

# NFPA 481

## Standard for the Production, Processing, Handling, and Storage of Titanium

1995 Edition

NFPA Technical Committee  
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National Fire Protection Association, 1 Batterymarch Park, PO Box 9101, Quincy, MA 02269-9101  
An International Codes and Standards Organization

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## **NFPA 481**

### **Standard for the**

## **Production, Processing, Handling, and Storage of Titanium**

### **1995 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 Metal Dusts and acted on by the National Fire Protection Association, Inc., at its Annual Meeting held May 22-25, 1995, in Denver, CO. It was issued by the Standards Council on July 21, 1995, with an effective date of August 11, 1995, and supersedes all previous editions.

This edition of NFPA 481 was approved as an American National Standard on August 11, 1995.

### **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.

The 1987 edition was a reconfirmation of the 1982 edition.

For this 1995 edition, the Committee has completely revised the standard to update the fire and dust explosion prevention measures and the requirements for safe handling of titanium solids and powders. The Committee revision has also incorporated editorial and style revisions to comply with the NFPA Manual of Style and to assist in making the document more usable, adoptable, and enforceable.

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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.

**Committee Scope:** This Committee shall have primary responsibility for documents on safeguards against fire and explosion in the manufacturing, processing, handling, and storage of combustible metals, powders, and dusts.

## Contents

<b>Chapter 1 General</b> .....	481- 4	5-3 Titanium Dust Collection .....	481- 6
1-1 Scope .....	481- 4	5-4 Compressed Air Fittings .....	481- 6
1-2 Purpose .....	481- 4	<b>Chapter 6* Scrap Storage</b> .....	481- 7
1-3 Equivalency .....	481- 4	6-1 Storage .....	481- 7
1-4 Applicability .....	481- 4	<b>Chapter 7* Titanium Powder Production and Use</b> .	481- 7
1-5 Definitions .....	481- 4	7-1 Drying and Storage of Titanium Powder ..	481- 7
<b>Chapter 2 Sponge Production</b> .....	481- 4	7-2 Titanium Powder Handling .....	481- 7
2-1 Plant Construction .....	481- 4	7-3 Personnel Safety Precautions .....	481- 7
2-2 Processing Equipment .....	481- 5	<b>Chapter 8 Fire Prevention and Fire Protection</b> . . . .	481- 7
2-3 Storage of Raw Materials .....	481- 5	8-1 Fire Prevention .....	481- 7
2-4 Dust Collection .....	481- 5	8-2 Fire Protection .....	481- 8
2-5 Personnel Safety Precautions .....	481- 5	<b>Chapter 9 Referenced Publications</b> .....	481- 8
2-6 Sponge Storage .....	481- 5	<b>Appendix A Explanatory Material</b> .....	481- 8
<b>Chapter 3* Titanium Melting</b> .....	481- 5	<b>Appendix B Supplementary Information</b>	
3-1 Explosion Prevention .....	481- 5	on Titanium .....	481-13
3-2 Casting .....	481- 5	<b>Appendix C Referenced Publications</b> .....	481-15
<b>Chapter 4* Mill Operations</b> .....	481- 6	<b>Index</b> .....	481-16
4-1 Fire Prevention .....	481- 6		
<b>Chapter 5 Machining and Fabrication</b> .....	481- 6		
5-1 Machining Operations .....	481- 6		
5-2 Welding .....	481- 6		

## NFPA 481

## Standard for the

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

Information on referenced publications can be found in Chapter 9 and Appendix C.

## Chapter 1 General

## 1-1 Scope.

**1-1.1** This standard shall apply to the production, processing, handling, and storage of titanium.

**1-1.2** This standard shall also apply to finished parts and those materials, including scrap, that exhibit the burning characteristics of titanium.

**1-1.3** This standard shall not apply to the transportation of titanium in any form on public highways and waterways, or by air or rail.

**1-1.4** This standard shall not apply to those laboratories handling hazardous chemicals as defined in NFPA 45, *Standard on Fire Protection for Laboratories Using Chemicals*.

**1-2\* Purpose.** The purpose of this standard shall be to provide requirements addressing the fire and explosion hazards of titanium and titanium alloys and to outline requirements for fire prevention and protection.

**1-3 Equivalency.** Nothing in this standard shall be intended to prevent the use of systems, methods, or devices of equivalent or superior quality, strength, fire resistance, effectiveness, durability, and safety over those prescribed by this standard, provided technical documentation is made available to the authority having jurisdiction to demonstrate equivalency and the system, method, or device is approved for the intended purpose.

**1-4 Applicability.** The provisions of this document shall be considered necessary to provide a reasonable level of protection from loss of life and property from fire and explosion. They reflect situations and the state-of-the-art prevalent at the time the standard was issued. Unless otherwise noted, it shall not be intended that the provisions of this document be applied to facilities, equipment, structures, or installations that were existing or approved for construction or installation prior to the effective date of the document, except in those cases where it is determined by the authority having jurisdiction that the existing situation involves a distinct hazard to life or adjacent property.

**1-5 Definitions.** For the purpose of this standard, the following terms shall have the meanings given below.

**Approved.\*** Acceptable to the authority having jurisdiction.

**Authority Having Jurisdiction.\*** The organization, office, or individual responsible for approving equipment, an installation, or a procedure.

**Labeled.** Equipment or materials to which has been attached a label, symbol, or other identifying mark of an organization that is 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.

**Media Collector.** Refers to either a bag house or a filter-type cartridge collector used for collecting dust.

**Shall.** Indicates a mandatory requirement.

**Should.** Indicates a recommendation or that which is advised but not required.

**Titanium.** Refers to either pure metal or alloys having the generally recognized properties of titanium metal, including the fire or explosion characteristics of titanium in its various forms.

**Titanium Chips.\*** Particles produced from a cutting, machining, or grinding operation that are not oxidized and that are not diluted by noncombustible materials.

**Titanium Dust.\*** Any finely divided titanium material 420 microns or smaller in diameter (material passing U.S. No. 40 Standard Sieve) that presents a fire or explosion hazard when dispersed and ignited in air.

**Titanium Fines.** Titanium particles typically 20 mesh and below that can be ignited in a static layer.

**Titanium Powder.\*** See Titanium Dust and Titanium Fines.

**Titanium Sponge.\*** Titanium metal after it has been won from the ore but before it is melted into ingot.

**Titanium Swarf.** Particles produced from a cutting, machining, or grinding operation that causes partial oxidation of the parent material or dilution by other inert materials.

