Cristal: one company, five continents

For decades the Cristal family of organizations has invested in the future of titanium.

From October 2012, we make our commitment to the brilliance of titanium clearer when we bring all our companies under one name: Cristal.
Cristal: complete titanium specialists

Mineral sands mining
- Leucoxene
- Rutile
- Zircon
- Ilmenite

Titanium Dioxide (TiO₂)
- TiONA® TiO₂

Titanium performance chemicals
- CristalACTiV™
- Ultratine TiO₂
- Titanium Tetrachloride

Titanium metals and alloy powders
- CP
- Ti6Al4V
Cristal cares

Safety and care are at the core of everything we do.

We are committed to looking after the people and places we work with, and to making the world a cleaner, brighter place through the brilliance of titanium.

- Cristal is in the top quartile of chemical companies in safety performance
- All workplace injuries, illnesses and adverse environmental impacts are preventable: we will never accept them
- We are continually improving our environmental performance, from waste disposal to sustainable product development
Titanium Powder Handling

- Cristal’s focus is on customer awareness, understanding the risks associated with processing titanium powder

- Few companies have extensive experience working with Ti though some have experience working with other types of powders

- “There is a lot of information on what not to do, but few guidelines on safe practices”

- These guidelines are neither inclusive nor instructive of all necessary precautions for handling titanium powders, but are intended to promote awareness and the safe handling and processing of titanium powder. Cristal makes no any warranty, express or implied, or assumes any legal liability or responsibility with respect to the information contained within this presentation. It is the responsibility of each individual handling and processing titanium powder to do so in a safe and responsible manner.
Requirements for **Fire** and Explosion Hazard - Explosion Pentagon

- **Ignition Source**
  - (Heat, Sparks, Static Electricity, Frictional Heating)
- **Dispersion of Dust Particulates**
- **Combustible Dust (Fuel)**
- **Confinement of Dust Cloud**
- **Oxygen in Air Oxidizer**
Flammable Solids
Testing to Determine Combustibility

• Preliminary screening test employed to determine fire risk (combustibility)
  Referenced in NFPA 484 2012 Standard for Combustible Metals

• Prescreening test:
  Unbroken powder train about 250 mm (9.84”) L x 20 mm (0.79”) W x 10 mm (0.39”) H on a low heat conducting base
  Hot flame from a gas burner (min. temperature 1000°C) until powder ignites, or for 5 minutes
  Must burn within 5 minutes, and propagate over 200 mm (7.87”) within 20 minutes
Flammable Solids
Testing to Determine Combustibility

• Results of pre-screening test:
  No reaction
  Glowing but no propagation
  Propagation but greater than 20 minutes
  Propagation in under 20 minutes

• If propagates under 20 minutes, burn rate test is employed on a triangular cross-section of powder
  Powder is classified within division 4.1, and considered as readily combustible if it can be ignited and reaction spreads over entire sample length within 10 minutes

• Packing group criteria for readily combustible materials of Division 4.1 are assigned as follows:
  (i) Packing Group II - reaction spreads over entire length of sample in 5 minutes or less.
  (ii) Packing Group III - reaction spreads over entire length between 5 and 10 minutes
Explosibility Determination

Testing and powder properties related to ability of dust to explode

Explosibility classification – screening test
Determine if a material is capable of initiating and sustaining an explosion
20 L chamber per ASTM E-1226

Minimum ignition energy (MIE)
Minimum ignition temperature (MIT)

Maximum explosion pressure
Maximum rate of pressure rise
K_{st} value

Limiting oxygen concentration (LOC)
Minimum explosible concentration (MEC) (g/m^3)

- MIE - indicates the ease of igniting a suspended dust cloud
- MIT - temperature to cause suspended dust to auto-ignite
- K_{st} is the deflagration index, measures relative explosion severity to other dusts
- LOC - minimum amount of oxygen needed to sustain an explosion
- MEC - minimum amount of dust to cause a significant pressure rise: “How easily can a dust cloud be formed”
## Explosion Severity

<table>
<thead>
<tr>
<th>Dust Explosion Class</th>
<th>$K_{st}$ (bar.m/s)</th>
<th>Characteristic</th>
<th>Typical Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>St 0</td>
<td>0</td>
<td>No Explosion</td>
<td>Silica</td>
</tr>
<tr>
<td>St 1</td>
<td>&gt;0 and &lt;200</td>
<td>Weak Explosion</td>
<td>Iron 50, CP Ti 92, Granulated Sugar (fine) 140, Zinc 176</td>
</tr>
<tr>
<td>St 2</td>
<td>&gt;200 and &lt;300</td>
<td>Strong Explosion</td>
<td>Acrawax 275</td>
</tr>
<tr>
<td>St 3</td>
<td>&gt;300</td>
<td>Very Strong Explosion</td>
<td>Aluminum 400, Magnesium 508</td>
</tr>
</tbody>
</table>

