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NFPA 481
Production, Processing, Handling, and Storage of Titanium
1987 Edition

NFPA

National Fire Protection Association Batterymarch Park, Quincy, MA 02269

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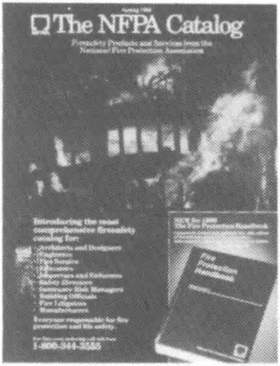

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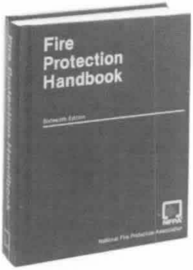

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NFPA 481

Standard for the

Production, Processing, Handling, and Storage of

Titanium

1987 Edition

This edition of NFPA 481, *Standard for the Production, Processing, Handling, and Storage of Titanium*, was prepared by the Technical Committee on Combustible Metals, and acted on by the National Fire Protection Association, Inc. at its Fall Meeting held November 17-20, 1986, in Denver, Colorado. It was issued by the Standards Council on December 10, 1986, with an effective date of December 30, 1986, and supersedes all previous editions.

The 1987 edition of this standard has been approved by the American National Standards Institute.

Origin and Development of NFPA 481

This standard was initiated in 1955, tentatively adopted in 1957 and, with certain amendments, was adopted by the National Fire Protection Association in May, 1958. Amendments were adopted in 1959 and 1961.

A complete revision of the 1961 edition was adopted in 1972. Amendments to the 1972 edition were adopted in 1974.

In 1980, the 1974 edition was completely revised primarily to comply with the NFPA Manual of Style. Minor technical corrections were also made at this time. The completely revised edition was adopted by the Association at its 1981 Fall Meeting, and the revision was designated the 1982 edition.

This 1987 edition is a reconfirmation of the 1982 edition.

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NOTE: Membership on a Committee shall not in and of itself constitute an endorsement of the Association or any document developed by the Committee on which the member serves.

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NFPA 481

Standard for the

Production, Processing, Handling, and Storage of

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NOTICE: An asterisk (*) following the number or letter designating a paragraph indicates explanatory material on that paragraph in Appendix A.

Information on referenced publications can be found in Chapter 8 and Appendix C.

Chapter 1 General

1-1 Scope. This standard shall apply to the production, processing, fabrication, handling, and storage of titanium.

1-2 Purpose. The purpose of this standard is to provide reasonable requirements addressing the fire and explosion hazards of titanium and to outline requirements and recommendations for fire prevention and protection, as well as safe personnel practices. The information is based on the present state of the art developed through more than 25 years of commercial production and use. (*See Appendix B for supplementary information on titanium.*)

1-3 Definitions. For the purpose of this standard, the following terms shall have the meanings given below.

Approved. Acceptable to the "authority having jurisdiction."

NOTE: The National Fire Protection Association does not approve, inspect or certify any installations, procedures, equipment, or materials nor does it approve or evaluate testing laboratories. In determining the acceptability of installations or procedures, equipment or materials, the authority having jurisdiction may base acceptance on compliance with NFPA or other appropriate standards. In the absence of such standards, said authority may require evidence of proper installation, procedure or use. The authority having jurisdiction may also refer to the listings or labeling practices of an organization concerned with product evaluations which is in a position to determine compliance with appropriate standards for the current production of listed items.

Authority Having Jurisdiction. The "authority having jurisdiction" is the organization, office or individual responsible for "approving" equipment, an installation or a procedure.

NOTE: The phrase "authority having jurisdiction" is used in NFPA documents in a broad manner since jurisdictions and "approval" agencies vary as do their responsibilities. Where public safety is primary, the "authority having jurisdiction" may be a federal, state, local or other regional department or individual such as a fire chief, fire marshal, chief of a fire prevention bureau, labor department, health department, building official, electrical inspector, or others having statutory authority. For insurance purposes, an insurance inspection department, rating bureau, or other insurance company representative may be the "authority having jurisdiction." In many circumstances the property owner or his designated agent assumes the role of the "authority having jurisdiction"; at government installations, the commanding officer or departmental official may be the "authority having jurisdiction."

Ingot. The product of arc-melted sponge with or without the addition of other metallic alloying agents.

Labeled. Equipment or materials to which has been attached a label, symbol or other identifying mark of an organization acceptable to the "authority having jurisdiction" and concerned with product evaluation, that maintains periodic inspection of production of labeled equipment or materials and by whose labeling the manufacturer indicates compliance with appropriate standards or performance in a specified manner.

Listed. Equipment or materials included in a list published by an organization acceptable to the "authority having jurisdiction" and concerned with product evaluation, that maintains periodic inspection of production of listed equipment or materials and whose listing states either that the equipment or material meets appropriate standards or has been tested and found suitable for use in a specified manner.

NOTE: The means for identifying listed equipment may vary for each organization concerned with product evaluation, some of which do not recognize equipment as listed unless it is also labeled. The "authority having jurisdiction" should utilize the system employed by the listing organization to identify a listed product.

Sponge. A term used to identify the titanium metal after it has been won from the ore but before it is melted into ingot. Sponge is a relatively finely divided form of the metal, nominally ½ in. (1.27 cm) or less in size.

Swarf. Finely divided metal particles produced by sawing and cutting operations.

Titanium. A nontoxic metallic element used principally in commercially pure and alloy forms.

Chapter 2 Sponge Production

2-1 Plant Construction.

2-1.1 Buildings housing reduction furnaces, boring and crushing facilities, and magnesium refining operations shall be constructed of noncombustible materials. Consideration shall be given to the provision of explosion venting, designed according to information contained in NFPA 68, *Guide for Explosion Venting*, and in the U.S. Bureau of Mines Reports of Investigations 3722 and 4835.

2-1.2 All buildings shall have adequate ventilation.

2-1.3 Building exits shall comply with NFPA *101*®, *Life Safety Code*®.

2-1.4* Floors in reduction, boring, and crushing buildings shall be noncombustible, preferably of concrete, brick, or steel plates.

2-2 Processing Equipment.

2-2.1 Reduction furnaces shall be air-cooled or an alternative method of cooling acceptable to the authority having jurisdiction shall be used. Furnaces shall be kept dry and free of iron scale and spillage.

2-2.2 Fuel supply lines to gas- or oil-fired furnaces shall have control valves at an easily accessible location remote from the reduction furnaces.

2-2.3 Fans handling combustible dust or gas and air mixtures shall be constructed in accordance with NFPA 91, *Standard for the Installation of Blower and Exhaust Systems*.

2-2.4 All electrically operated or controlled processing equipment shall be installed in accordance with NFPA 70, *National Electrical Code®*.

2-3 Storage of Raw Materials.

2-3.1 Magnesium ingots for use in the Kroll process shall be stored in accordance with NFPA 480, *Standard for the Processing, Handling and Storage of Magnesium*.

2-3.2* Chlorine containers shall be handled and stored in accordance with recommendations published in the *Chlorine Manual*. (*See Chapter 8.*)

2-3.3 Containers of titanium tetrachloride ($TiCl_4$) shall be stored in a cool, well-ventilated dry place away from areas of acute fire hazard. Containers shall be plainly labeled and tightly sealed until used.

2-3.4 Acids in quantity shall be stored in specially designed tank farms provided with personnel safety equipment.

2-4 Dust Collection.

2-4.1* Magnesium chloride dust resulting from the boring and crushing of titanium sponge shall be collected in bag houses or wet scrubbers.

2-4.2 Bag houses shall be kept warm and dry.

2-4.3 Collectors shall be emptied daily.

2-5 Fire Prevention.