## 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 in accordance with current accepted practices.

**2-1.2** Building exits shall comply with NFPA 101®, *Life Safety Code*®.

**2-1.3\*** Floors in reduction, boring, and crushing buildings shall be made of noncombustible materials, such as concrete, brick, or steel plates.

**2-1.4** Magnesium refining and casting operations shall be protected from rain, and all possibilities of water spillage shall be avoided.

## **2-2 Processing Equipment.**

**2-2.1** Reactor vessels shall be air-cooled.

*Exception: Magnesium reduction-sealed vessels shall be permitted to be water-cooled and designed to prevent water from entering the reaction vessel.*

**2-2.2** Furnaces shall be kept dry and free of iron scale and metal spillage.

**2-2.3** Fuel supply lines to gas-fired furnaces shall have an emergency shutoff valve located within easy access outside of the building that contains the reduction furnaces.

NOTE: For information on emergency gas shutoff valves, see NFPA 54, *National Fuel Gas Code*.

**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 Storage, Handling, and Processing of Magnesium Solids and Powders*.

**2-3.2\*** Chlorine shall be handled and stored in accordance with accepted industry practice.

**2-3.3\*** Bulk containers of liquid titanium tetrachloride ( $\text{TiCl}_4$ ) shall be stored in a well-ventilated place located away from areas of acute fire hazard. Containers shall be plainly identified and tightly sealed until used.

## **2-4 Dust Collection.**

**2-4.1** Dust resulting from the crushing of titanium sponge shall be safely managed to minimize the risk of fires and explosions.

**2-4.2** Media collectors shall not be used for the collection of titanium sponge fines.

**2-4.3** Dry collectors shall be emptied before or when 80 percent of the storage capacity of the collector is attained. The maximum volume of titanium fines collected before emptying shall not exceed 5 gal (19 L).

**2-4.4\*** Dust collectors for Kroll-distilled material shall be located outside buildings and shall be provided with explosion vents.

**2-4.5\*** Fans that handle combustible dust and air mixtures shall be constructed of nonsparking materials and shall be constructed in accordance with NFPA 91, *Standard for Exhaust Systems for Air Conveying of Materials*.

**2-5\* Personnel Safety Precautions.** Personnel involved in reduction furnace tapping, removal of molten magnesium chloride, and magnesium refining and casting shall wear tight-fitting, above-the-ankle shoes, flame-retardant clothing, heat-resistant gloves, and face shields.

## **2-6 Sponge Storage.**

**2-6.1** Titanium sponge shall be stored in closed metal containers with a maximum capacity that are capable of being moved by available equipment.

**2-6.2** 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.

**2-6.3** Where drums are used, storage shall be limited to one-drum tiers per pallet, and no more than four pallet loads high. Stacked storage shall be positioned in such a manner as to ensure stability.

**2-6.4** Aisles shall be provided for maneuverability of material-handling equipment, accessibility, and to facilitate fire-fighting operations.

# **Chapter 3\* Titanium Melting**

## **3-1 Explosion Prevention.**

**3-1.1** The water supply to crucibles shall be monitored continuously by a system that automatically interrupts power to the furnace upon a drop in water pressure or flow. In addition, an emergency source of cooling water shall be provided and shall be actuated automatically by flow interlock in the event of interruption of the primary cooling water.

**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 if an explosion occurs.

**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 if water enters 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 (138 kPa gauge) maximum. Large low-pressure ports shall not be used.

**3-1.5** A clearance shall be maintained at all times between the electrode and the crucible wall to minimize arcing to the crucible wall.

**3-1.6** The furnace shall be equipped with a device that continuously senses pressure within the furnace. The device shall automatically interrupt power to the melting heat source in the event of an expected sudden rise in pressure.

**3-1.7** The furnace shall be equipped with:

- (a) Water flow, temperature, and pressure sensors on all cooling systems;
- (b) Arc voltage and melting power recorders;
- (c) Electrode position indicators;
- (d) Furnace pressure sensors and recorders; and
- (e) Set point alarms on all systems to warn of abnormal conditions.

## **3-2\* Casting.**

**3-2.1\*** The water supply to crucibles shall be monitored continuously by a system that automatically interrupts power to the melting heat source upon a drop in water pressure or flow. In addition, an emergency source of cooling water shall be provided and shall be actuated automatically by flow interlock in the event of interruption of the primary cooling water.



**3-2.2** Molds for titanium casting shall be made of material that is compatible with molten titanium. Molds shall be dried thoroughly and stored carefully to prevent accumulation of moisture in the molds.

**3-2.3** The casting chamber shall be cooled or shall be sufficiently massive, or both, to accommodate a spill, since mold breaks are inevitable.

**3-2.4** Control consoles for water-cooled melting and casting operations shall be located remote from melting areas and outside of furnace vaults.

**3-2.5\*** Residue from casting furnaces shall be placed in steel boxes and moved outside the building.

## Chapter 4\* Mill Operations

### 4-1 Fire Prevention.

**4-1.1** Tanks in which flammable or combustible solvents are used for degreasing shall comply with NFPA 30, *Flammable and Combustible Liquids Code*.

**4-1.2\*** Sawing, grinding, and cutting equipment shall be grounded.

**4-1.3** All titanium chips shall be collected in closed-top metal containers and removed daily, as a minimum, to a safe storage or disposal area.

**4-1.4** Forge presses, heavy grinders, and other milling equipment operated by hydraulic systems shall use a less hazardous hydraulic oil with a flash point greater than 200°F (93°C) if oil leaks are anticipated.

**4-1.5** Nonflammable coolants shall be used for wet grinding, cutting, or sawing operations. The coolant shall be filtered on a continuous basis and the collected solids shall not be permitted to accumulate in quantities greater than 5 gal (19 L) and shall be moved to a safe storage or disposal area.

**4-1.6** Flammable and combustible liquids coatings applied to ingots or billets shall meet the requirements of NFPA 34, *Standard for Dipping and Coating Processes Using Flammable or Combustible Liquids*.

**4-1.7** Oily crushed lathe turnings, raw turnings, and swarf shall be collected in closed-top metal containers and removed daily, as a minimum, to a safe storage or disposal area.

**4-1.8** Furnaces or other heating equipment used for heating titanium shall be free of iron scale or residue that could react exothermically with the metal being heated.

## Chapter 5 Machining and Fabrication

**5-1\* Machining Operations.** Cutting tools shall be of proper design and shall be kept sharp for satisfactory work with titanium.

