

NFPA 482

Standard for the Production, Processing, Handling, and Storage of Zirconium

1996 Edition



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 482

Standard for the

Production, Processing, Handling, and Storage of Zirconium

1996 Edition

This edition of NFPA 482, *Standard for the Production, Processing, Handling, and Storage of Zirconium*, 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 20–23, 1996, in Boston, MA. It was issued by the Standards Council on July 18, 1996, with an effective date of August 9, 1996, and supersedes all previous editions.

This edition of NFPA 482 was approved as an American National Standard on July 26, 1996.

Origin and Development of NFPA 482

NFPA 482 was originally developed as a manual under the designation NFPA 482M, *Zirconium*. NFPA 482M was prepared by the Committee on Combustible Metals and officially adopted by the NFPA in 1959. It was amended in 1961, and the 1961 edition was reconfirmed in 1974.

In reviewing the 1974 edition, the Committee on Combustible Metals determined that NFPA 482M could be rewritten as a standard. Thus, where appropriate, all recommendations were expressed as requirements. Supplementary information was relocated to the appendices. The text was also rearranged to comply with the NFPA *Manual of Style*. This major rewrite resulted in the 1982 edition.

The 1987 edition was a reconfirmation of the 1982 edition.

For the 1996 edition, the committee has completely revised the standard to update the fire and dust explosion prevention measures and the requirements for safe handling of zirconium 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 and adoptable.

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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.

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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 zirconium.

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

1-1.3 This standard shall not apply to the transportation of zirconium 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 is to provide requirements addressing the fire and explosion hazards of zirconium and zirconium alloys in all forms and to outline requirements for fire prevention and protection.

1-3 Equivalency. Nothing in this standard is intended to prevent the use of systems, methods, or devices that are equivalent or superior in quality, strength, fire resistance, effectiveness, durability, and safety to those prescribed by this standard, provided technical documentation is made available to the authority having jurisdiction that demonstrates 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 is not intended that the provisions of this document be applied to facilities, equipment, structures, or installations that existed or were 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 be defined as follows:

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, materials, or services included in a list published by an organization acceptable to the authority having jurisdiction and concerned with evaluation of products or services that maintains periodic inspection of production of listed equipment or materials or periodic evaluation of services and whose listing states either that the equipment, material, or service meets identified standards or has been tested and found suitable for a specified purpose.

Media Collector. 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.

Zirconium. Pure metal or alloys having the generally recognized properties of zirconium metal, including the fire or explosion characteristics of zirconium in its various forms.

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

Zirconium Dust.* Any finely divided zirconium material 420 microns or smaller in diameter (material passing through a U.S. No. 40 standard sieve) that presents a fire or explosion hazard when dispersed and ignited in air.

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

Zirconium Powder.* See Zirconium Dust and Zirconium Fines.

Zirconium Sponge.* Zirconium metal after it has been won from the ore but before it is melted.

Zirconium 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 Magnesium Operations. All magnesium storage, handling, and processing operations in zirconium sponge production operations shall be in accordance with the requirements of NFPA 480, *Standard for the Storage, Handling, and Processing of Magnesium Solids and Powders*.

2-2 Plant Construction.

2-2.1* 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 deflagration venting in accordance with current accepted practices.

2-2.2 Building exits shall comply with NFPA 101®, *Life Safety Code*®.

2-2.3* Floors in reduction, boring, and crushing facilities shall be made of noncombustible materials, such as concrete, brick, or steel plate.

2-2.4 Fittings used on compressed air and inert gas line outlets shall not be interchangeable to prevent potential explosions caused by inadvertently using compressed air in place of low pressure inert gas.

2-3 Processing Equipment.

2-3.1 Chlorinators and reduction vessels shall be designed and maintained to prevent water from entering the reaction chamber.

2-3.2 Furnaces shall be kept dry and free of iron scale and other foreign material.

2-3.3 Fuel supply lines to gas-fired furnaces or other gas-fired equipment shall be installed and maintained in accordance with NFPA 54, *National Fuel Gas Code*.

2-3.4* Furnaces shall comply with NFPA 86C, *Standard for Industrial Furnaces Using a Special Processing Atmosphere*, and NFPA 86D, *Standard for Industrial Furnaces Using Vacuum as an Atmosphere*.

2-3.5 All electrically operated or controlled processing equipment shall be installed in accordance with NFPA 70, *National Electrical Code*®.

2-3.6 Back-up methods or systems shall be provided to allow for the safe and orderly shutdown of critical processes in the case of primary system failure.