2-5.1 Because of the great affinity of titanium and magnesium for oxygen, particularly at elevated temperatures, and the potential for magnesium or sodium ignition in air, the reduction process shall be carried out in an enclosed, oxygen-free vessel. (*See NFPA 69, Standard on Explosion Prevention Systems.*)

2-5.2 Precautions shall be taken to always have available an adequate supply of inert gas to meet anticipated demand. A reserve supply shall be available for emergency use.

2-5.3 All pipes, valves, and fittings in the inert gas distribution system shall be checked to ensure an uninterrupted flow of gas to the reactors and elsewhere, as needed.

2-5.4 Since titanium fines (normally, everything under 48 mesh) can be ignited by a small spark, accumulations of fines in crushing and drying systems shall be prevented.

2-5.5 Sponge discharged from dryers shall be collected in lots no larger than tote bins or 55-gal (208-L) drums. The collection area shall be well-ventilated and free of combustible material. A forklift industrial truck or other suitable handling vehicle shall be available at all times for quick removal of burning containers. Sponge containers shall not be stored in this area.

2-5.6 All systems shall be thoroughly cleaned of titanium fines and sponge before attempting maintenance work. All equipment and adjacent areas shall be washed down with water before proceeding with any welding or cutting on the processing equipment or in the immediate area.

2-5.7 All containers used to receive molten metal, molten magnesium, molten magnesium chloride, or liquid sodium shall be thoroughly cleaned and dried before using. All pieces of magnesium metal shall be clean and dry when charged to reactors.

2-5.8 Good housekeeping is essential. Supplies shall be stored in an orderly manner with properly maintained aisles to permit regular inspection and segregation of incompatible materials. Supplies of material in the reactor rooms and drying rooms shall be limited to amounts necessary for normal operation.

2-5.9 Ordinary combustible material, such as paper, wood, cartons, packing material, etc., shall not be stored or allowed to accumulate near furnaces, dryers, or other ready sources of ignition.

2-5.10 Smoking shall be prohibited in all areas where titanium sponge is bored, crushed, dried, or stored and in all areas where titanium fines are produced or stored. Areas shall be clearly posted with No Smoking signs.

2-5.11 Boring, crushing, and drying equipment shall be properly grounded to prevent accumulation of static electricity. (*See NFPA 77, Recommended Practice on Static Electricity.*)

2-6* Fire Protection.

2-6.1 If required by the authority having jurisdiction, automatic sprinkler protection, installed according to NFPA 13, *Standard for the Installation of Sprinkler Systems*, shall be provided for offices, warehouses, and repair shops.

2-6.2 Fire extinguishers approved for use on combustible metal fires, dry sodium chloride, or other dry chemicals suitable for extinguishment or containment of titanium fires shall be stored in sufficient quantity in sealed containers in all areas where titanium fines and sponge are bored, crushed, dried, blended, or stored. Shovels shall be kept readily available adjacent to the sealed containers. All extinguishing agent storage areas shall be clearly identified.

2-6.3* Titanium fines or sponge shall be segregated by storage in noncombustible drums or tote bins. Burning drums or tote bins shall be moved away from processing equipment and out of buildings as rapidly as possible.

2-6.4* When a fire occurs in processing equipment, material feed to the equipment shall be stopped. The equipment shall be kept in operation, if possible, until all burning material is removed.

2-7 Personnel Safety Precautions.

2-7.1* All personnel exposed to titanium tetrachloride leaks or spills in titanium tetrachloride plants, storage, and transfer areas, and laboratories shall wear protective clothing, goggles, or face shields and shall carry approved respiratory protection at all times. Respirators shall be worn while drawing samples or making transfers.

2-7.2 A supply of clean, soft rags shall be kept available in clearly marked areas in titanium tetrachloride plants, laboratories, and storage and transfer areas. Safety showers shall be installed at critical locations. Eyewash fountains or bottles shall also be located at critical locations.

2-7.3 The protection required by 2-7.1 and 2-7.2 shall also apply to the handling of caustic soda, caustic potash, hydrochloric acid, nitric acid, and sulfuric acid. Rubber coats and gloves shall be used for handling all corrosives.

2-7.4* Personnel working in chlorine handling or storage areas shall carry respiratory protection at all times. Liquid chlorine shall be handled and stored in accordance with recommendations published in the *Chlorine Manual*. (*See Chapter 8.*)

2-7.5 Personnel involved in reduction furnace tapping, removal of molten magnesium chloride, and magnesium refining shall wear tight above-ankle shoes, flame-retardant clothing, heat-resistant gloves, and face shields. Respirators shall be carried at all times.

2-7.6* Tight above-ankle shoes, flame-retardant clothing, heat-resistant gloves, and face shields shall be worn by all personnel involved in magnesium refining and casting operations. Respirators shall also be carried at all times.

2-7.7* Personnel involved in the use, handling, and storage of liquid sodium shall wear protective shoes, clothing, gloves, and face shields.

2-7.8* Protective clothing, gloves, and respirators shall be worn by personnel involved in the handling of magnesium chloride. Skin affected by magnesium chloride shall be promptly washed with water.

2-7.9 Chemical safety goggles or face shields and protective clothing shall be worn by all maintenance personnel when any joint or connection containing a potentially dangerous liquid or gas is being opened.

2-7.10 To prevent potential explosions caused by inadvertently using high-pressure compressed air in place of low-pressure inert gas, fittings used on compressed air and inert gas line outlets shall not be interchangeable.

2-7.11 Magnesium refining and casting operations shall be protected from rain and all possibilities of water spillage shall be avoided.

2-8 Sponge Storage and Shipping Requirements.

2-8.1 Long-term storage of titanium sponge shall be in 55-gal (208-L) steel galvanized drums with tight-fitting clamp-on sealable lids. Short-term storage may be in aluminum tote bins holding not more than 10,000 lb (45 350 kg).

2-8.2 Titanium fines shall be stored in tightly sealed noncombustible 55-gal (208-L) drums.

2-8.3 Titanium storage areas shall be kept free of combustible materials, well ventilated, equipped with required fire protection equipment and plainly marked with No Smoking signs. Storage of drums shall be on steel pallets no more than two drums high.

Chapter 3* Sponge Melting

3-1 Explosion Prevention.

3-1.1 The water supply to crucibles shall be continuously monitored by a system that will automatically interrupt power to the furnace upon a drop in water pressure or flow. An emergency secondary source of cooling water shall be provided and shall be actuated automatically by an interlock with power interruption.

3-1.2 The use of a magnetic field to deflect the electric arc away from the crucible wall shall be considered.

3-1.3 Water-cooled furnaces shall be located in a protective concrete vault or the crucible and its water jacket shall be isolated to protect personnel and to minimize damage should an explosion occur.

3-1.4 The upper chamber of the furnace shall be provided with a pressure relieving device, such as a rupture disc, to aid in safely relieving pressure should water enter the furnace. Means shall be provided to prevent influx of air through the pressure-relief port. The release pressure of the rupture disc shall be 20 psig (137.9 kPa gage) maximum. Large low-pressure ports shall not be used.

3-1.5 A minimum 2-in. (50.8-mm) clearance shall be maintained at all times between the electrode and the crucible wall by proper design and proper alignment of the electrode.

3-1.6 The furnace shall be equipped with a device that continuously senses pressure within the furnace and shall automatically interrupt power if the pressure rises to a minimum of 5 psig (34.5 kPa gage).

3-1.7 The furnace shall be equipped with:

(a) water flow, temperature, and pressure sensors on all cooling systems;

(b) arc voltage and amperage recorders;

(c) electrode position indicators;

(d) furnace pressure sensors and recorders.

Set point alarms shall be provided on all systems to warn of abnormal conditions.

3-2* Casting.

3-2.1 Caution shall be used in the handling and storage of ingots that have been wetted during the melting process. Such ingots contain internal stresses which may cause them to shatter, even up to several days after being wetted.

3-2.2 Suitable interlocks shall be provided to prevent operation of the casting crucible without adequate coolant flow.