### 5-2 Welding.

**5-2.1** All welding of titanium shall be carried out under an inert atmosphere, such as helium, argon, or under vacuum.

**5-2.2** 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 washed thoroughly.

### 5-3 Titanium Dust Collection.

**5-3.1\*** Titanium dust shall be collected by means of hoods or enclosures at each dust-producing operation. The hoods or enclosures shall be connected to liquid precipitation separators, and the suction unit shall be installed so that the dust is converted to sludge without contact, in the dry state, with any high-speed moving parts. [See Figures A-5-3.1(a) through (e).]

**5-3.2** 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 in accordance with NFPA 91, *Standard for Exhaust Systems for Air Conveying of Materials*.

**5-3.3** Titanium dust-producing equipment shall be connected to dust-separating equipment. Multiple pieces of titanium dust-producing equipment shall be permitted to be connected to a single titanium dust-separating unit. An evaluation shall be made to determine if multiple pieces of dust-producing equipment can be safely served by a single dust-separating unit.

**5-3.4\*** If the titanium dust-separating unit is to be used for other materials, it shall be thoroughly cleaned of all incompatible materials prior to and after its use.

**5-3.5** The power supply to the dust-producing equipment shall be interlocked with the airflow from 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 device shall be provided on the dust-producing equipment to prevent starting of its motor drive until the separator is in complete operation.

### 5-3.6 Housekeeping.

**5-3.6.1** Systematic cleaning of the entire building containing dust-producing equipment, including roof members, pipes, conduits, etc., shall be conducted as conditions warrant. Cleaning methods shall be limited to those methods that minimize the probability of having a fire or explosion, as determined by a person knowledgeable in the properties of titanium dust.

**5-3.6.2** Due to the inherent hazards associated with the use of fixed vacuum-cleaning systems for finely divided titanium dust, special engineering considerations shall be given to the design, installation, maintenance, and use of such systems.

**5-3.7** Sludge from dust separators and vacuum-cleaning system precipitators shall be removed daily as a minimum. Covered, vented steel containers shall be used to transport collected sludge to a safe storage area or for disposal. Sludge shall be disposed of in accordance with federal, state, and local regulations.

**5-4 Compressed Air Fittings.** 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.

## Chapter 6\* Scrap Storage

### 6-1 Storage.

**6-1.1** Open storage of sheet, plate, forgings, or massive pieces of scrap presents no fire risk and shall be permitted.

**6-1.2** Open storage of sponge, chips, fines, and dust that are readily ignitable shall be isolated and segregated from other combustible materials and titanium scrap to prevent propagation of a fire.

*Exception: Storage of materials in closed noncombustible containers shall not be subject to the requirements of 6-1.2.*

## Chapter 7\* Titanium Powder Production and Use

### 7-1 Drying and Storage of Titanium Powder.

**7-1.1** Wetted powder shall be dried at a temperature not exceeding 230°F (110°C).

**7-1.2\*** 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** Titanium powder shall be stored in sealed containers in well-ventilated areas, and shall be kept free of combustibles. The containers shall be protected from damage.

### 7-2 Titanium Powder Handling.

**7-2.1** Special care shall be taken to prevent spills or dispersions that produce dust clouds.

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

**7-2.3\*** To minimize the risk of fire or explosion hazards in the handling of dry titanium powders, the equipment and processes shall be designed by people knowledgeable in the hazards of titanium powders.

**7-2.4 Electrical Installations.** All titanium powder production, drying, and packing areas shall be evaluated for fire and explosion hazards associated with the operation and shall be provided with approved electrical equipment for the hazardous location present, which shall be installed in accordance with the requirements of NFPA 70, *National Electrical Code*.

**7-3 Personnel Safety Precautions.** Personnel handling dry titanium powder shall wear nonsparking shoes and noncombustible or flame-retardant clothing without pockets, cuffs, laps, or pleats in which powder can accumulate.

## Chapter 8 Fire Prevention and Fire Protection

**8-1 Fire Prevention.** The provisions of Chapter 8 shall apply to all titanium production process, handling, and storage operations.

**8-1.1** Buildings shall comply with the applicable provisions of NFPA 101, *Life Safety Code*.

**8-1.2** Sponge discharged from dryers shall be collected in containers that have no larger than a 4000-lb (1814-kg) capacity. The collection area shall be well-ventilated and free from other combustible material.

**8-1.3** Hot work permits shall be required in designated areas that contain exposed titanium fines, dust, or sponge where hot work is conducted. All hot work areas that require a permit shall be thoroughly cleaned of titanium fines, dust, or sponge before hot work is performed.

**NOTE:** For information on cutting and welding practices, see NFPA 51B, *Standard for Fire Prevention in Use of Cutting and Welding Processes*.

**8-1.4\*** All containers used to receive molten metal, molten magnesium, molten magnesium chloride, or liquid sodium shall be cleaned and dried thoroughly before using. All pieces of magnesium metal shall be clean and dry when charged to reactors.

**8-1.5** Good housekeeping practices shall be maintained. Supplies shall be stored in an orderly manner with properly maintained aisles to permit regular inspection and segregation of incompatible materials. Supplies of materials in titanium processing areas shall be limited to amounts necessary for normal operation.

**8-1.6** Ordinary combustible materials, such as paper, wood, cartons, and packing material, shall not be stored or permitted to accumulate in titanium processing areas unless necessary for the process, and then only in designated areas.

**8-1.7** Regular, periodic cleaning of titanium dust and fines from buildings and machinery shall be carried out as frequently as conditions warrant. Dust and fines shall be removed to a safe storage or disposal area. Consideration shall be given to the potential ignition sources associated with the operation of equipment during the cleaning operation.

**8-1.8** Regular inspections shall be conducted to detect the accumulation of excessive titanium dust, chips, or fines on any portions of buildings or machinery not regularly cleaned in daily operations. Records shall be kept of these inspections.

**8-1.9** Combustible materials shall not be discarded in containers used for the collection of dust, swarf, or turnings.

**8-1.10** Oil spills shall be cleaned up immediately.

**8-1.11** Smoking shall be permitted only in designated areas. No smoking areas shall be posted with No Smoking signs.

**8-1.12\*** Boring, crushing, and drying equipment shall be properly electrically bonded and grounded to prevent accumulation of static electricity.

**8-1.13** All electrical equipment and wiring in titanium production, processing, handling, and storage facilities shall comply with NFPA 70, *National Electrical Code*.