2-4 Storage of Raw Materials.

2-4.1* Chlorine shall be handled and stored in accordance with accepted industry practice.

2-4.2 Storage and handling of flammable and combustible liquids shall be in accordance with NFPA 30, *Flammable and Combustible Liquids Code*.

2-4.3* Bulk containers of zirconium tetrachloride ($ZrCl_4$) and silicon tetrachloride ($SiCl_4$) shall be stored in a well-ventilated area located away from areas of acute hazard. Containers shall be identified plainly and tightly sealed until used.

2-5 Dust Collection.

2-5.1 Dust resulting from the crushing of zirconium sponge shall be managed safely to minimize the risk of fires and explosions.

2-5.2 Media collectors shall not be used for the collection of zirconium sponge fines.

2-5.3 Nonmedia based dry collectors shall be emptied before, or when, 80 percent of the storage capacity is attained. The maximum volume of zirconium fines collected before emptying shall not exceed 5 gal (19 L).

2-5.4* Dust collectors for Kroll-distilled material shall be located outside buildings and shall be provided with deflagration vents.

2-5.5* 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*.

2-6* 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.

2-7 Sponge Storage.

2-7.1* Dry zirconium sponge shall be stored in closed metal containers with a maximum capacity that is capable of being moved by available equipment. Wet zirconium sponge shall be stored in nonsealing, covered, metal containers with a maximum capacity that is capable of being moved by available equipment.

2-7.2 Zirconium storage areas shall be kept free of combustible materials, well-ventilated, equipped with the required fire protection equipment, and plainly marked with "no smoking" signs.

2-7.3 Where drums are used, storage shall be limited to one-drum tiers per pallet with a height of no more than four pallet loads. Stacked storage shall be arranged to ensure stability.

2-7.4 Aisles shall be provided for maneuverability of material-handling equipment, for accessibility, and to facilitate fire-fighting operations.

Chapter 3* Zirconium Melting

3-1 Explosion Prevention.

3-1.1 The water supply to crucibles shall be continuously monitored 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 Water-cooled furnaces shall have the crucible and its water jacket located in a protective noncombustible enclosure that provides a means of isolation to protect personnel and to minimize damage if an explosion occurs.

3-1.3* The upper chamber of the furnace shall be provided with a pressure-relieving device to aid in safely relieving pressure if water enters the furnace. The release pressure of the pressure-relieving device shall be a maximum of 20 psig (138 kPa gauge).

3-1.4* A clearance shall be maintained at all times between the electrode and the crucible wall to minimize arcing to the crucible wall.

3-1.5 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 unexpected sudden rise in pressure.

3-1.6 The furnace shall be equipped with the following:

- (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 zirconium casting shall be made of material that is compatible with molten zirconium. Molds shall be dried thoroughly and stored carefully to prevent accumulation of moisture in the molds.

3-2.3 Since mold breaks are inevitable, the casting chamber shall be cooled or shall be large enough to serve as a heat sink, or both, in order to provide the protection necessary in the event of a spill.

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

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 Flammable or combustible liquids shall be handled in accordance with NFPA 30, *Flammable and Combustible Liquids Code*.

4-1.2* All electrically-driven equipment used for sawing, cutting, or grinding operations shall be grounded in accordance with NFPA 70, *National Electrical Code*.

4-1.3 Zirconium chips shall be collected in covered 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).

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 or combustible liquid coatings applied to zirconium shall be used in accordance with 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 chips shall be collected in covered 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 zirconium 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.

5-1.1 Cutting tools shall be of proper design and shall be kept sharp for satisfactory work with zirconium.

5-1.2 Nonflammable coolants or lubricants shall be used to minimize heat generated by the cutting operation.

5-2 Welding.

5-2.1 All welding of zirconium shall be carried out under a helium or argon atmosphere, or under vacuum.

5-2.2* Hot work such as electric arc or gas torch welding shall not be permitted in areas where zirconium powder or chips are produced, handled, packaged, or stored until all exposed chips or powder have been removed and exposed equipment has been cleaned thoroughly.

5-3 Zirconium Dust Collection.

5-3.1* Zirconium 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 making 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 practicable, 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 Zirconium dust-producing equipment shall be connected to dust-separating equipment. Multiple pieces of zirconium dust-producing equipment shall be permitted to be connected to a single zirconium 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 zirconium 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 shuts 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 and several air changes have swept out any residual hydrogen.

5-3.6 Housekeeping (Dust).

