



Precautionary Handling Advice for Zirconium, Zirconium Hydride, Titanium, Titanium Hydride and Zr/Ni- Alloys in Powder Form

The following information should enable persons handling such powders to have a better understanding of the potential dangers.

All information is given to the best of our knowledge and according to present state of the art, but this does not exclude the user from his responsibility to check all risks of application and handling himself.

It is recommended that processes in which handling of such powders is involved should be reviewed by occupational safety specialists.

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1. General Safety Information

- Zirconium, zirconium hydride, titanium, titanium hydride and Zr/Ni-alloys in powder form are highly flammable.
- Dry metal powder can be ignited by sparks, friction or very low electric discharge energy.
- Dry metal powder presents a dust explosion hazard.
- Partly wet material is most dangerous as it is easily ignited and burns at explosive speed.

2. Fire

Burning powders may be controlled by covering with plenty of dry sand, limestone (calcium oxide), zirconium oxide or by special dry extinguishing powder for metal fires, class D.

DO NOT USE water, carbon dioxide or carbon halides!

Small fires should be isolated and allowed to burn off, persons should stay away. Dry powders burn quickly but quietly even in bulky quantity with evolution of much heat. Burning powders decompose water by explosion. Partly wet powders burn explosively, dispersing burning particles.

3. General Characteristics

3.1. Pyrophoricity

Powders with bare metallic surface and particle sizes below 10 microns such as obtained by dehydrogenation processes are pyrophoric and can decompose water. In contrast, powders which are derived from a wet chemical process have a passivating oxide and nitride film on their surface which protects the metal from further oxidation and from reaction with water.

Extremely fine powders containing particles below 1 micron may react slowly with water generating some hydrogen. In a qualified production of such powders, fines below 1 micron as well as colloidal particles are carefully washed out to produce a stable, safe to handle product.

Impurities, which can act as destabilizing poisons for the passivating oxide film, are strictly excluded. The passivating and electrically nonconductive oxide film on the particles may cause electrostatic charging if the particles undergo friction to each other. Charging preferably occurs in operations like dry milling, mixing, sieving, pouring into other vessels etc. and can lead to self-ignition.

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3.2. Dry Metal powder / Dust Explosion Hazard

Dry zirconium or titanium powders with particle sizes below 10 microns can be ignited by friction sparks or by electrostatic discharge energies as low as 2 - 5 micro joules. Thus the average discharge energy of a person (0.1 - 2.5 milli-joule) is more than sufficient to ignite zirconium powder. Upon heating in air, zirconium powder ignites at temperatures between 150 - 250 degrees C, depending upon particle size, hydrogen content and impurities. Generally speaking, zirconium hydride, titanium hydride and Zr/Ni-alloys are not so sensitive as pure zirconium or titanium metal powders, but sudden ignition caused by electrostatic discharge must always be taken into consideration. Values for the minimum electrical discharge ignition energy are given in table A.

Like any finely divided combustible material dry powders present a dust explosion hazard. If the powders are whirled up, the electrostatic energy developing during separation of the single particles is sufficient to self-ignite the dust cloud. In closed systems maximum dust explosion pressures (7 bar) and pressure rise time for class St 2 (200 - 400 bar/second) are determined. The lower explosion limit value for dry zirconium dust in air is 40 g/m³.

Dry zirconium powder whirled up and ignited in an open system deflagrates with a white flash and a flame temperature above 3000 degrees C. Such sudden flare-up can occur during spillage, for instance, when an open tin can filled with zirconium powder falls on the floor.

3.3. Wet Material / Dust Explosion Hazard

The reactivity of wet powder slurries depends on the amount of water contained. Powders mixed into more than 30 weight % of water, well slurried, are safe to handle as they are sufficiently wet to prevent ignition. However, compared to this partly wet material with about 2 - 10 weight % of water is most dangerous! Such material is easily ignited and will burn explosively, decomposing water and dispersing burning particles over the surrounding area. Partly wet material will result during drying operations or after a long storage time when wet powders have settled and dried out in the container to form a hard cake. In sedimented material the water concentration can drop below 10 % thus making the powder very sensitive. In this case do not attempt to dig up the material by an instrument or spatula as friction could ignite it!

Best method for removing wet powders from a container is to reslurry them by mechanical rolling on a suitable ball-mill-type roller or by shaking the container in a tumbler. Persons should stay away during such operations. Residues can be washed out by a stream of water. Instructions for drying wet material are given in chapter 7.

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4. Safety Equipment

Persons handling dry or wet powders should be equipped for fire prevention. Fire resistant or non-flammable clothing and gloves together with a face-shield are recommended. Non sparking ground connected metallic apparatus should be used, preferably made of stainless steel, brass or copper. Working area, machinery and clothes must be kept perfectly clean, all residues or wastes should be destroyed by burning them at a safe place. Inhalation of dust should be avoided by good ventilation or use of a dust mask although zirconium and titanium are considered to be not harmful. For handling zirconium/nickel alloys a protective dust mask class P3 is recommended as the toxicology of these nickel-containing alloys is not fully known.