**8-1.14** Nonsparking tools and utensils shall be used in handling titanium powder.

**8-1.15\*** All metal objects or equipment used in titanium operations shall be properly electrically bonded and grounded to prevent accumulations of static electricity.

**8-1.16** Where titanium is collected or stored in containers, material-handling equipment with sufficient capability to remove any container from the immediate area in the case of an emergency shall be readily available.

**8-1.17** Areas used for torch-cutting of massive pieces of scrap shall be kept free of combustible materials.

## **8-2\* Fire Protection.**

**8-2.1\*** Buildings or portions of buildings of noncombustible construction used principally for titanium storage or handling shall not be permitted to be equipped with automatic sprinkler protection.

*Exception:* Sprinkler systems installed in accordance with NFPA 13, *Standard for the Installation of Sprinkler Systems*, shall be permitted in areas where combustibles other than titanium create a more severe hazard than the titanium and where acceptable to an authority having jurisdiction who is knowledgeable of the hazards associated with titanium.

**8-2.2** If required by the authority having jurisdiction, automatic sprinkler protection, installed in accordance with NFPA 13, *Standard for the Installation of Sprinkler Systems*, shall be provided for offices, repair shops, and warehouses not used for the storage of titanium sponge, fines, or chips.

## **8-2.3\* Portable Fire Extinguishers.**

**8-2.3.1** Portable fire extinguishers shall be provided in accordance with NFPA 10, *Standard for Portable Fire Extinguishers*. Water-based or CO<sub>2</sub> extinguishers shall not be provided in areas containing titanium sponge, fines, or chips.

**8-2.3.2** If portable extinguishers are to be used on metal fires, they shall be approved for use on Class D fires.

**8-2.4\*** Dry sodium chloride, or other dry chemicals or compounds suitable for extinguishment or containment of titanium fires, shall be permitted to be substituted for Class D fire extinguishers. These alternative agents shall be stored in a manner that ensures the agent's effectiveness. Shovels or scoops shall be kept readily available adjacent to the containers. All extinguishing agent storage areas shall be clearly identified.

**8-2.5** Titanium fines shall be segregated by storage in noncombustible drums or tote bins. Drums or tote bins of burning materials shall be moved away from processing equipment and out of buildings as rapidly as possible.

**8-2.6\*** When a fire occurs in processing equipment, material feed to the equipment shall be stopped. The equipment shall be kept in operation, unless continued operation will spread the fire.

## **Chapter 9 Referenced Publications**

**9-1** The following documents or portions thereof are referenced within this standard and shall be considered part of the requirements of this document. The edition indicated for each reference is the current edition as of the date of the NFPA issuance of this document.

**9-1.1 NFPA Publications.** National Fire Protection Association, 1 Batterymarch Park, P.O. Box 9101, Quincy, MA 02269-9101.

NFPA 10, *Standard for Portable Fire Extinguishers*, 1994 edition.  
NFPA 13, *Standard for the Installation of Sprinkler Systems*, 1994 edition.

NFPA 30, *Flammable and Combustible Liquids Code*, 1993 edition.  
NFPA 34, *Standard for Dipping and Coating Processes Using Flammable or Combustible Liquids*, 1995 edition.

NFPA 45, *Standard on Fire Protection for Laboratories Using Chemicals*, 1991 edition.

NFPA 70, *National Electrical Code*, 1996 edition.

NFPA 91, *Standard for Exhaust Systems for Air Conveying of Materials*, 1995 edition.

NFPA 101, *Life Safety Code*, 1994 edition.

NFPA 220, *Standard on Types of Building Construction*, 1995 edition.

NFPA 480, *Standard for the Storage, Handling, and Processing of Magnesium Solids and Powders*, 1993 edition.

## **Appendix A Explanatory Material**

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

**A-1-2** See Appendix B for supplementary information on titanium.

**A-1-5 Approved.** 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, 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 that is in a position to determine compliance with appropriate standards for the current production of listed items.

**A-1-5 Authority Having Jurisdiction.** 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, or 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 or her 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.

**A-1-5 Listed.** 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.

**A-1-5 Titanium Chips.** Titanium chips vary in ease of ignition and rapidity of burning, depending on size and geometry. A light, fluffy chip ignites easily and burns vigorously while a

heavy, compact chip ignites with difficulty and burns quite slowly.

**A-1-5 Titanium Dust.** See NFPA 497B, *Recommended Practice for the Classification of Class II Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*, or NFPA 497M, *Manual for Classification of Gases, Vapors, and Dusts for Electrical Equipment in Hazardous (Classified) Locations*, for information on explosibility parameters of combustible dusts.

**A-1-5 Titanium Powder.** See NFPA 497B, *Recommended Practice for Classification of Class II Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*, or NFPA 497M, *Manual for Classification of Gases, Vapors, and Dusts for Electrical Equipment in Hazardous (Classified) Locations*, for information on explosibility parameters of combustible dusts.

**A-1-5 Titanium Sponge.** Titanium sponge can contain dust and fines that can become airborne when the material is handled. If present in sufficient quantity, the dust and fines can cause increased fire risk.

**A-2-1.1** NFPA 68, *Guide for Venting of Deflagrations*, contains information on the subject of explosion venting.

**A-2-1.3** Floors should be slightly crowned to prevent accumulation of water in the vicinity of reduction furnaces.

**A-2-3.2** For information on guidelines for handling and storing chlorine, see *The Chlorine Manual* (see C-1.2.4).

**A-2-3.3** 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 should be wiped immediately and then flushed with a large amount of water. Eyes splashed with titanium tetrachloride also should be flushed with copious amounts of water.

**A-2-4.4** A high-efficiency cyclone-type collector presents less hazard than a bag- or media-type collector and, except for extremely fine powders, usually operates with fairly high collection efficiency. Where cyclones are used, the exhaust fan discharges to atmosphere away from other operations. It should be recognized that there are some instances in which a centrifugal-type collector might be followed by a fabric or bag- or media-type collector or by a scrubber-type collector where particulate emissions are kept at a low level. The hazards of each collector should be recognized and protected against. In each instance, the fan is the last element downstream in the system. Because of the extreme hazard involved with a bag- or media-type collector, consideration should be given to a multiple-series cyclone with a liquid final stage.

Industry experience has clearly demonstrated that an eventual explosion can be expected where a bag- or media-type collector is used to collect titanium fines. Seldom, if ever, can the source of ignition be positively identified. In those unusual instances where it becomes necessary to collect very small fines for a specific commercial product, it is customary for the producer to employ a bag- or media-type collector. Since this presents a strong explosion potential, the bag- or media-type collector should be located a safe distance from buildings and personnel.