5-3.6.1 Systematic cleaning of the entire building containing dust-producing equipment, including roof members, pipes, conduits, and other components, shall be conducted as conditions warrant. Cleaning methods shall be limited to those methods that minimize the probability of fire or explosion, as

determined by a person knowledgeable in the properties of zirconium dust.

5-3.6.2 Due to the inherent hazards associated with the use of vacuum-cleaning systems for finely divided zirconium 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, and shall be kept thoroughly wet. Nonsealing, covered, metal 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.

Chapter 6* Scrap Storage

6-1 Storage.

6-1.1 Open storage of sheet, plate, forgings, or massive pieces of scrap shall be permitted.

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

Chapter 7* Zirconium Powder Production and Use

7-1 Drying and Storage of Zirconium 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 practicable from other operations. Deflagration venting for drying rooms shall be considered.

7-1.3 Zirconium powder shall be stored in sealed containers in well-ventilated areas and shall be kept segregated from other combustibles. The containers shall be protected from damage.

7-2 Zirconium Powder Handling.

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

7-2.2* Sintering furnaces that handle zirconium parts that are fabricated from powder shall be installed and operated in accordance with NFPA 86C, *Standard for Industrial Furnaces Using a Special Processing Atmosphere*. Powder or dust shall not be permitted to accumulate in the furnace or near the heating elements. Furnaces shall be operated with inert atmospheres of helium or argon or under vacuum.

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

7-2.4 Electrical Installations. All zirconium 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 suitable for the hazardous location. The electrical equipment shall be installed in accordance with the requirements of NFPA 70, *National Electrical Code*.

7-3 Personnel Safety Precautions. Personnel handling zirconium powder shall wear nonsparking shoes and noncombustible or flame-retardant clothing that is designed to minimize the accumulation of zirconium powder.

7-4 Housekeeping Practices. Good housekeeping practices shall be followed so that accumulations of powder are minimized. Special attention shall be paid to powder accumulations in crevices and joints between walls and floors.

Chapter 8 Fire Prevention and Fire Protection

8-1 Fire Prevention. The provisions of Chapter 8 shall apply to all zirconium production processes, 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 with a maximum capacity of 4000 lb (1814 kg). The collection area shall be well-ventilated and free from other combustible materials.

8-1.3* Hot work permits shall be required in designated areas that contain exposed zirconium chips, powder, or sponge. All hot work areas that require a permit shall be thoroughly cleaned of zirconium chips, powder, or sponge before hot work is performed.

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 use. All pieces of magnesium metal shall be clean and dry where charged to reduction furnaces.

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

8-1.6 Ordinary combustible materials, such as paper, wood, cartons, and packing material, shall not be stored or allowed to accumulate in zirconium processing areas.

Exception: This requirement shall not apply where ordinary combustible materials are necessary for the process and are stored in designated areas.

8-1.7* Periodic cleaning of zirconium sponge, chips, or powder from buildings and machinery shall be carried out as frequently as conditions warrant. Sponge, chips, or powder shall be removed to a safe storage or disposal area.

8-1.8 Periodic inspections shall be conducted, as frequently as conditions warrant, to detect the accumulation of excessive zirconium sponge, chips, or powder on any portions of buildings or machinery not regularly cleaned during daily operations. Records of these inspections shall be kept.

8-1.9* Ordinary combustible materials shall not be discarded in containers used for the collection of sponge, chips, or powder.

Exception: Floor sweepings from zirconium operations shall be permitted to contain small amounts of ordinary combustible materials.

8-1.10 Areas in which flammable and combustible liquids are used shall be in accordance with the requirements of NFPA 30, *Flammable and Combustible Liquids Code*.

8-1.11 Smoking shall not be permitted in areas where ignitable zirconium sponge, chips, or powder is present. Such areas shall be posted with "no smoking" signs.

Exception: Where smoking is prohibited throughout the entire plant, the use of signage shall be at the discretion of the facility management.

8-1.12 All electrical equipment and wiring in zirconium production, processing, handling, and storage facilities shall comply with NFPA 70, *National Electrical Code*.

8-1.13 Where using tools and utensils in areas handling zirconium powder, consideration shall be given to the risks associated with generating impact sparks and static electricity.

8-1.14* Processing equipment used in zirconium operations shall be electrically bonded and grounded properly in order to prevent accumulations of static electricity.

8-1.15 Where zirconium 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.

8-1.16 Areas used for torch-cutting of massive pieces of scrap shall be kept free of combustible materials.