Operations in which formation of dust clouds cannot be avoided (mixing, sieving etc.) must be carried out under an atmosphere of argon or helium gas. Special purification of the noble gases is not necessary, trace impurities of oxygen or nitrogen etc. (< 0.5 %) will not support combustion. Do not use nitrogen or carbon dioxide for inertisation, both gases react vigorously with zirconium, titanium, their hydrides and the Zr/Ni-alloys upon heating. Control of inertisation by an oxygen meter is recommended especially in glove box operations; oxygen content should be kept below 0.5 vol. %.

5. Spill

Small amounts of spilled dry powder should be carefully swept together and taken up into metallic vessels. Avoid friction sparks and remove all sources of ignition. Vacuum cleaning is not advisable because of the risk of dust explosion by self-ignition, see chapter 3.2. and 7.

If plenty of material is spilled, cover it with dry sand or calcium oxide (Limestone), then carefully sweep together, being aware of ignition by friction. Keep material dry, fill into dry, tightly closed containers and later burn it at a safe place. Small residues of spilled powders, e. g. analytical samples may be flushed off by plenty of water.

If wet zirconium or other wet powders are spilled, put all material contaminated by the slurry together into a metallic vessel, e.g. a barrel. Keep material wet, eventually by pouring a lot of water on it, minimum water content must be kept at 30 weight %. Be aware of the risk that combustible material like paper or cloth, contaminated by the powders or slurries, can self-ignite when drying.

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6. Storage and Transportation

If properly stored in the original containers, both dry and suspended metal powders have a shelflife of at least 2 years. The degree of oxidation of the product depends upon the average particle size of the material, storage temperature and the kind and quality of package. The powders should be stored in a dry cool place. Freezing of wet zirconium should be avoided as there is a risk of electrostatic charging during freezing or melting. Containers with wet zirconium should be inspected from time to time for possible leakage or buildup of pressure by slow hydrogen generation.

Some of the powders may be packed and stored under methanol, ethanol or other alcohols. The sensitivity of such preparations against ignition is somewhat diminished compared to dry material. On the other hand potential hazards from organic solvents must be considered, such as toxicity, explosion risks from vapor-air-mixtures, electrostatic charging during decanting etc. Powders should not be mixed with solvents with which they can react, e. g. halogenated hydrocarbons! Transportation of the powders is ruled by international regulations for dangerous goods. Details are given in this delivery program within the description of each type.

7. Drying, Mixing, Sieving, Milling

Batches for drying should be kept as small as possible, preferably below 1000 grams each. Metallic ground connected apparatus should be used wherever possible. Keep in mind: During filtering and drying operations of wet powder the dangerous state of partly wet/dry material is not avoidable!

One possible method for safe drying is to pour the reslurried suspension (see 3.3) into a flat stainless steel tray which is put on a heating element or heat-exchanger preferably heated by hot water. Temperatures should not exceed 60 - 70 degrees C. If electric heating or steam is applied, the installation must be explosion-proof and a reliable temperature control is required to exclude local overheating above 70 degrees C. Time for drying can be saved if most of the water is removed from the suspension prior to drying by filtration. A Buchner funnel or similar apparatus made of stainless steel is used to suck off water. The operator should avoid air passing through the filter cake. The wet cake is poured on a stainless steel tray and dried as described above. During such filtering operations persons should be equipped with fire resistant clothing and a face shield. Personnel should stay away until the powder is perfectly dry (12 - 24 hours). Dryness can be confirmed by heating a 1 or 5 gram sample to 110 degrees C for half an hour determining the change of weight on an analytical balance.

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All sources of ignition must be removed and dust formation avoided. The batches must be kept separately from each other to avoid conflagration. After drying the material must be allowed to cool to room temperature before further processing. Residues and filter paper are to be burnt at a safe place immediately. If very quick drying of small batches is required, the powder can be filtered off on the Buchner funnel as described above, replacing the rest of water by an alcohol like ethanol or isopropanol. The material can then be dried quickly by evaporation of the volatile organic solvent at room temperature or slightly elevated temperature. However formation of unhealthy solvent vapors or explosive air-vapor mixtures must be taken into consideration.

Vacuum drying of wet powder is possible but not recommended owing to potential dangers. Main danger during vacuum drying is local overheating or sudden ignition during back-filling with air. A sudden unexpected leakage during vacuum drying would lead to a severe dust explosion as whirled up powder will explode by self ignition. Back-filling of the vacuum chamber should be done only after cooling to room temperature either slowly by air, allowing heat from the passivating reaction to dissipate, or better by argon with subsequent gradual exposure of the material to the atmosphere.

