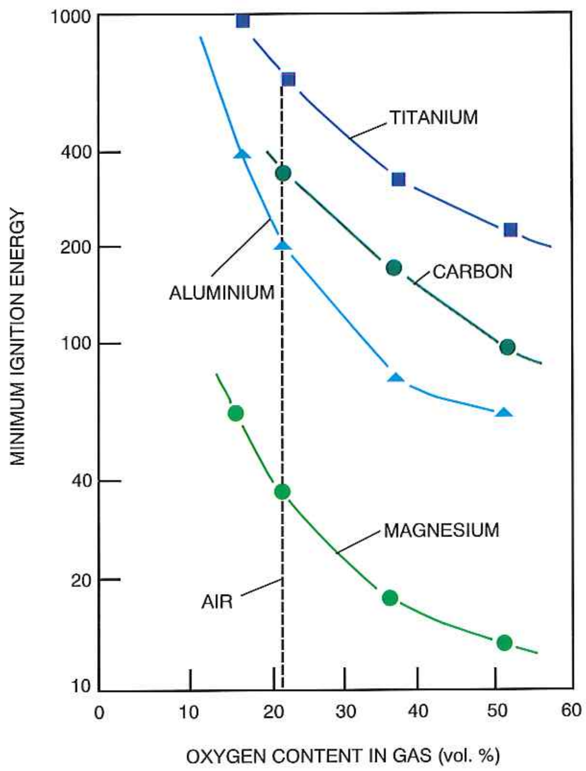

Figure 6
Influence of oxygen content on minimum ignition energy of various materials.[2]

2.3 Source of Ignition

A combustible dust cloud will ignite only when fuel, oxygen and an ignition source are present simultaneously, hence it is important to identify and isolate each of the above mentioned parameters. Fuel (combustible dust) can be easily identified in the process. Oxygen exists in the atmosphere but ignition source identification is not as easy as the other two.Ignition sources in powder manufacturing industries are as follows :

1. Smoldering or burning dust
2. Hot surface
3. Mechanically produced sparks
4. Static electricity
5. Chemical ignition sources
6. Electrical equipment

The most commonly encountered sources of ignition in powder industries are :

Smoldering or burning dust : Combustible dust deposited in a heap develops internal combustion resulting in high temperatures. A dust deposit containing such a hot reaction zone is called a "smoldering nest". When this smoldering nest is disturbed and dispersed by an air blast or mechanical action, the burning dust can easily initiate a dust explosion.

Open flames : Flames from welding torches, cutting burners and wooden matches are sufficient for ignition in most combustible dusts.

Hot surfaces : Hot surfaces can ignite combustible dust by direct contact.

Mechanical impact and friction : Friction is a process of fairly long duration occurring when objects rub against each other forming hot surfaces, for example, removing powder from a tray using a scraper. Whereas impact is a short duration interaction between two solid bodies under condition of large transient mechanical forces, here small fragments of solid material may be torn off and if made of metal may burn in air due to the heat absorbed from the impact process. There is also a possibility of hot spots being generated at the point of impact.

Electric sparks and arc, electrostatic discharge : Electric sparks and arcs that occur during normal operation of commutator motors, circuit breakers, switches and fuses can ignite combustible dust. Electrostatic discharges occur in all operations involving moving of powder, and it is the accumulation of these charges that can give rise to a spark capable of igniting combustible dust.

2.4 Tantalum Powder Process

Once all the factors that affect dust combustion or explosion are identified, then the next step is to identify risk factors involved in tantalum production and take the necessary precautionary measures. A brief description of tantalum production is as follows :

Raw materials are potassium fluo-tantalate and sodium. These raw materials are charged into a reactor. After reduction the reaction cake is chipped, leached and dried. Screened material is then agglomerated in a vacuum furnace and deoxidized. Deoxidized powder is blended and sent for packing.

The above steps from sodium reduction to drying/screening represent the primary stage of powder production where very fine powders with high surface area and high reaction sensitivity are produced. The secondary stage is agglomeration. Here powder has reduced surface area and is less sensitive to ignition. After deoxidization, the final stage, the powder once again is sensitive to ignition.