If a bag- or media-type collector is used, the shaking system or dust removal system can be such as to minimize sparking

due to frictional contact or impact. Pneumatic or pulse-type shaking is more desirable because no mechanical moving parts are involved in the dusty atmosphere. If the bags are provided with grounding wires, they can be positively grounded through a low-resistance path to ground. Where bags are used, it is customary that the baghouse be protected by an alarm that indicates excessive pressure drop across the bags. An excess air temperature alarm is also frequently used. A bag- or media-type collector is customarily located at least 50 ft (15 m) from any other building or operation. It is not customary to permit personnel to be within 50 ft (15 m) of the collector during operation or when shaking bags. Explosion vents are usually built into the system, as described in NFPA 68, *Guide for Venting of Deflagrations*. Care is customarily exercised in locating the vents because of the possibility of blast damage to personnel or adjacent structures.

**A-2-4.5** Information on spark-resistant fans and blowers can be found in AMCA Standards Handbook 99-0410-86, *Classification for Spark-Resistant Construction*, 1986.

**A-2-5** Molten magnesium and molten magnesium chloride present an extremely dangerous fire and fume hazard, in addition to an explosion hazard, if in contact with water or residual moisture.

**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, is 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 developed to meet quality and process requirements. 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; and 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 is water-cooled.

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-3-1.4** The explosion that can occur due to the rapid phase transformation of water trapped below molten material takes place over a time span of approximately  $10^{-5}$  to  $10^{-4}$  seconds. This is faster than a condensed phase detonation. The required pressure-relief device would not be effective in safely relieving the rapid pressure build-up caused by the rapid phase transformation. It should be noted that the required pressure-relieving device is intended to safely relieve only much slower increases in pressure, such as might occur from small incursions of water onto the top of the molten metal.

**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 exposed to the electric arc or the molten metal.

**A-3-2.1** Such ingots contain internal stresses that can cause them to shatter, even up to several days after being wetted.

**A-3-2.5** Personnel entering furnace shells to conduct inspections or repair work should first make certain that any inert gas has been purged from the shell and that all pyrophoric residue has been removed. These residues might be combustible or pyrophoric and caution should be exercised.

**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 can vary from 1600°F to 2300°F (871°C to 1260°C). The rate of heat-up and final temperature must often be controlled precisely to achieve specific metallurgical and physical properties. Slabs, billets, and bar stock are produced by forging.

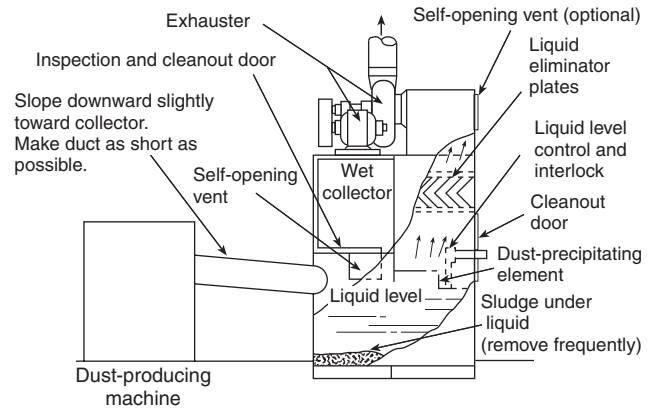
Large rounds of titanium are produced by lathe turning or by grinding forges. A considerable amount of titanium strip, coil, and duct, down to foil thickness, is produced from slabs on both continuous and hand mills. Wide sheets and plates of various thicknesses are produced on hand mills or plate-rolling mills. Temperature control during rolling is important. Shearing and straightening operations are necessary to trim sheets and plates to size, to straighten or flatten plates, 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.

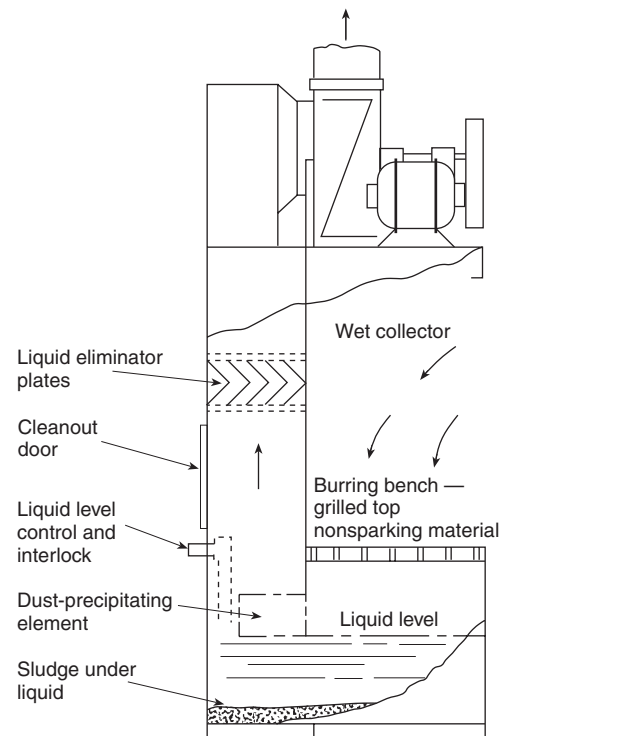
Cold saws and abrasive cut-off saws are used to cut billet and bar stock to length. Swarf, or finely divided metal particles, is produced by all sawing and grinding operations.

**A-4-1.2** See NFPA 77, *Recommended Practice on Static Electricity*.

**A-5-1** Improperly designed or dulled tools can produce high temperatures at the interface, causing ignition at the turnings, if an adequate coolant flow is not used.



**Figure A-5-3.1(a) Typical liquid precipitation separator for fixed dust-producing equipment.**



**Figure A-5-3.1(b) Typical liquid precipitation separator for portable dust-producing equipment.**

NOTE: These drawings are schematic and are intended only to indicate some of the features that are incorporated into the design of a separator. The volume of all dust-laden airspace is as small as possible.

**A-5-3.4** For example, iron oxide dusts are known to be incompatible with titanium due to the potential for an exothermic reaction. The dust-separating unit should be cleaned unless it has been determined that the materials exhibit no incompatibility.