Dry mixing, blending or milling of the powders is to be done only under argon atmosphere. Aggressive dry milling can produce pyrophoric material. The powders are non-reactive with aliphatic or aromatic hydrocarbons, alcohols and water under normal conditions. Wet mixing and milling can be carried out in non-oxidizing organic solvents or in more than 30 weight % of water. Very aggressive and rapid milling of aqueous suspensions with formation of colloidal or sub-micron particles should be avoided, as such material can react with water explosively even at room temperature. Material should be well slurried and wetted, inclusion of air or clods of dry material can lead to ignition and explosive reactions. During wet milling of aqueous slurries a slight generation of hydrogen from passivating reactions is possible. Good ventilation of the working area is required.

Wet powders with more than 30 weight % of water are easily sieved through stainless steel or brass sieves using a stream of water. Unexpected drying up e. g. formation of dried-up crusts at the rim of the sieve must be avoided. Dry sieving should be done only under argon-or helium-atmosphere in ground connected, metallic equipment. Very small batches of the

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powders, e. g. analytical samples can of course be sieved in air by hand using metallic ground connected apparatus and a metallic support, operators being aware of possible sudden ignition.

Mixing, milling and sieving of zirconium, titanium, zirconium hydride, titanium hydride or ZrNi-alloys together with oxidizing agents like chromates, perchlorates, nitrates or similar reactive agents will produce highly explosive, even detonative compositions and the specific processing is only under the responsibility of the user. Also the processing of the powders with plastic binders, organic solvents etc. should be done with utmost care and precaution. As an example, mixtures of zirconium with Teflon®, a material normally considered to be extremely stable and unreactive, are easily ignited, burn violently and may even explode. As a rule all halogenated hydrocarbons will form very dangerous mixtures with zirconium and the other metal or hydride powders.

8. Wastes and Environmental Pollution Aspects

Zirconium, titanium, their hydrides and the Zr/Ni-alloys are non-toxic and normally do not present an environmental pollution problem because of their insolubility and resistance against chemical attack. Accumulation of wastes and dust must be avoided because of fire risk. Combustible material like paper or cloth contaminated by zirconium should be treated with special care as self ignition or sudden flare-up can occur. Such wastes are to be destroyed immediately by burning them at a safe place. Dry zirconium and zirconium hydride burns quickly but quietly forming stable non-toxic zirconium oxide and zirconium nitride. The same is true for titanium which forms titanium dioxide and titanium nitride. These combustion residues can be treated like normal waste as they are nontoxic and insoluble in water. In contrast to zirconium and titanium the zirconium-nickel-alloys form toxic nickel oxide when burnt. Combustion products of Zr/Ni-alloys must be treated like toxic chemical waste (see local regulations valid for waste removal of nickel or nickel-oxide).

9. Toxicology

Zirconium and titanium are known to possess low toxicity in elemental form as well as in their compounds. The MAK-value for Zr and Zr-compounds is 5 mg/m³, for TiO₂ 6 mg/m³. Little is known about the toxicology of ZrNi-alloys. The great chemical stability and the total insolubility of these alloys in water make toxic effects unlikely. Because of the nickel content, however, inhalation of the alloy powders or their combustion fumes is to be avoided. Zr/Ni-alloy powders should be regarded and handled with care like any other incompletely investigated chemical substance.

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Table A: Critical electrostatic ignition energy

Type of metal powder		Average particle size acc. Blaine (microns)	Ignition energy	
Zr	CX	1.7	1.8	μJ
	CA	2.0	1.8	μJ
	FA	2.3	3.2	μJ
	MX	2.2	3.2	μJ
	ZM	2.5	5.6	μJ
	ZE	4.0	10.	μJ
	ZS	3.0	10	μJ
	GA	5.5	18	μJ
	GH	5.5	56	μJ
ZrH₂	F	2.5	56	μJ
	S	3.0	3200	μJ
	G	5.5	5600	μJ
Zr/Ni	70/30A	4	0.1	mJ
	30/70 A	5	3.3	mJ
	70/30 B	4	18	mJ
	30/70 C	5	56	mJ
Ti	E	3.0	0.32	mJ
	S	9.0	1.0	mJ
	sponge granules	> 200 mesh	180	mJ
TiH₂	standard grade	5.0	56	mJ
B	grade I 95-97 %	0.7 – 1.0	560	mJ
	grade II 90-92 %	0.5 – 0.9	1.8	J
	grade III 86-88 %	0.8 – 1.5	1.8	J

Measured by the method of an approaching electrode, reference:

B. Berger, J. Gyseler: Methode zur Prüfung der Empfindlichkeit von Explosivstoffen gegenüber elektrostatischen Entladungen. Technology of Energetic Materials, page 55 - 1 to 55 - 14. 18th Int. Annual Conference of ICT 1987. Fraunhofer Institut für Treib- und Explosivstoffe, Karlsruhe/ Germany.