MATERIAL	FLAMMABILITY	SMOLDER TEMPERATURE (°C)	AUTOIGNITION START*** (°C)	IMPACT SENSITIVITY	CLOUD IGNITION TEMPERATURE (°C)	DUST EXPLOSIBILITY
40000 cV/g PRIMARY POWDER	6	NONE	—	NONE	310	ST1 (HARTMANN)
23000 cV/g PRIMARY POWDER	6	NONE	—	NONE	340	ST1 (HARTMANN)
15000 cV/g PRIMARY POWDER	6	NONE	—	NONE	400	ST1 (HARTMANN)
23000 cV/g SINTERED POWDER	6	NONE	—	NONE	400	ST1 (HARTMANN)
15000 cV/g SINTERED POWDER	6	NONE	—	NONE	380	ST1 (HARTMANN)
40000 cV/g FINISHED POWDER	6	NONE	—	NONE	360	ST1 (HARTMANN)
23000 cV/g FINISHED POWDER	6	NONE	—	NONE	370	ST1 (HARTMANN)
15000 cV/g FINISHED POWDER	6	NONE	—	NONE	400	ST1 (HARTMANN)

***Test still in progress

Table 1 : Tantalum powder dust hazard testing

To identify the ignition sensitivity at the three stages of tantalum powder production, tests were conducted on samples of three products as listed below

40000 cV/g-	Primary powder Finished powder	High capacitance
23000 cV/g-	Primary powder Agglomerated powder Finished powder	Medium capacitance
15000 cV/g-	Primary powder Agglomerated powder Finished powder	Low capacitance

by the Analytical Research Group (polymer division), Miles Inc. The test results are shown in Table 1.

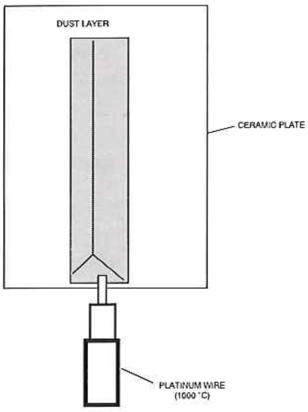

Figure 7
Flammability of dust layers

Combustibility test (Flammability test) : The test equipment consists of an electrically heated platinum wire, transformer and ceramic plate. The sample is contacted by the platinum wire heated to redness.Products are rated by their ability to spread a fire on a combustion scale of 1 to 6. Table 2 describes the combustion class number. Of particular concern is the high flammability rating (class 6) of all samples. There was essentially no difference in the way different samples burned. All burned violently.

COMBUSTION CLASS NUMBER	TEST RESULTS	FLAME PROPAGATION	REFERENCE SUBSTANCE
1	NO IGNITION	NO SPREADING OF FIRE	TABLE SALT
2	BRIEF IGNITION, RAPID EXTINCTION	NO SPREADING OF FIRE	TARTARIC ACID
3	LOCALIZED COMBUSTION OR GLOWING WITH PRACTICALLY NO SPREADING	NO SPREADING OF FIRE	LACTOSE
4	GLOWING WITHOUT SPARKS OR SLOW DECOMPOSITION WITHOUT FLAMEFIRE	FIRE SPREADS	1-AMINO-8-NAPTHOL-3,6-DISULFONIC ACID
5	BURNING LIKE FIREWORKS OR SLOW QUIET BURNING WITH FLAMES	FIRE SPREADS	SULFUR
6	VERY RAPID COMBUSTION WITH FLAME PROPAGATION OR RAPID DECOMPOSITION WITHOUT FLAME	FIRE SPREADS	BLACK POWDER

Table 2 : Description of combustion class numbers for combustibility test

Smolder test : in this test a powder sample is placed on a hot plate with rising temperature.None of the samples showed any change in physical appearance and no smoldering was evident up to a temperature of 360 °C.

Autoignition test : in this test, the powder sample is loaded into a stainless steel container placed in an oven.Heated air enters the lower part of the oven and passes through the test sample in a controlled manner.Temperatures of the test samples are recorded.The point at which the sample temperature first exceeds that of the reference is recorded.

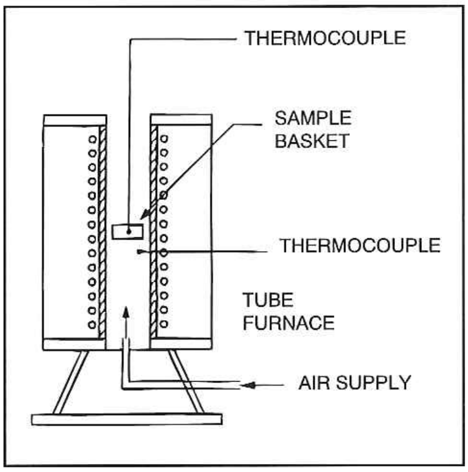

Figure 8
Tube furnace for determining autoignition temperature of a dust layer

Impact sensitivity : none of the samples showed impact sensitivity in presence or absence of aluminium foil.In this test, a hammer drops onto a sample.The work done by the hammer is 39.2 newton meters.

Ignition temperature test : in this test, samples were blown into the BAM apparatus with variable temperature controller. The lowest temperature at which dust ignites or explodes is reported (see Table 1).

Dust explosibility test : this test is carried out using a modified Hartmann apparatus with electric arc as an ignition source.