3-2.3 Molds for titanium casting may be of metal, graphite, ceramic, or a combination of these materials. In all cases, molds shall be thoroughly dried and carefully stored to prevent accumulation of moisture in the molds.

3-2.4 Mold breaks are inevitable. Therefore, the casting section shall be cooled or shall be sufficiently massive to accommodate a spill, or both.

3-3 Fire Prevention.

3-3.1 Titanium sponge and alloys shall be stored in drums or tote bins with lids in place at all times.

3-3.2 Ordinary combustibles, such as paper, wood, cartons, packing material, etc., shall not be stored or allowed to accumulate in sponge blending, melting, or casting buildings.

3-3.3 Residue from melting furnaces, especially from first melts of magnesium-reduced sponge, shall be moved outside the building and placed in steel boxes for haulage to dumping areas. Collection boxes shall be kept a safe distance from all buildings. Other combustible wastes shall be placed in a separate noncombustible container and not mixed with melting residue.

3-3.4 Dry dust collectors used in collecting fines from blending, splitting, and pressing operations shall be emptied daily.

3-3.5 All sponge handling equipment shall be thoroughly cleaned, preferably by washing with water, before attempting any welding on the equipment or close to it. All welding shall be controlled by a permit system.

3-3.6 All sponge handling and storage areas shall be clearly posted with No Smoking signs.

3-4 Fire Protection.

3-4.1* Portable fire extinguishers shall be provided according to NFPA 10, *Standard for Portable Fire Extinguishers*.

3-4.1.1 Only extinguishers suitable for use on Class D fires shall be used on metal fires. A water-base extinguisher (soda-acid, foam, or pressurized water) shall not be used.

3-4.2 Small titanium fires may be controlled by the use of dry metal powder, flux, or dry salt. Burning material shall be removed from the equipment and the building as fast as possible.

3-4.3* Automatic sprinkler protection, if required by the authority having jurisdiction, shall be installed according to NFPA 13, *Standard for the Installation of Sprinkler Systems*.

3-5 Personnel Safety Precautions.

3-5.1 Control consoles for water-cooled melting and casting operations shall be located remote from melting areas and outside of furnace vaults.

3-5.2 Personnel shall be prevented from entering furnace vaults or pits of water-cooled furnaces during melting operations.

3-5.3 Personnel entering furnace shells to conduct inspections or repair work shall first make certain that any inert gas has been purged from the shell and that all pyrophoric residue has been removed.

3-5.4 Personnel working around NaK-cooled furnaces shall wear face shields in addition to other protective clothing when loading, unloading, or repairing furnaces.

3-6 Ingot Storage and Shipment.

3-6.1 Since all commercial titanium ingots are round, special tongs shall be used for handling.

3-6.2 When lying on the floor, ingots shall be kept in saddles to prevent rolling.

Chapter 4* Mill Operations

4-1 Fire Prevention.

4-1.1 Good housekeeping shall be required. Ordinary combustibles shall not be stored or discarded around mill equipment or in working areas of mill operations, especially dry grinding operations where hot sparks are prevalent.

4-1.2 Fuel lines to gas- or oil-fired furnaces or other heating equipment shall be equipped with emergency shutoff valves installed at an accessible location remote from equipment being served. All lines and fittings shall be inspected regularly to detect corrosion or mechanical damage that might permit leaks to develop. (*See NFPA 86, Standard for Ovens and Furnaces.*)

4-1.3 Open tanks in which flammable solvents are used for degreasing or pickling shall comply with NFPA 34, *Standard for Dipping and Coating Processes Using Flammable or Combustible Liquids*.

4-1.4 When mobile bins on casters are used to transport oily crushed turnings, raw lathe turnings, or swarf, bin-to-floor ground straps shall be used to minimize possible sparking from static electricity. Sawing, grinding, and cutting equipment shall also be grounded. (*See NFPA 77, Recommended Practice on Static Electricity.*)

4-1.5 Oily crushed lathe turnings, raw turnings, and swarf shall be collected in closed-top metal containers and removed daily to a safe storage or disposal area.

4-1.6 Forge presses, heavy grinders, and other milling equipment operated by hydraulic systems shall use a nonflammable oil. Oil leaks shall be repaired immediately and leakage kept to a minimum. Cleanliness is required in areas where hot metal is handled or where sparks are produced and bits of scale are continuously being dropped.

4-1.7 No welding or torch cutting shall be peformed in the mill process area unless authorized by a permit system.

4-1.8 Smoking shall not be permitted in operating, storage, or disposal areas.

4-1.9 Nonflammable water-soluble coolants shall be used for wet grinding, cutting, or sawing operations. Coolant shall be filtered on a continuous basis and filter cake shall be removed daily to a safe storage or disposal area.

4-1.10 Dry grinding and cutting operations shall be equipped with liquid precipitation separators and fume collection equipment. Sludge shall be removed daily to a safe, remote storage or disposal area. Fume ducts shall be flushed with water at regular intervals. (*See Section 5-6.*)

4-2 Fire Protection.

4-2.1 Dry salt or dry powder suitable for use on Class D fires shall be used to control and extinguish titanium fires.

4-2.2 Carbon dioxide extinguishers may be used to stop reignition of fires on small, hot forgings or sheets during processing.

4-2.3 All mill buildings shall be provided with portable fire extinguishers according to NFPA 10, *Standard for Portable Fire Extinguishers.* (*See A-3-4.1.*)

4-3* Personnel Safety Precautions. Personnel operating mill equipment shall wear face shields, gloves, and proper protective clothing.

4-4 Mill Product Storage.

4-4.1 Finished products awaiting shipment shall be stored in an orderly manner with adequate aisle spacing.

4-4.2 The storage area shall be kept free of combustible materials.

Chapter 5 Machining and Fabrication

5-1 Machining Operations.

5-1.1 Titanium may be turned, milled, bored, sawed, ground, or abrasive cut with standard metalworking equipment.

5-1.2* Cutting tools shall be of proper design and shall be kept sharp for satisfactory work with titanium. The use of water-soluble cutting oils is considered standard for use with titanium.

5-2 Pressing and Forming.

5-2.1 Proper handling equipment and temperature-controlled heating furnaces shall be used for hot forging of titanium.

5-2.2 Normal fabrication techniques may be used for both cold and hot forming of titanium.

5-3 Welding.

5-3.1 All welding of titanium shall be carried out under an inert atmosphere, such as helium or argon, to avoid air contamination.

5-3.2 Welding of small assemblies may be carried out in inert gas-filled chambers.

5-3.3 Special shielding devices shall be used for larger assemblies where chambers are impractical.

5-4 Fire Prevention.

5-4.1 Work areas shall be cleaned daily and residue from operations shall be removed to a safe storage or disposal area.

5-4.2 Accumulations of swarf from sawing, grinding, machining, or abrasive cutting shall be cleaned up daily and removed to a safe storage or disposal area.

5-4.3 Combustible materials shall not be discarded in containers used for the collection of dust, swarf, or turnings.

5-4.4 Combustible materials shall not be stored in titanium working areas. Oil spills shall be cleaned up immediately, particularly in areas where dry grinding is done.

5-4.5 Smoking shall be prohibited in titanium working areas or in scrap collection and storage areas.

5-4.6 No open flames or electric or gas cutting or welding equipment shall be used for repair of machinery or for other purposes in titanium work areas while machinery is operating.

5-4.6.1 If the use of cutting or welding equipment becomes absolutely necessary, all machines that produce fines or dust shall be shut down and the entire area where the cutting or welding is to be done shall be thoroughly cleaned by a water flush to remove all accumulations of fines, dust, and other combustible material.

5-4.6.2 The provisions of 5-4.6.1 also shall apply to fume exhaust and dust collection ductwork.

5-4.6.3 All cutting or welding shall be done under the supervision of a responsible person who has adequate fire fighting apparatus at his/her disposal and who is thoroughly trained in its use. That person shall be assigned no other duties during the cutting or welding operations.