8-2* General Fire Protection.

8-2.1 A fire protection plan shall be provided for all areas where zirconium is processed, handled, used, and stored.

8-2.2* Buildings or portions of buildings of noncombustible construction principally used for zirconium 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 zirconium create a more severe hazard than the zirconium and where acceptable to an authority having jurisdiction who is knowledgeable of the hazards associated with zirconium.

8-2.3 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 zirconium sponge, powder, or chips.

8-2.4 As an alternative, a specially engineered fire protection system specifically designed to be compatible with the hazards present in the zirconium operation area shall be permitted to be installed in areas where combustible loading is essential to the process operation.

8-3 Extinguishing Agents and Application Techniques.

8-3.1 Only listed or approved Class D extinguishing agents or those tested and shown to be effective for extinguishing zirconium

fires shall be permitted. A supply of extinguishing agent for manual application shall be kept within easy reach of personnel while they are working with zirconium. The quantity of extinguishing agents shall be sufficient to contain anticipated fires.

8-3.2 Agents intended for manual application shall be kept in identified containers. Container lids shall be secured in place to prevent agent contamination and to keep the agent free of moisture. Where large quantities of agent are expected to be needed, a clean, dry shovel shall be provided with the container. Where small amounts are needed, a hand scoop shall be provided with each container.

8-3.3 Portable or wheeled extinguishers approved for use on zirconium fires shall be permitted and shall be distributed in accordance with NFPA 10, *Standard for Portable Fire Extinguishers*.

8-3.4* Portable fire extinguishers shall be provided in accordance with NFPA 10, *Standard for Portable Fire Extinguishers*. Water-based or CO₂ extinguishers shall not be provided in areas containing zirconium sponge, chips, or powder.

Exception: CO₂ extinguishers shall be permitted in areas containing zirconium for use on electrical fires. Such CO₂ extinguishers shall be clearly marked "not for use on zirconium fires."

8-3.5 The following agents shall not be used as extinguishing agents on a zirconium fire because of adverse reaction:

- (a) Water;
- (b) Gaseous-based foams;
- (c) Halon; and
- (d) Carbon dioxide.

8-3.6 An ABC dry chemical extinguisher and a B:C dry chemical extinguisher shall not be used as a zirconium fire extinguishing agent, but shall be permitted to be used on other classes of fires in the area where zirconium is present.

8-3.7* Dry sodium chloride, or other dry chemicals or compounds suitable for extinguishment or containment of zirconium 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.

8-3.8 Zirconium fines shall be segregated by storage in noncombustible drums.

8-3.9* Where a fire occurs in processing equipment, material feed to the equipment shall be stopped. When feed is stopped, the equipment shall be kept in operation.

Exception: Where continued operation of equipment would cause the spread of fire, it shall be stopped.

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*, 1996 edition.

NFPA 30, *Flammable and Combustible Liquids Code*, 1996 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*, 1996 edition.

NFPA 54, *National Fuel Gas Code*, 1996 edition.

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

NFPA 86C, *Standard for Industrial Furnaces Using a Special Processing Atmosphere*, 1995 edition.

NFPA 86D, *Standard for Industrial Furnaces Using Vacuum as an Atmosphere*, 1995 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-1-1.1 See Appendix B for supplementary information on zirconium.

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

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 Zirconium Chips. Zirconium chips vary in ease of ignition and rapidity of burning, depending on their 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 Zirconium 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 the explosibility parameters of combustible dusts.

A-1-5 Zirconium Powder. 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 the explosibility parameters of combustible dusts.

A-1-5 Zirconium Sponge. Zirconium 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-2-2.1 NFPA 68, *Guide for Venting of Deflagrations*, contains information on the subject of deflagration venting.

A-2-2.3 Floors should be slightly crowned or drained to prevent the accumulation of water in the vicinity of reduction furnaces.

A-2-3.4 For additional information on ovens and furnaces, see NFPA 86, *Standard for Ovens and Furnaces*.

A-2-4.1 For information on guidelines for handling and storing chlorine, see *The Chlorine Manual*.

A-2-4.3 Zirconium 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, zirconium tetrachloride in contact with the eyes or skin results in a double burn, one caused by the acid, the other caused by the heat of reaction. Any skin that comes in contact with zirconium tetrachloride should be wiped immediately and then flushed with a large amount of water. Eyes splashed with zirconium tetrachloride also should be flushed with copious amounts of water.