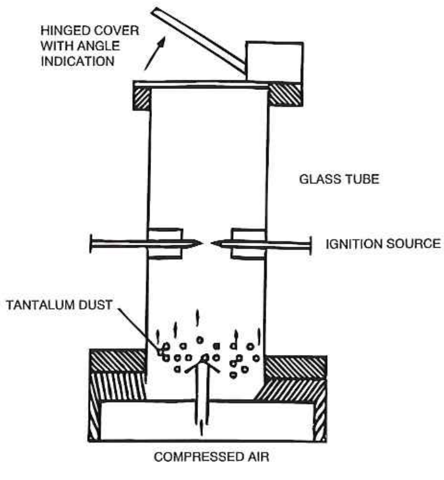

Figure 9
A modified Hartmann tube for determining the explosiveness of a dust

The following table lists the results of hinged lid deflection as a function of dust concentration.

SAMPLE	CONCENTRATION g/m³				
LABEL	30	100	200	500	1000
40000cV/g PRIMARY POWDER	0	0	0	0	1
23000cV/g PRIMARY POWDER	0	0	0	0	0
23000cV/g PRIMARY POWDER	0	0	0	0	1
23000cV/g SINTERED POWDER	0	0	0	1	1
15000cV/g SINTERED POWDER	0	0	0	1	1
40000cV/g FINISHED POWDER	0	0	0	0	1
23000cV/g FINISHED POWDER	0	0	0	1	1
23000cV/g FINISHED POWDER	0	0	0	0	1

Table 3 : Dust explosibility : hinged lid deflection as a function of concentration using a modified Hartmann tube

It has been noted that all tests were characterized by spark formation in the vicinity of the arc regardless of whether the hinged lid deflected or not.Flames were observed at all concentrations greater than $30g/m^3$ in all tests.

Dust explosibility classification is as shown in table 4 :

DUST CLASS	Kst (bar-m/s)
ST-1	<201
ST-2	201-300
ST-3	>300

Table 4

Here, ST-1 rating means that the material is explosible and that measures must be taken to prevent or mitigate an explosion in the equipment.Table 1 summarizes all the test results.

3. RECOMMENDATIONS FOR PREVENTION AND MITIGATION OF DUST COMBUSTION AND EXPLOSION

In summary, all test samples were flammable and explosive at specific dust concentrations.Major differences between product types and stages of the process were not found, although higher surface area material was more active.

It is important that ignition sources must be eliminated.Incorporation of explosion suppression, pressure relief and explosion isolator systems is highly recommended.Electrical classification for all process areas must be a minimum of Class 1, Group G, Division 2 as described in the National Electrical code (NFPA National Fire Code 70).

Some of the general protective measures used in handling of fine metal powder in practice are as follows

3.1 GENERAL PROTECTIVE MEASURES

- Avoid dust generation.
- Good housekeeping to avoid dust accumulation around equipment and in the plant.
- Grounding of all conductive parts of plant and equipment.
- Use "Ground Monitor" to verify the integrity of electrical grounds.
- Static measurement and monitoring of equipment and personnel is essential; i.e., using electrostatic field detectors to identify the magnitude of the charge accumulation.
- Add grounding mats where appropriate.
- Limiting Oxygen - Concentration of dust/air mixture by inertization.

3.2 PROTECTIVE MEASURES FOR EQUIPMENT

Statistics have shown that the majority of pieces of equipment involved in dust combustion and explosion are dust collecting systems.Let me add some specific safety recommendations.

1. Dust Collector — Individual dust collectors are preferred to central dust collection systems.Fans should be installed in the clean air stream or behind the dust collector.Filter cloth should be made of electrostatic conductive material.It must be ensured that the electrical properties, such as dissipation of electrostatic charge, must be conserved when it is washed or soiled during long usage.Conductive parts must be grounded.
2. Vacuum Cleaners — Conductive parts must be grounded.Additional path to the ground is advisable because this neutralizes any difference in the electrostatic charge between the vacuum cleaner and the equipment being cleaned. Use industrial explosion-proof vacuum cleaners because these motors are protected against short-circuit sparking of brushes and overheating.

4. CONCLUSION

All organic and metallic dusts are capable of combustion and even explosion under specific conditions. Tantalum powder used as an example in this presentation is not a specifically hazardous material compared to other metals. It just follows the reaction pattern of any fine material.Because of this and the ongoing trend of the industry to produce finer and finer tantalum powders, production and processing areas should reflect safety precautions requested.

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1) Dust explosion course, prevention, protection by Wolfgang Bartknecht, pub. Springer-Verlag 1989.
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4) Electrostatic Hazard in Powder Handling by Martin Glor, pub. John Wiley & sons Inc 1988.
5) NFPA 57, 61, 651, 70.