5-4.7 All scrap material shall be stored according to the requirements of Chapter 6.

5-5 Fire Protection.

5-5.1 Suitable extinguishing agents for titanium fires shall be kept within easy reach of every operator performing machining, grinding, or other operations on titanium.

5-5.2 Extinguishing agents shall be kept in substantial containers with easily removable covers. A hand scoop shall be provided at each container for applying the agent.

5-5.3 Containers of extinguishing agents shall be clearly labeled.

5-5.4 Where automatic sprinkler protection is provided for areas where titanium parts or assemblies are machined, fabricated, or stored, finely divided titanium metal or swarf shall not be stored.

5-6 Dust Collection.

5-6.1 Dust shall be collected by means of suitable hoods or enclosures at each dust-producing operation. The hoods or enclosures shall be connected to liquid precipitation separators and the suction unit installed so that the dust is converted to sludge without contact, in the dry state, with any high-speed moving parts. [*See Figures 5-6.1 (a), (b), and (c).*]

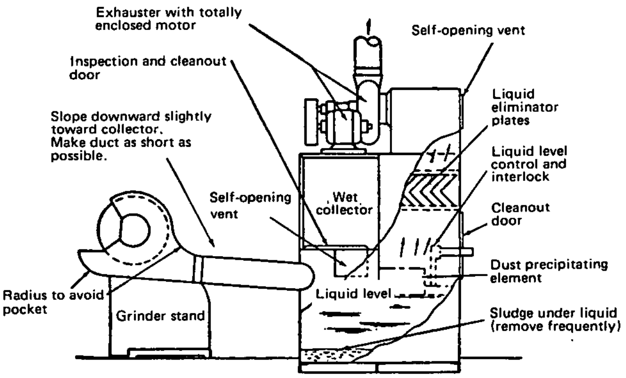

Figure 5-6.1 (a) Typical Liquid Precipitation Separator for a Fixed Grinding Unit.

NOTE: This drawing is schematic and intended only to indicate some of the features that are incorporated in the design of a separator. The volume of all dust-laden air spaces is as small as possible.

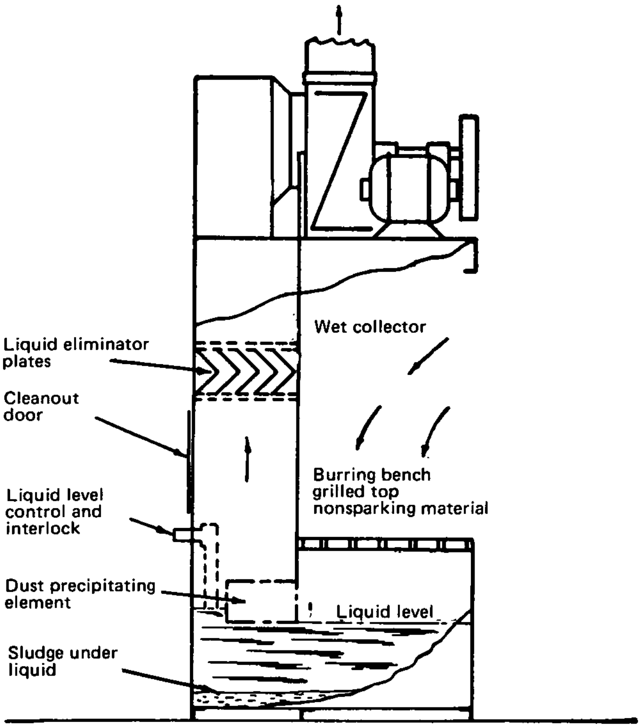

Figure 5-6.1 (b) Typical Liquid Precipitation Separator for a Portable Grinding Unit. [*See Note under Figure 5-6.1 (a).*]

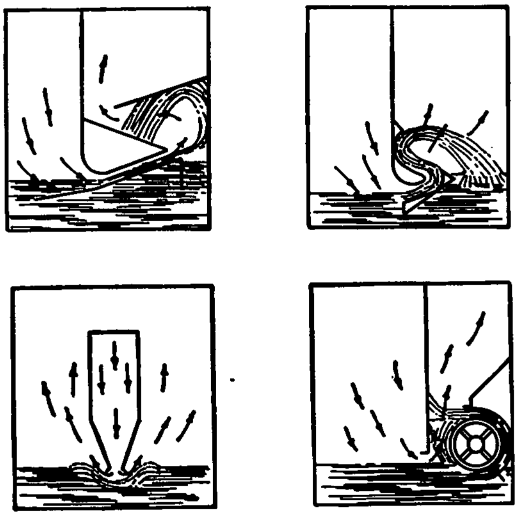

Figure 5-6.1 (c) Diagram of Four Methods of Precipitating Dust Used in Precipitators such as Those Shown in Figures 5-6.1 (a) and (b).

5-6.2 Connecting ducts or suction tubes between points of collection and separators shall be completely bonded and grounded. Ducts and tubes shall be as short as possible, with no unnecessary bends. Ducts shall be fabricated and installed according to NFPA 91, *Standard for the Installation of Blower and Exhaust Systems.*

5-6.3 Each dust-producing machine shall be equipped with its own dust-separating unit.

Exception: With multiunit machines, two dust-producing machines may be served by a single separator.

5-6.4 Not more than four portable dust-producing machines in a single enclosure or stand may be served by a single separator.

5-6.5 The power supply to the dust-producing equipment shall be interlocked with the motor driving the exhaust blower and the liquid level controller of the separator so that improper functioning of the dust collection system will shut down the equipment it serves. A time delay switch or equivalent devices shall be provided on the dust-producing equipment to prevent starting of its motor drive until the separator is in complete operation and several air changes have swept out any residual hydrogen.

5-6.6 Systematic cleaning of the entire building containing dust-producing equipment, including roof members, pipes, conduits, etc., shall be conducted daily or as conditions warrant. Cleaning shall be done by soft brushes and nonsparking scoops and containers or by fixed suction pipe vacuum cleaning systems.

5-6.6.1 Vacuum cleaning systems shall be used only if the dust collector is a liquid precipitation separator and if the suction piping system consists of mild steel pipe and standard recessed drainage fittings with a check valve at each outlet. Implements and hose shall be bonded and grounded. A rupture diaphragm shall be provided in the piping at its connection to the inlet side of the separator so that a possible explosion in the suction pipe system may be safely vented.

5-6.7 Sludge from dust separators and vacuum cleaning system precipitators shall be removed daily. Covered, vented steel containers shall be used to transport collected sludge to a safe storage area or for disposal by mixing with sand (in a ratio of one part sludge to five parts sand) and buried.

5-7 Personnel Safety Precautions.

5-7.1 Safety glasses or goggles and protective clothing shall be required for all operating personnel. Maintenance personnel and material handlers shall wear hard hats and safety shoes.

5-7.2 All working areas and aisleways shall be properly lighted and kept free of obstructions.

5-7.3 Personnel working in dusty areas or operating dust-producing equipment shall wear respiratory protection.

5-7.4 Welding and cutting areas shall be properly ventilated.

Chapter 6* Scrap Generation, Processing, and Storage

6-1 Fire Prevention and Storage.

6-1.1 Titanium fines shall be solvent-wetted to reduce the fire and dust explosion hazard.

6-1.2 Areas used for torch cutting of massive pieces of scrap shall be kept free of combustible materials. Swarf shall be collected daily and removed to a disposal area.

6-1.3* Oily lathe turnings and swarf shall be stored in small covered containers no larger than bucket size in well-ventilated areas or in enclosed outside areas remote from buildings.

6-1.4 No Smoking signs shall be posted around all scrap processing and storage areas.

6-1.5 Open storage of sheet, plate, forgings, or massive pieces of scrap presents no fire problems and shall be permitted.

6-1.6 Fire protection requirements shall be as set forth in Section 2-6.

6-2 Personnel Safety Precautions.