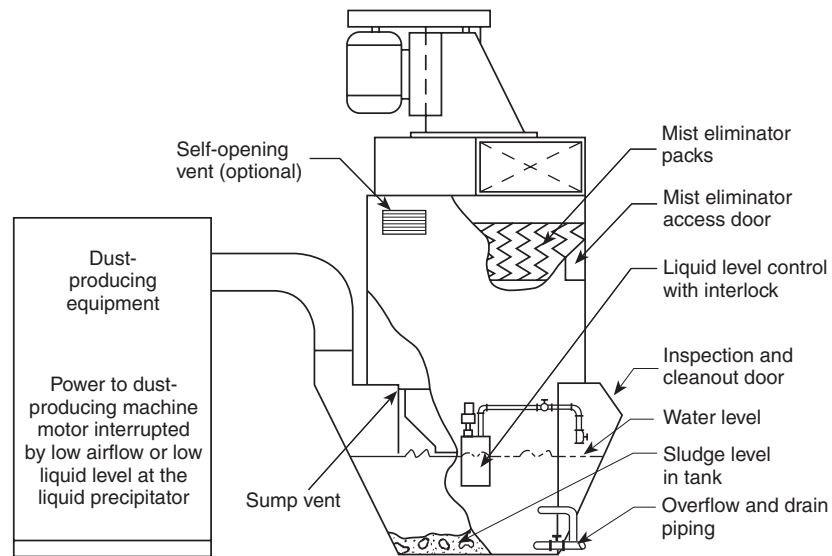


Figure A-5-3.1(c) Typical liquid precipitation separator for fixed dust-producing equipment.

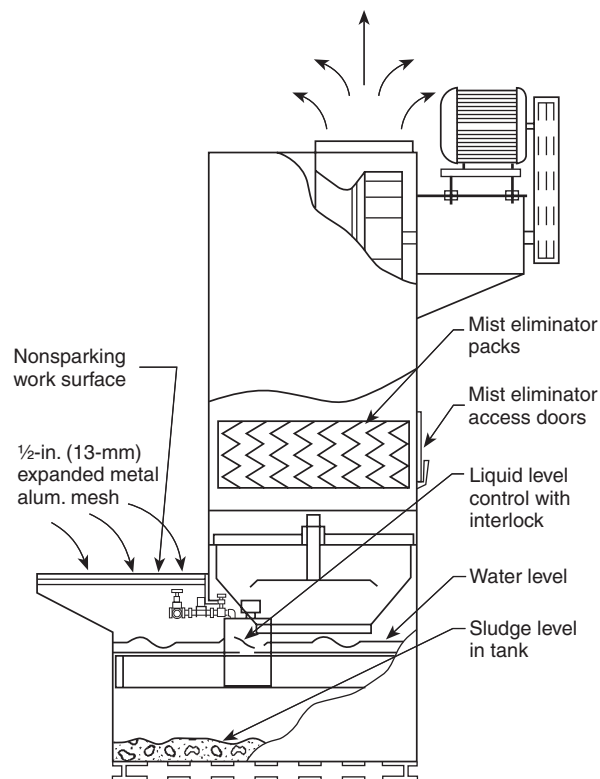


Figure A-5-3.1(d) Typical liquid precipitation separator for portable dust-producing equipment.

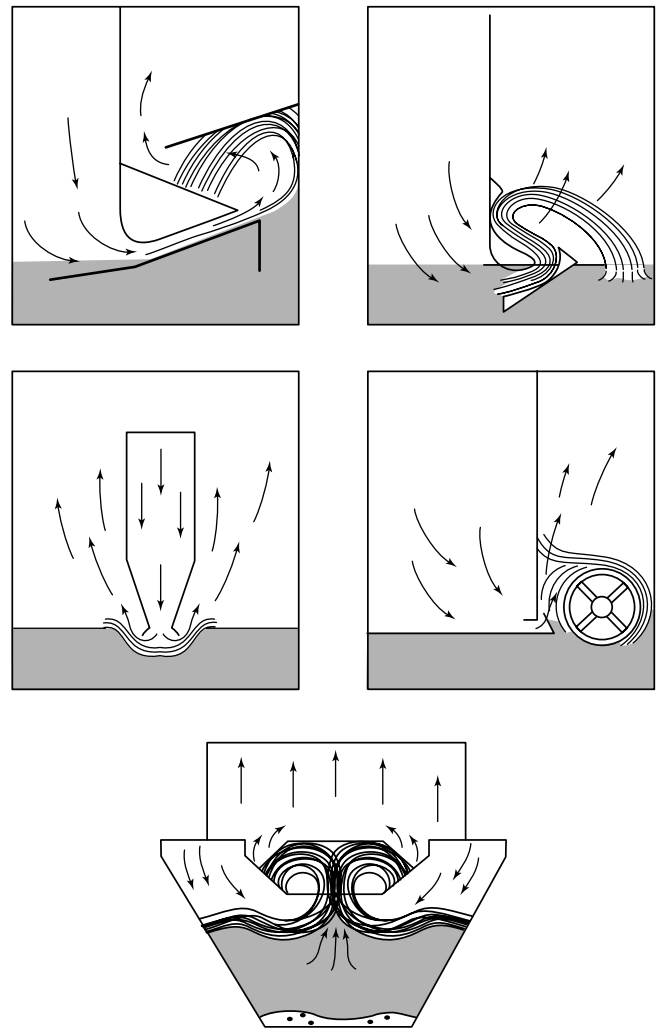


Figure A-5-3.1(e) Diagram of five methods of precipitating dust used in precipitators such as those shown in Figures A-5-3.1(a), (b), (c), and (d).

**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 clippings.

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-7** Not all methods of producing metal powder are applicable to titanium. Reduction of titanium hydride and some forms of milling generally are used to produce the limited amounts of powder now required commercially. To reduce oxidation and possible ignition hazards, milling can be performed underwater 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°C to 590°C (626°F to 1094°F). The minimum explosive concentration is 0.045 oz/ft<sup>3</sup> (0.045 kg/m<sup>3</sup>). Maximum pressure produced in explosions in a closed bomb at a concentration of 0.5 oz/ft<sup>3</sup> (0.5 kg/m<sup>3</sup>) ranged from 46 psi to 81 psi (317 kPa to 558 kPa). The average rate of pressure rise in these tests ranged from 250 psi/sec to 4300 psi/sec (1724 kPa/sec to 29 650 kPa/sec); the maximum rate of pressure rise ranged from 550 psi/sec to 10,000 psi/sec (3792 kPa/sec to over 68 950 kPa/sec). The minimum energy of electrical condenser discharge sparks required for ignition of a dust cloud was 10 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-7-1.2** For information on designing explosion venting, see NFPA 68, *Guide for Venting of Deflagrations*.