20L test chamber for explosivity testing – ASTM E-1226
Powder Handling Guide

• Cristal created a powder handling guide that gives handling guidance for working with titanium powders

• Handling guide is sent to each customer prior to supplying powder
Storage of Powder

• Store in a closed container when possible to prevent accidental dust generation and to prevent possible contamination

• Protect containers from physical damage

• Welding, grinding, or other processing that can generate heat and sparks should not be performed around any titanium powder. Smoking shall not be permitted in storage areas

• Storage containers of titanium powders must be kept separate from other chemicals in a storage area
Storage of Powder

• Water from automatic sprinkler systems can contribute to material hazard in the event of a powder fire. Contact of burning titanium with water in a fire event will evolve flammable hydrogen gas, which may result in fire or detonation of hydrogen, and the potential to disturb more powder and spread the fire. If you choose to disable the sprinkler system to eliminate this potential hazard, be sure to discuss with your insurance carrier before doing so.

• NFPA 484 requires that in areas where titanium dust may be present, all electrical equipment must comply with Class 2, Division 1, Group E of the National Electrical Code.

• Review with local building authority for restrictions on building, storage piles, and total allowable quantities.

• Where powered fork-trucks and fork-lifts will be employed, reference NFPA 505.
Housekeeping

• Continuous housekeeping and cleaning must be maintained to minimize accumulation of titanium powder on floors and horizontal surfaces such as ducts, pipes, hoods, ledges, beams, suspended ceilings and other concealed surfaces within the facility. Equipment must be maintained to minimize the escape of dust.

• Review NFPA 484 for general housekeeping practices for titanium powders

• Vacuuming should never be performed, even with an explosion-proof vacuum cleaner, to pick up any waste or spilled powder. Fires or explosions while vacuuming may occur.

• A natural-fiber broom and non-sparking (i.e., aluminum) dust pan should be employed for removing powder. Shovel or sweep material into a metal waste container with a sealing lid. Use non-sparking tools and equipment.

• Surfaces must be cleaned in a manner that minimizes the generation of dust clouds. Vigorous sweeping or use of compressed air must be avoided as they may produce hazardous dust clouds.
Handling/Use

• Electrically ground powder storage drum while using material

• The following are some of the steps that can be taken to prevent static charge accumulation:
  • conductive flooring and footwear
  • personnel-grounding devices
  • anti-static or conductive clothing

• Suggest using ground-connected metallic apparatus to prevent electrostatic charges from causing ignition. All equipment used to process titanium powder should be electrically bonded and grounded to prevent accumulation of static electricity.

• Use proper personal protection equipment (PPE) guidelines when working with powder. Fire resistant clothing, full leather footwear, safety glasses and/or full face shield, and leather gloves.
Handling/Use

- Use non-metallic (non-sparking), non-static inducing scoops and tools (such as aluminum or beryllium-copper).

- When powder is being processed, argon gas blanketing of processing equipment will reduce combustion risks and minimize oxygen pick-up.

- While loading powder into any processing equipment, keep main supply of feed material at least four feet from entrance or discharge of equipment.

- Keep a well supplied stock of suitable extinguishing media nearby during processing. Suitable media include dry sand, talc, salt, and Class D extinguishing agents.

- Where Class A, B, C fire extinguishers are present in the areas where titanium is stored or processed, they must be marked “Not for use on Combustible Metal Fires.”
## Metal Fire Extinguishing Agents per NFPA 484

<table>
<thead>
<tr>
<th>Extinguishing Agents</th>
<th>Alkali Metals (Calcium, Sodium)</th>
<th>Lithium</th>
<th>Aluminum</th>
<th>Iron &amp; Steel</th>
<th>Magnesium</th>
<th>Niobium</th>
<th>Tantalum</th>
<th>Titanium</th>
<th>Zirconium</th>
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</thead>
<tbody>
<tr>
<td>Coke (carbon microspheroids)</td>
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<td>Yes</td>
<td>Yes</td>
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<td>Met-L-X</td>
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</table>

*Preferred extinguishing agent
Emergency Precautions

- Maintain a safe perimeter around equipment to insure adequate access to eliminate power to equipment in an emergency.

- Maintain a safe perimeter to insure adequate space to back away from equipment and/or powder in the event of a fire.

- Do not spray any titanium fires with water; contact with water in fire event will evolve flammable hydrogen gas - resulting in fire and/or explosion.

- Extinguishing agents should be applied in a manner that does not disturb or disperse accumulated dust to form a dust cloud. In the case a dust cloud is produced as a result of the fire fighting, a deflagration hazard will be present.

- All burnt materials and sand, once cooled, should be shoveled into a metal drum and allowed to sit and complete cooling undisturbed. The lid should be locked into place and the drum disposed of following all federal and local guidelines.
Questions/Comments?