6-2.1 Personnel operating scrap torch cutting equipment shall wear gloves, face shields, high-top shoes, and protective clothing.

6-2.2 Personnel involved in pickling of massive pieces of scrap shall wear gloves, face shields, and protective clothing.

Chapter 7* Powder Production and Use

7-1 Shipping and Storage.

7-1.1 Because of the flammable and explosive character of titanium powder, special precautions shall be observed.

7-1.1.1 When conditions permit, titanium powder shall be shipped wet with not less than 20 percent water in tightly closed cans packed within a damageproof overpack.

7-1.1.2 Where specifications do not allow wet shipment, the powder shall be shipped in a steel container that has been flushed with argon prior to filling. The powder containers shall be packed within a similar steel container.

7-1.2 Drying of wetted powder shall be accomplished at a temperature not exceeding 110°C.

7-1.2.1 Drying rooms shall be of Type I construction, as defined by NFPA 220, *Standard on Types of Building Construction*. They shall be segregated as far as possible from other operations. Explosion venting for drying rooms shall be considered.

7-1.3 Storage of titanium powder shall be in sealed containers in well-ventilated areas, kept free of combustibles. The containers shall be protected from damage.

7-2 Handling.

7-2.1 Special care shall be taken to prevent spills or dispersions that may produce dust clouds. Requirements of Section 7-1 shall be complied with.

7-2.2 Special temperature controls shall be required on sintering furnaces handling titanium parts fabricated from powder. Powder or dust shall not be allowed to accumulate in the furnace or near the heating elements. Furnaces shall be provided with inert atmospheres.

7-3 Fire Prevention.

7-3.1 All electrical equipment in production, drying, and packing areas shall be approved for Class II, Group E atmospheres and shall be installed according to the requirements of NFPA 70, *National Electrical Code*.

7-3.2 Nonsparking tools and utensils shall be used in handling titanium powder. All metal objects or equipment shall be properly bonded and grounded to prevent accumulations of static electricity. (*See NFPA 77, Recommended Practice on Static Electricity.*)

7-3.3* All mixing and blending of dry titanium powder under 300 mesh particle size shall be done in an inert atmosphere. Coarse powders (under 100 mesh) may be safely blended in a standard U-type blender without inert atmosphere.

7-3.4 All possible precautions shall be taken to prevent the formation of dust clouds and to eliminate sources of ignition.

7-3.5 Where titanium powder presents a dust explosion hazard, the requirements of NFPA 651, *Standard for the Manufacture of Aluminum and Magnesium Powder*, shall be complied with.

7-3.6 Smoking shall be prohibited in any area or room where titanium powder is produced, handled, packaged, or stored.

7-3.7 Electric arc or gas torch welding shall not be permitted in any room where titanium powder is produced, handled, packaged, or stored until all powder has been removed and all equipment thoroughly washed.

7-4 Fire Protection.

7-4.1 Very small fires in titanium powder shall be controlled and extinguished by extinguishing agents approved for Class D fires. Burning titanium powder shall be isolated as much as possible to prevent spread of fire.

7-4.2 Water shall not be used as an extinguishing agent.

7-4.3 A fire within an individual container may be extinguished or controlled with a flush of argon gas.

7-5 Personnel Safety Precautions.

7-5.1 Personnel handling dry titanium powder shall wear nonsparking shoes and noncombustible or flame retardant clothing without pockets, cuffs, laps, or pleats in which powder may accumulate.

7-5.2 Personnel shall also use goggles or face shields that will provide protection against flash burns.

Chapter 8 Referenced Publications

8-1 The following documents or portions thereof are referenced within this document and shall be considered part of the requirements of this document. The edition indicated for each reference shall be the current edition as of the date of the NFPA issuance of this document. These references shall be listed separately to facilitate updating to the latest edition by the user.

8-1.1 NFPA Publications. National Fire Protection Association, Batterymarch Park, Quincy, MA 02269.

NFPA 10-1984, *Standard for Portable Fire Extinguishers*

NFPA 13-1987, *Standard for the Installation of Sprinkler Systems*

NFPA 34-1987, *Standard for Dipping and Coating Processes Using Flammable or Combustible Liquids*

NFPA 70-1987, *National Electrical Code*

NFPA 91-1983, *Standard for the Installation of Blower and Exhaust Systems for Dust, Stock and Vapor Removal or Conveying*

NFPA *101*-1985, *Life Safety Code*

NFPA 220-1985, *Standard on Types of Building Construction*

NFPA 480-1987, *Standard for the Processing, Handling, and Storage of Magnesium*

NFPA 651-1987, *Standard for the Manufacture of Aluminum and Magnesium Powder.*

8-1.2 Other Publication.

The Chlorine Manual, Chlorine Institute, Inc., 342 Madison Avenue, New York, NY 10017.

Appendix A

This Appendix is not a part of the requirements of this NFPA document, but is included for information purposes only.

A-2-1.4 Floors should be slightly crowned to prevent accumulation of water in the vicinity of reduction furnaces.

A-2-3.2 Chlorine is a toxic nonflammable gas. (*For hazards, see NFPA 49, Hazardous Chemicals Data.*) It exists in both the liquid and gaseous phases in pressurized containers. All containers used in the transportation of chlorine, as well as the means of transportation, are controlled by the U.S. Department of Transportation.

A-2-4.1 Dry cyclone collectors are recommended where sponge is continuously fed from dryers.

A-2-6 Water and other liquids have proven ineffective in extinguishing titanium sponge fires. Streams of water intensify the fire by feeding oxygen to it. There is also the possibility of causing a steam or hydrogen explosion, particularly if large amounts of sponge are involved. The great affinity of high-temperature titanium for oxygen will free a considerable amount of hydrogen, which may reach explosive concentrations in confined spaces. Entrapment of water under any burning or hot metal may result in a steam explosion.

Experience has shown that dry sodium chloride is one of the most effective chemicals for containing titanium sponge or fines fires. Another effective chemical is a nonmetallic flux compound consisting of potassium chloride, magnesium chloride, and calcium fluoride. Commercial dry fire extinguishants approved for use on combustible metals are also effective. Covering the fire completely reduces the accessible oxygen supply, thereby slowing the burning rate so that eventual extinguishment is reached.

While automatic sprinkler systems may be used for offices, warehouses, and shops, they are not recommended for titanium sponge storage or processing areas, magnesium refineries, sodium storage areas, chlorinators, or blending facilities.

The use of inert gas (argon or helium) to extinguish titanium fires is practical only where small quantities of titanium are confined to small spaces.

A-2-6.3 Application of dry salt or a dry powder will tend to minimize the fire and contain it, but any container in which a fire occurs will usually become a total loss, along with the material contained.

A-2-6.4 Keeping the equipment in operation until all burning material is removed actually reduces damage to the equipment. Small amounts of burning material can be handled with a shovel to facilitate removal.

A-2-7.1 Titanium tetrachloride in contact with moist air or water hydrolyzes to form hydrogen chloride gas and hydrochloric acid. Hydrogen chloride is toxic and highly irritating to the respiratory tract. If not immediately removed, titanium tetrachloride in contact with the eyes or skin will result in a double burn, one caused by the acid, the other caused by the heat of reaction. Any skin that is contacted by titanium tetrachloride must be wiped immediately and then flushed with a large amount of water. Eyes splashed with titanium tetrachloride must also be flushed with copious amounts of water.

A-2-7.4 Chlorine gas is highly irritating to the eyes and respiratory tract. Canister-type gas masks are effective only to a maximum concentration of 1000 ppm.

A-2-7.6 Molten magnesium presents a potentially dangerous fire and fume hazard, in addition to an explosion hazard, if contacted with water.

A-2-7.7 Liquid sodium splashed on the skin should be wiped off with a soft cloth immediately and the affected area covered with mineral oil.

A-2-7.8 Magnesium chloride dust can be highly irritating to skin, especially if perspiration is present. Also, magnesium chloride will readily absorb moisture to create a slipping hazard.