**A-7-2.3** The handling of dry titanium powder presents a fire and explosion hazard. The hazard increases as the size of the titanium particles decreases. The equipment and processes should be designed with consideration for the need to minimize the damage to property and risk to life resulting from fires and explosions involving titanium powders. Design con-

siderations should include the use of deflagration venting, proper dust collection systems, inerting, or a combination of these methods. The inert gas used should be determined by test to be appropriate for the titanium powder being handled. Titanium powder can react exothermically in pure carbon dioxide atmospheres and in pure nitrogen atmospheres.

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

This data was obtained from U.S. Bureau of Mines, Report of Investigations 3722, *Inflammability and Explosibility of Metal Powders*.

**A-8-1.4** Molten magnesium and molten magnesium chloride present an extremely dangerous fire and fume hazard, in addition to an explosion hazard, if contacted with water or residual moisture.

**A-8-1.12** See NFPA 77, *Recommended Practice on Static Electricity*.

**A-8-1.15** See NFPA 77, *Recommended Practice on Static Electricity*.

**A-8-2** The principal intent in fighting titanium fires is isolation and containment, rather than extinguishment. 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 can reach explosive concentrations in confined spaces. Entrapment of water under any burning or hot metal can result in a steam explosion.

**A-8-2.1** Automatic sprinkler protection should not be recommended for blending and melting buildings.

**A-8-2.3** Water-based 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-8-2.4** Experience has shown that dry sodium chloride is one of the most effective chemicals for containing fires involving titanium sponge or fines. Fire-fighting salts should be checked periodically to ensure that they have not become caked from moisture. Another effective chemical is a nonmetallic flux compound consisting of potassium chloride, magnesium chloride, and calcium fluoride. Commercial dry powder fire extinguishers or agents 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.

**A-8-2.6** Keeping the equipment in operation until all burning material is removed can reduce damage to the equipment. Small amounts of burning materials can be handled with a shovel to facilitate removal.

## Appendix B Supplementary Information on Titanium

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

### B-1 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 might 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 among countries in the former Soviet Union. Three basic processes have been developed for commercial refining of titanium from rutile ore. The most widely used processes employ 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-2 Properties.

Titanium is a silver-gray 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 can 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 (540°C) and can become embrittled after extended exposure to air at temperatures above 800°F (430°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 resistance 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 might 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 dissolve as temperature increases. Excessive oxidation can cause embrittlement.

### B-3 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 gray-white marks on the glass.

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

### B-4 Applications.

While titanium has many uses, production is still largely consumed by commercial and military aircraft applications 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 communications 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-5 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 630°F to 1090°F (330°C to 590°C). Ignition of dust layers occurred at temperatures from 720°F to 950°F (380°C to 510°C). In some cases, dust clouds ignited at lower temperatures than static layers of the same dust. (See U.S. Bureau of Mines Report of Investigations 3722 and 4835, listed in Appendix C.) 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 can spread rather rapidly immediately after ignition.

Heavy castings or ingots of titanium can 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 900°F (480°C) and as a layer at 880°F (470°C), also ignited as a layer in pure carbon dioxide at 1260°F (680°C). At red heat, about 1300°F (704°C), titanium will decompose steam to free hydrogen and oxygen. Above 1470°F (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 (2410 kPa gauge) when a fresh surface is created. The actual hazard in air is much less than that for aluminum.

### B-6 Special Hazards.

In spite of titanium's superior resistance to corrosion, as discussed in Section B-2, titanium can 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 involving 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 can 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 *ASM International Handbook*, Chapter on 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 can react and, in some cases, become pyrophoric.

### B-7 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 should 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 can 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 *Appendix C*.)

### B-8 Process Description.

Current titanium production processes involve reduction of titanium tetrachloride to titanium metal. The titanium tetrachloride ( $\text{TiCl}_4$ ) 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 underway. 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 1290°F (700°C) and 1650°F (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 recy-

cling 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 American Institute of Chemical Engineers (AIChE) *Chemical Engineering Progress*, November, 1954. (See Appendix C.)

In the sodium reduction process, liquefied sodium is used as the reducing agent. In this process, the reaction vessel is heated to approximately 1830°F (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 standard for informational purposes only and thus are not considered part of the requirements of this document. The edition indicated for each reference is the current edition as of the date of the NFPA issuance of this document.

**C-1.1 NFPA Publications.** National Fire Protection Association, 1 Batterymarch Park, P.O. Box 9101, Quincy, MA 02269-9101.

NFPA 51B, *Standard for Fire Prevention in Use of Cutting and Welding Processes*, 1994 edition.

NFPA 54, *National Fuel Gas Code*, 1992 edition.

NFPA 68, *Guide for Venting of Deflagrations*, 1994 edition.

NFPA 77, *Recommended Practice on Static Electricity*, 1993 edition.

NFPA 491M, *Manual of Hazardous Chemical Reactions*, 1991 edition.

NFPA 497B, *Recommended Practice for the Classification of Class II Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*, 1991 edition.

NFPA 497M, *Manual for Classification of Gases, Vapors, and Dusts for Electrical Equipment in Hazardous (Classified) Locations*, 1991 edition.

### C-1.2 Other Publications.

**C-1.2.1 American Institute of Chemical Engineers Publication.** American Institute of Chemical Engineers, 345 E. 47th St., New York, NY 10017.

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

**C-1.2.2 AMCA Publication.** Air Movement and Control Association, 30 W. University Drive, Arlington Heights, IL 60004-1893.

AMCA Standards Handbook 99-0410-86, *Classification for Spark-Resistant Construction*, 1986.

**C-1.2.3 ASM International Publication.** American Society of Metals, 9639 Kinsman, Materials Park, OH 44073-0002.

ASM International Handbook, Chapter on Metals Properties, 1980.

**C-1.2.4 The Chlorine Institute Publication.** The Chlorine Institute, Inc., 2001 L Street, NW, Washington, DC 20036.

*The Chlorine Manual*, 5th edition, 1986.

**C-1.2.5 U.S. Bureau of Mines Publications.** U.S. Bureau of Mines, Cochran Mill Road, Pittsburgh, PA 15236-0070.

RI 3722, *Inflammability and Explosibility of Metal Powders*, I. Hartman, M.J. Nagy, and H.R. Brown, 1943.

RI 4835, *Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium and their Hydrides*, 1951.

RI 4879, *Recent Practice at the Bureau of Mines*, Boulder City, NV, Plant, 1951.