A-3 Unlike other metals which can be melted, cast, or molded without unusual complications, titanium, because of its strong affinity for oxygen, hydrogen, and nitrogen and its tendency to become contaminated, must be melted in special water or NaK-cooled copper crucibles under a vacuum or with an inert gas blanket of argon or helium. During the early years of the titanium industry, melting was done with a nonconsumable electrode, usually carbon.

The consumable electrode process using direct current electricity was soon developed to meet quality and process equipments. Nonconsumable copper electrode furnaces are now being used to process scrap.

During the 1950s, several titanium melting furnace explosions occurred when water inadvertently entered the melting crucibles during the melting operation. Three distinct types of explosions were evident: steam explosions produced by water contacting molten metal; chemical reaction between the molten metal and water; explosion of free hydrogen generated by the chemical reaction. Also, if air entered the crucible at the same time, an air-hydrogen explosion would sometimes occur. All three types of explosions could occur in the same incident. The explosion hazard is present with any crucible that uses water as the coolant.

The use of liquid metal NaK (sodium-potassium alloy) as a crucible coolant has been developed for both laboratory and commercial installations. While the danger of furnace explosion due to leakage into the melt zone is reduced, the handling of NaK has its own inherent hazards. The reaction between NaK and water is violent.

A-3-2 The general process for shape casting of titanium is the "skull-casting" process where the material to be cast is melted as a consumable electrode in a tilting crucible. The power applied is normally somewhat higher than typical for ingot melting in order to develop a deep pool of molten metal. At the appropriate time in the melting cycle, the electrode is withdrawn and the casting poured. Vacuum or inert gas is provided to protect the metal from atmospheric contamination. The furnace crucible is made of copper and has water or NaK cooling. Due to the high power levels used, seams in the crucible should not be visible to the electric arc or the molten metal.

A-3-4.1 Water-base extinguishers suitable for use on Class A fires should only be used on fires in ordinary combustibles. Extinguishers suitable for Class B fires are recommended for fires in oil, grease, and most flammable liquids. Extinguishers suitable for Class C fires should be used for fires in electrical equipment.

A-3-4.3 Automatic sprinkler protection is not recommended for blending and melting buildings.

A-4 Forging remains the most popular method of forming titanium because it is generally simpler and less costly than other forming processes. Gas or electric furnaces with accurate heat control are used to heat the metal into the proper forging range, which may vary from 1600 to 2300°F (871 to 1260°C). The rate of heat-up and final temperature must often be precisely controlled to achieve specific metallurgical and physical properties. Slabs, billets, and bar stock are produced by forging.

Large rounds of titanium are produced by lathe turning or by grinding forges. A considerable amount of titanium strip, coil, and duct, down to foil thickness, is produced from slabs on both continuous and hand mills. Wide sheets and plates of various thicknesses are produced on hand mills or plate rolling mills. Temperature control during rolling is important. Shearing and straightening operations are necessary to trim sheet and plate to size, to straighten or flatten plate, or to straighten forged bar stock or extrusions. Titanium wire is produced from coils of rolled bar by drawing operations. Fastener stock is produced from coils of wire. Titanium tubing is produced by inert gas seam welding of rolled narrow strip. Heavy wall seamless tubing is produced by extrusion.

Special types of grinding operations are performed in mills. Swing grinders are used to spot grind ingots, slabs, billets, and bar stock. Centerless grinders are used to finish round bar and fastener stock. Strip in coil form is ground continuously and sheets are individually ground.

Cold saws and abrasive cut-off saws are used to cut billet and bar stock to length. Swarf, or finely divided metal particles, is produced by all sawing and grinding operations.

A-4-3 The wearing of hard hats, safety glasses or goggles, and safety shoes is recommended.

A-5-1.2 Improperly designed or dulled tools may produce high temperatures at the interface, causing ignition at the turnings, if an adequate coolant flow is not used.

A-6 Generation of titanium scrap from the sponge and melting processes through milling and fabrication is an inherent part of the titanium business. Scrap sponge, including some fines, is generated in the reduction, boring, crushing, leaching, and blending operations due to contamination and spills. Solid pieces of scrap titanium result in the melting process due to air or water contamination or due to malfunctions that cause interrupted melts.

During milling and fabrication, solid pieces of scrap result from forge, welding, and fabrication shops. Other scrap includes lathe turnings and sheet clippings. Swarf is produced by sawing and grinding operations.

Before recycling, lathe turnings and clippings are usually crushed and degreased with a water-soluble detergent. Solid scrap is more difficult to handle. In one process, large pieces are torch cut, then tumbled to remove slag, after which they are descaled in a basic chemical solution, washed in a sulfuric acid bath, and water-rinsed. Hydrogenation and crushing completes the preparation for recycling. Another method of handling fairly large chunks of titanium scrap is to weld them to the sides of consumable electrodes prior to melting.

A more recent development is the nonconsumable electrode furnace for melting scrap into ingot form. Equipped with a continuous feed through a vacuum interlock, these furnaces are capable of handling scrap pieces of baseball size.

A-6-1.3 When stored in the open for any length of time, the water-soluble oils gravitate to the base of the pile. The water evaporates, leaving the oily residue. If exposed to an ignition source, the oil may ignite and create enough heat to ignite the titanium. Sparks from the blades of earth-moving equipment have been known to cause ignition, followed by an explosive reaction in piles of turnings.

A-7 Not all methods of producing metal powder are applicable to titanium. Reduction of titanium hydride and some forms of milling are generally used to produce the limited amounts of powder now required commercially. To reduce oxidation and possible ignition hazards, milling may be performed under water or in an inert atmosphere of helium or argon. Some powders are given a very light copper coating during the manufacturing process.

Like many other metal powders, titanium is capable of forming explosive mixtures in air. The ignition temperatures of dust clouds, under laboratory test conditions, range from 330° to 590°C. The minimum explosive concentration is 0.045 oz per cu ft (0.045 kg per m^3). Maximum pressure produced in explosions in a closed bomb at a concentration of 0.5 oz per cu ft (0.5 kg per m^3) ranged from 46 to 81 psi (317 to 558 kPa). The average rate of pressure rise in these tests ranged from 250 to 4300 psi per sec (1724 to 29,650 kPa/sec); the maximum rate of pressure rise ranged from 550 to 10,000 psi per sec (3792 to over 68,950 kPa/sec). The minimum energy of electrical condenser discharge sparks required for ignition of a dust cloud was 10.0 millijoules; for a dust layer, the minimum value was 8 microjoules. Some samples of titanium powder were ignited by electric sparks in pure carbon dioxide, as well as in air. In some cases, titanium at elevated temperatures was found to react in nitrogen as well as in carbon dioxide. Titanium powder is considered a flammable solid. (*See NFPA 491M, Manual of Hazardous Chemical Reactions.*)

A-7-3.3 Tests have shown that the maximum oxygen concentrations allowed for different inert gases to prevent explosions are:

Carbon Dioxide	0 percent Oxygen
Nitrogen	6 percent Oxygen
Argon	4 percent Oxygen
Helium	8 percent Oxygen

Appendix B

Supplementary Information on Titanium

This Appendix is not a part of the requirements of this NFPA document, but is included for information purposes only.

B-1 History.

Titanium was discovered by William Gregor, an English clergyman who was an amateur chemist. The element he discovered in the black sands of Cornwall attracted no scientific interest at the time. A few years later, Klaproth extracted titanium from an ore called rutile. He named the element "Titanic Earth," for the Titans of Greek mythology.

Titanium was first produced in the United States in 1910 by Dr. M. A. Hunter of Rensselaer Polytechnic Institute. The basic process for producing titanium was developed by Wilhelm Kroll, a native of Luxembourg. His patent was vested by the U.S. Government during World War II. Experimentation was continued by the U.S. Bureau of Mines and, in 1946, the operation of a pilot plant producing titanium by the Kroll process was announced.

B-2 Commercial Production.

Commercial production of titanium began in 1948 in a plant whose capacity was less than 20 tons (18 140 kg) per year. By 1951, the fulfillment of the needs of the military had brought about tremendous strides in the titanium industry. Large-scale commercial production had become a reality.

Titanium-bearing ores are plentiful and widely scattered throughout the world, including the United States, the principal ores being rutile and ilmenite. At present, rutile is the more desirable of the two for recovery of titanium. However, it is the ore in shortest supply, coming primarily from deposits in Australia, South Africa, and Sierra Leone.

It is generally recognized that, in time, the greatest tonnage of titanium may be processed from ilmenite ore. Ilmenite mines in the United States are located at Tahawas, NY; Highland, Starke, and Green Cove Springs, FL; and Manchester, NJ.

Titanium sponge is currently produced in the United States, Japan, England, and the Soviet Union. Three basic processes have been developed for commercial refining of titanium from rutile ore. The most widely used processes use magnesium or sodium to reduce titanium tetrachloride. An electrolytic process has been proven to be practical and development of a commercial version is underway.

Titanium ingot is produced by arc-melting a consumable electrode of compacted sponge, or sponge and alloy, into a cooled copper mold under a low vacuum or an inert atmosphere.

B-3 Properties.

Titanium is a silver-grey light metal, about 60 percent heavier than aluminum, but only 56 percent as heavy as alloy steel. Its atomic weight is 47.90, specific gravity is 4.5, and melting point is 3140°F (1727°C). Titanium-based alloys are stronger than aluminum alloys and most alloy steels and have excellent ductility. They are superior to all the usual engineering metals and alloys in strength-weight ratio. Their fatigue resistance (ability to resist repeated flexures) is above that of heat-treated alloy steels and far greater than those of nonferrous metals. Titanium alloys are harder than aluminum and almost as hard as the high alloy steels. Surface hardness comparable to nitrided steel is obtainable.

Titanium is highly corrosion-resistant, being greatly superior to aluminum, considerably better than many specialty steels, and unique, compared to commonly available metals, in its immunity to saltwater and marine atmospheres. It is the only known structural metal that is highly resistant to simultaneous exposure to seawater and air. However, it is subject to stress corrosion cracking in methanol containing less than 0.8 percent water. Also, crevice corrosion can be expected in chlorine systems.

Titanium-based alloys may be subject to cracking during hot-forming operations if they are in contact with halide salts. Manufacturers' recommendations should be sought if applications are considered where high strength alloys are expected to come in contact with halide salts at temperatures above 500°F (260°C).

Impact resistance (capacity to withstand shock) of titanium is superior to that of aluminum; some titanium alloys approach heat-treated steel in impact resistance. Titanium alloys commonly lose strength above 1000°F (605°C) and may become embrittled after extended exposure to air at temperatures above 800°F (427°C).

Normal compositions of some widely used titanium alloys are:

Titanium 90 percent, Aluminum 6 percent, Vanadium 4 percent;

Titanium 92.5 percent, Aluminum 5 percent, Tin 2.5 percent;

Titanium 90 percent, Aluminum 8 percent, Molybdenum 1 percent, Vanadium 1 percent;

Titanium 86 percent, Aluminum 6 percent, Vanadium 6 percent, Tin 2 percent;

Titanium 92 percent, Manganese 8 percent.

Titanium presents some fire hazards during production of the raw sponge, melting of the sponge, casting, machining that produces fine turnings or chips, powder production and handling, and disposal of scrap containing chips or fines. However, because of its high temperature properties in solid form, titanium sheet is extensively used for fire walls in jet aircraft and spacecraft.

In molten form, titanium either dissolves or is contaminated by every known refractory.

Slight contaminations apparently have little effect on the flammable characteristics of chips, turnings, or powder produced in machining operations, but may have an important bearing on ignition and explosion hazards associated with acid or salt baths.

Titanium combines readily with oxygen, nitrogen, and hydrogen at temperatures considerably below its melting point. Freshly exposed surfaces tend to form an adherent oxide coating quickly. This oxide coating is evidenced by discoloration that will be dissolved as temperature increases. Excessive oxidation may cause embrittlement.

B-4 Tests for Titanium.

Two relatively simple methods are used to distinguish titanium from other metals.

(a) *Spark Test.* Distinctive sparks are thrown off when a piece of titanium is held against a grinding wheel. The white lines traced by the flying sparks end with a burst that produces several brilliant white rays or branches.

(b) *Glass Test.* The softer grades of titanium and titanium alloys are able to wet glass and can be identified by rubbing a moistened piece of the metal on a piece of glass. If the metal is relatively soft titanium, it will leave distinctive grey-white marks on the glass.

A portable metal spectroscope will better serve the purpose when attempting to identify titanium scrap by grade.

B-5 Applications.

While titanium has many uses, production is still largely consumed by commercial and military aircraft production for use in jet engines, aircraft frames, and outer skin covering on subsonic and supersonic aircraft. Titanium is also being used in space vehicles and communication satellites. Other military uses include armor plate, electrical components, pontoons, cables, structural braces, fire walls, personnel helmets, and protective vests.

Titanium's virtually complete immunity to atmospheric and saltwater corrosion and to such agents as wet chlorine, nitric acid, and most oxidizing chemicals makes it attractive for chemical process applications such as heat exchangers, dryers, mixers, and other equipment.

Specially prepared, very finely divided titanium powders find limited application in powder metallurgy and other relatively small-scale uses.

B-6 Combustibility and Explosibility.

In tests conducted by the U.S. Bureau of Mines with titanium powders of less than 200 mesh, ignition of dust clouds in air was obtained at temperatures from 330°C to 590°C. Ignition of dust layers occurred at temperatures from 380°C to 510°C. In some cases, dust clouds ignited at lower temperatures than static layers of the same dust. (*See Report of Investigations 3722 and 4835, listed in Appendix C-1.2.*) Titanium fines, nominally under 48 mesh, a by-product of sponge production and handling, and coarser particles, such as swarf from sawing and grinding operations, can be ignited by a spark.

Tests conducted by Underwriters Laboratories Inc. showed that dry ductile titanium in the form of thin chips and fine turnings could be ignited with a match. Normal size machine chips and turnings ignited and burned when heated in the flame of a Bunsen or blast burner. When ignited, titanium sponge or coarse turnings burn slowly with the release of a large quantity of heat, although a sponge fire may spread rather rapidly immediately after ignition.

Heavy castings or ingots of titanium may give some indication of burning when being cut with an oxyacetylene torch, but when enough surface is available to permit radiation cooling below the ignition temperature, burning ceases when the torch is removed.

Titanium can burn in atmospheres other than air. For example, one titanium powder sample, which ignited in air as a cloud at 480°C and as a layer at 470°C, also ignited as a layer in pure carbon dioxide at 680°C. At red heat, about 704°C, titanium will decompose steam to free hydrogen and oxygen. Above 801°C, titanium burns readily and vigorously in atmospheres of pure nitrogen.

Titanium will burn in the presence of dry chlorine or oxygen at room temperature. In oxygen, the combustion is not spontaneous and only occurs with oxygen concentration above 35 percent at pressures over 350 psig (2445 kPa gage) when a fresh surface is created. The actual hazard in air is much less than that for aluminum.

B-7 Special Hazards.

In spite of titanium's superior resistance to corrosion, as discussed in Section B-5, titanium may react vigorously or even explosively with some hazardous materials. For example, extreme care should be taken when using titanium metal or powder in red fuming nitric acid. While no problems have been reported with normal nitric acid, explosions have occurred in laboratory tests with titanium and red fuming nitric acid. These incidents have never been completely explained, although it is believed that the strength of the acid is a controlling factor and that some pyrophoric material is produced which, when disturbed, releases enough heat to permit rapid oxidation of the metal. Potentially hazardous reactions between titanium and various chemicals are listed in NFPA 491M, *Manual of Hazardous Chemical Reactions.*

Low melting eutectics may form when titanium or its alloys are in contact with metals such as iron, nickel, or copper at high temperatures. Phase diagrams for titanium, such as those in the *ASME Handbook: Metals Properties*, should be consulted in such potential situations.