**C-1.2.6 Other Publications.** Forbath, T.P., "Sodium Reduction Route Yields Titanium," *Chemical Engineering*, McGraw Hill Publications Co., March 1958, pp. 124-127.

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

# Index

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- A-**
  - Applications, of titanium ..... B-4
  - Approved (definition) ..... 1-5, A-1-5
  - Authority having jurisdiction (definition) ..... 1-5, A-1-5
- B-**
  - Bag- or media-type collectors ..... A-2-4.4
- C-**
  - Casting ..... 3-2, A-3-2
  - Chlorine, storage and handling ..... 2-3.2, A-2-3.2
  - Combustibility ..... B-5
  - Commercial production ..... B-1
  - Compressed air fittings ..... 5-4
  - Cyclone-type collectors ..... A-2-4.4
- D-**
  - Definitions ..... 1-5, A-1-5
  - Dry sodium chloride ..... 8-2.4, A-8-2.4
  - Dust collection ..... 2-4, 5-3 to 5-3.5, A-2-4.4, A-2-4.5
- E-**
  - Electrical installations ..... 7-2.4
  - Explosibility ..... B-5
  - Explosion prevention
    - Compressed air fittings ..... 5-4
    - Dust collectors ..... 2-4.4, A-2-4.4
    - Dust cloud ignition temperatures ..... 2-4.4, A-7
    - Titanium melting ..... 3-1, A-3-1.4
    - Titanium powder handling ..... 7-2.3, A-7-2.3
    - Venting ..... A-7-1.2
- F-**
  - Fire fighting ..... A-8.2
  - Fire prevention
    - Titanium mill operations ..... 4-1 to 4-1.8, A-4-1.2
    - Titanium powder handling ..... 7-2.3, A-7-2.3
    - Titanium production process ..... Chap. 8, A-8-1.4, A-8-1.12, A-8-1.15
  - Fire protection, titanium production process ..... Chap. 8, A-8-1.4, A-8-2, A-8-2.1
  - Forging ..... A-4
  - Furnaces ..... 3-1 to 3-1.7, A-3
- G-**
  - Glass test ..... B-3(b)
- H-**
  - Hazards, special ..... B-6
  - Housekeeping ..... 5-3.6
- I-**
  - Ignition temperatures, dust clouds ..... A-7
  - Inert gases ..... A-7-2.3
  - Iron oxide dusts ..... A-5-3.4
- K-**
  - Kroll-Bureau of Mines process ..... 2-3.1, B-8
- L-**
  - Labeled (definition) ..... 1-5
  - Listed (definition) ..... 1-5, A-1-5
- M-**
  - Machining and fabrication ..... Chap. 5
    - Compressed air fittings ..... 5-4
    - Dust collection ..... 5-3
    - Housekeeping ..... 5-3.6
    - Operations ..... 5-1, A-5-1
    - Titanium scrap ..... A-6
    - Welding ..... 5-2
  - Magnesium ..... 2-1.4, 2-3.1, 2-5, 8-1.4, A-2-5, A-8-1.4
  - Media collector (definition) ..... 1-5
  - Mill operations ..... Chap. 4, A-4
    - Fire prevention ..... 4-1 to 4-1.8, A-4-1.2
    - Forging ..... A-4
- N-**
  - NaK (sodium-potassium alloy) coolant ..... A-3
- P-**
  - Personnel safety precautions ..... 2-5, 7-3
  - Portable fire extinguishers ..... 8-2.3, A-8-2.3, A-8-2.4, A-8-2.6
  - Pressure-relief devices ..... A-3-1.4
  - Production processes ..... A-4, B-8
    - Machining and fabrication ..... Chap. 5, A-5
    - Melting ..... Chap. 3, A-3
    - Mill operations ..... Chap. 4, A-4
    - Powder ..... Chap. 7, A-7
    - Sponge production ..... 2-2
  - Purpose of the standard ..... 1-2, A-1-2
- R-**
  - Recycling, titanium scrap ..... A-6
  - Referenced publications ..... Chap. 9, App. C
- S-**
  - Scope of the standard ..... 1-1
  - Shall (definition) ..... 1-5
  - Should (definition) ..... 1-5
  - "Skull-casting process," titanium melting ..... A-3-2
  - Spark test ..... B-3(a)
  - Special hazards ..... B-6
  - Sponge production
    - Dust collection ..... 2-4
    - Personnel safety precautions ..... 2-5, A-2-5
    - Plant construction ..... 2-1, A-2-1.3
    - Processing equipment ..... 2-2
    - Storage of raw materials ..... 2-3, A-2-3.2, A-2-3.3
    - Storage of sponge ..... 2-6

<b>Spontaneous combustion</b> .....	B-7
<b>Sprinkler systems</b> .....	8-2.1, 8-2.2, A-8.2.1
<b>Storage</b>	
Raw materials .....	2-3, A-2-3.2, A-2-3.3
Scrap .....	Chap. 6, A-6,
Titanium powder .....	7-1
Titanium sponge .....	2-6
<b>-T-</b>	
<b>Tests, for titanium</b> .....	B-3
<b>Titanium</b>	
Applications .....	B-4
Definition .....	1-5
Properties .....	B-2
<b>Titanium chips (definition)</b> .....	1-5, A-1-5
<b>Titanium dust</b>	
Collection .....	2-4, 5-3 to 5-3.5, A-5-3.1, A-5-3.4
Definition .....	1-5, A-1-5
<b>Titanium fines (definition)</b> .....	1-5
<b>Titanium melting</b> .....	Chap. 3, A-3
Casting .....	3-2, A-3-2, A-3-2.1, A-3-2.5
Explosion prevention .....	3-1, A-3-1.4

<b>Titanium powder</b>	
Definition .....	1-5, A-1-5
Drying and storage .....	7-1, A-7-1.2
Handling .....	7-2, A-7-2.3
Production and use .....	Chap. 7, A-7
<b>Titanium scrap</b>	
Storage .....	Chap. 6, A-6
<b>Titanium sponge</b>	
Definition .....	1-5, A-1-5
Production .....	Chap. 2
<b>Titanium swarf (definition)</b> .....	1-5
<b>Titanium tetrachloride (TiCl<sub>4</sub>)</b> .....	2-3.3, A-2-3.3, B-8

**-V-**

<b>Venting</b> .....	2-1.1, A-2-1.1, A-7-1.2
----------------------	-------------------------

**-W-**

<b>Welding</b> .....	5-2
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