Titanium engages in thermite-type reactions with iron oxides.

Caution should be exercised in introducing titanium into process environments not previously investigated, since titanium may react and, in some cases, become pyrophoric.

B-8 Spontaneous Combustion.

Spontaneous ignition has occurred in fine, water-soluble oil-coated titanium chips and swarf. Such fires, while probably due mostly to the presence of oil and certain contaminants, are very difficult to control and special precautions must be taken to have all fine scrap and oil-covered material removed from the plant and stored where any possible fire can be segregated and prevented from exposing other combustible material. Dry titanium fines collected in cyclones have, on occasion, ignited spontaneously when allowed to drop freely through the air. Also, sump fines will often ignite when they are dried.

During the early stages of the development of the titanium industry, thin titanium sheets were reported to have ignited spontaneously as they were removed from a sodium hydride descaling bath. However, the use of a potassium hydride solution in recent years has eliminated this problem.

Like any other metal in the high temperature molten state, titanium can cause a violently destructive explosion if water is present in any mold, pit, or depression into which the molten metal is poured or spilled. Under such circumstances, severe damage may be caused by steam pressure, an exothermic chemical reaction, or a low order hydrogen-air explosion.

In the 1950s, several violent explosions occurred in consumable electrode furnaces when water entered the furnace because of a crucible failure. The failures resulted from loss of cooling water flow and severe arc-through. A committee of industry representatives then prepared a set of general recommendations on design of melting furnaces to improve process safety. Their recommendations, given consideration in this standard, have been published by the Defense Metals Information Center of Battelle Memorial Institute. (*See Section C-1.2.*)

B-9 Process Description.

Current titanium production processes involve reduction of titanium tetrachloride to titanium metal. The titanium tetrachloride ($TiCl_4$) is made from rutile ore (approximately 95 percent titanium dioxide) by high temperature reaction with chlorine in the presence of a reducing agent, usually carbon. There are two basic commercially used processes for reduction of titanium: the Kroll-Bureau of Mines process, which uses magnesium as the reducing agent, and the Sodium process, which uses liquid sodium as the reducing agent. Pilot plant work to develop a commercial electrolytic process is under way. The resulting product of all of the processes is referred to as titanium sponge.

In the Kroll-Bureau of Mines process, purified titanium tetrachloride is fed into a steel reaction chamber containing molten magnesium. The reduction takes place under an inert gas blanket of argon or helium and at temperatures between 700° and 900°C. The products of the reduction are magnesium chloride and titanium sponge, so called because of the spongy appearance of the titanium. The magnesium chloride is drawn off in the molten state for recycle or for reprocessing to magnesium and chlorine. After cooling, the sponge mass is bored from the reactor vessel and crushed in a "dry room." Any residual magnesium or magnesium chloride is removed by acid leaching or vacuum distilling. A modified version of the Kroll process involves vacuum distillation in the reaction vessel before removal of the sponge, thus eliminating the dry room. A detailed description of the Kroll process and equipment is contained in the Bureau of Mines' Report of Investigations No. 4879. Another description by Powell appears in *Chemical Engineering Progress*, November, 1954. (*See Section C-1.2 for references.*)

In the sodium reduction process, liquefied sodium is used as the reducing agent. In this process, the reaction vessel is heated to approximately 1000°C and no withdrawal of by-product during the reduction cycle is required. After completion of the reduction cycle, the reactor contains a solid mixture of titanium sponge and sodium chloride (called "spalt"). After the cooling cycle, this solid mixture is usually bored from the reaction vessel. A dry room is not required. The spalt is vacuum dried after removal from the reaction vessel. The sodium reduction process is described by Forbath in *Chemical Engineering*, March, 1958.

In the electrolytic process being developed, titanium tetrachloride is fed into a cell containing a molten salt bath (usually sodium chloride), where it is reduced to crystalline metal by fused salt electrolysis. The crystalline mass must be crushed, leached, and dried after removal from the cell. Although this process is commercially feasible, it has not yet been used significantly.

The titanium sponge fire risk is affected by the process used. The sodium reduction process and the electrolytic process produce a sponge that is less apt to be pyrophoric than magnesium reduced sponge. The fines resulting from the crushing operation of these two processes, likewise, tend to be less pyrophoric.

Appendix C Referenced Publications

C-1 The following documents or portions thereof are referenced within this document for informational purposes only and thus are not considered part of the requirements of this document. The edition indicated for each reference should be the current edition as of the date of the NFPA issuance of this document. These references should be listed separately to facilitate updating to the latest edition by the user.

C-1.1 NFPA Publications. National Fire Protection Association, Batterymarch Park, Quincy, MA 02269.

NFPA 49-1975, *Hazardous Chemicals Data*

NFPA 68-1978, *Guide for Explosion Venting*

NFPA 69-1986, *Standard on Explosion Prevention Systems*

NFPA 77-1983, *Recommended Practice on Static Electricity*

NFPA 86-1985, *Standard for Ovens and Furnaces*

NFPA 491M-1986, *Manual of Hazardous Chemical Reactions.*

C-1.2 Other Publications.

ASME Handbook: Metals Properties, New York, NY, Society of American Mechanical Engineers, 1980

Chemical Engineering, March, 1958, Forbath, T.P., "Sodium Reduction Route Yields Titanium," pp. 124-127

Chemical Engineering Progress, November, 1954, Powell, R.L., pp. 578-581

Code of Federal Regulations, 49 CFR 100-199, Washington, DC, U.S. Department of Transportation, 1977

"Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium and their Hydrides," *Report of Investigations* 4835, Pittsburgh, PA, U.S. Bureau of Mines, 1951

General Recommendations on Design Features for Titanium and Zirconium Production Melting Furnaces, Columbus, OH, Defense Metals Information Center, Battelle Memorial Institute

"Inflammability and Explosibility of Metal Powders," *Report of Investigations* 3722, Pittsburgh, PA, U.S. Bureau of Mines, 1943

"Recent Practice at the Bureau of Mines," Boulder City, NV Plant, *Report of Investigations* 4879, Pittsburgh, PA, U.S. Bureau of Mines, 1951.

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SUBMITTING PROPOSALS ON NFPA TECHNICAL COMMITTEE DOCUMENTS

Contact NFPA Standards Administration for final date for receipt of proposals on a specific document.

INSTRUCTIONS

Please use the forms which follow for submitting proposed amendments.
Use a separate form for each proposal.

1. For each document on which you are proposing amendment indicate:
    (a) The number and title of the document
    (b) The specific section or paragraph.

2. Check the box indicating whether or not this proposal recommends new text, revised text, or to delete text.

3. In the space identified as "Proposal" include the wording you propose as new or revised text, or indicate if you wish to delete text.

4. In the space titled "Statement of Problem and Substantiation for Proposal" state the problem which will be resolved by your recommendation and give the specific reason for your proposal including copies of tests, research papers, fire experience, etc. If a statement is more than 200 words in length, the technical committee is authorized to abstract it for the Technical Committee Report.

5. Check the box indicating whether or not this proposal is original material, and if it is not, indicate source.

6. If supplementary material (photographs, diagrams, reports, etc.) is included, you may be required to submit sufficient copies for all members and alternates of the technical committee.

NOTE: The NFPA Regulations Governing Committee Projects in Paragraph 10-10 state: Each proposal shall be submitted to the Council Secretary and shall include:

(a) identification of the submitter and his affiliation (Committee, organization, company) where appropriate, and

(b) identification of the document, paragraph of the document to which the proposal is directed, and

(c) a statement of the problem and substantiation for the proposal, and

(d) proposed text of proposal, including the wording to be added, revised (and how revised), or deleted.