A-2-5.4 A high-efficiency cyclone-type collector presents less hazard than a bag-type or media-type collector and, except where collecting extremely fine powders, usually operates with fairly high collection efficiency. Where cyclones are used, the exhaust fan discharges to the 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-type 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 appropriate protection provided. In each instance, the fan is the last element downstream in the system. Because of the extreme hazard involved with a bag-type 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 explosion ultimately can be expected where a bag-type or media-type collector is used to collect zirconium 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-type or media-type collector. Since this presents a strong explosion potential, the bag-type or media-type collector should be located a safe distance from buildings and personnel.

If a bag-type or media-type collector is used, the shaking system or dust removal system can be such that it minimizes sparking due to frictional contact or impact. Pneumatic or pulse-type shaking is recommended, 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, the baghouse should be protected by an alarm that indicates excessive pressure drop across the bags. An excess air temperature alarm also is frequently used. A bag-type or media-type collector should be located at least 50 ft (15 m) from any other building or operation. Personnel should not be permitted to be within 50 ft (15 m) of the collector during operation or when shaking bags. Deflagration vents usually are built into the system, in accordance with NFPA 68, *Guide for Venting of Deflagrations*. Care should be exercised in locating the vents because of the possibility of blast damage to personnel or adjacent structures.

A-2-5.5 Information on spark-resistant fans and blowers can be found in AMCA Standards Handbook 99-0410-86, *Classification for Spark-Resistant Construction*.

A-2-6 Molten magnesium and molten magnesium chloride present an extremely dangerous fire and fume hazard, in addition to an explosion hazard, where they come into contact with water or residual moisture.

A-2-7.1 Wet zirconium sponge has the potential to generate hydrogen gas. Sealed covers have the potential to confine hazardous accumulations of hydrogen within the container.

A-3 Unlike other metals, which can be melted, cast, or molded without unusual complications, zirconium, because of its strong affinity for oxygen, hydrogen, and nitrogen and its tendency to become contaminated, is melted in special water or NaK (sodium-potassium alloy)-cooled copper crucibles under a vacuum or with an inert gas blanket of argon or helium. During the early years of the zirconium 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 specifications.

During the 1950s, several zirconium 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 a single incident. The explosion hazard is present with any crucible or electrode that is water-cooled.

The use of liquid metal NaK 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-3-1.3 The explosion that can occur due to the rapid phase transformation and dissociation reaction of water in contact with molten material takes place over a time span of approximately 10^{-5} seconds to 10^{-4} seconds. This is faster than a condensed phase detonation. The required pressure-relieving device is not 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 relieve safely only much slower increases in pressure, such as might occur from small incursions of water onto the top of the molten metal. Following a breach in the vacuum system, air enters the furnace, which could create a secondary explosion due to the presence of hydrogen generated by the molten metal/water reaction.

A-3-1.4 The use of a magnetic field to deflect the electric arc away from the crucible wall should be considered.

A-3-2 The general process for shape casting of zirconium 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 is poured. A vacuum or inert gas is provided to protect the metal from atmospheric contamination. The furnace crucible is made of copper and uses water or NaK for 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-3-2.5 Personnel entering furnace shells to conduct inspections or repair work should first make certain that any inert gas has been purged from the shell (*see Title 29, Code of Federal Regulations, Part 1910.146, "Permit Required Confined Spaces"*). All combustible or pyrophoric residues should be removed or deactivated. Residues from casting furnaces are known to be combustible or pyrophoric and caution should be exercised.

A-4 Forging remains the most popular method of forming zirconium 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 often should be controlled precisely to achieve specific metallurgical and physical properties. Slabs, billets, and bar stock are produced by forging.

Large rounds of zirconium are produced by lathe turning or by grinding forges. A considerable amount of zirconium strip, coil, and sheet in thicknesses as thin as those of foil is produced from slabs on both continuous mills 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. Zirconium wire is produced from coils of rolled bar by drawing operations. Fastener stock is produced from coils of wire. Zirconium 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*, in operations where static electricity presents a hazard.

A-5-1 If a sufficient coolant flow is not used, improperly designed or dull tools can produce high temperatures at the interface, causing ignition of the turnings.

A-5-2.2 Cleaning methodologies should consider the hazards of creating airborne dusts and the dangers associated with the use of vacuum cleaners.

A-5-3.1 See Figures A-5-3.1(a) through (e) for typical dust collector drawings.

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

A-5-3.4 For example, iron-oxide dusts are known to be incompatible with zirconium 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.

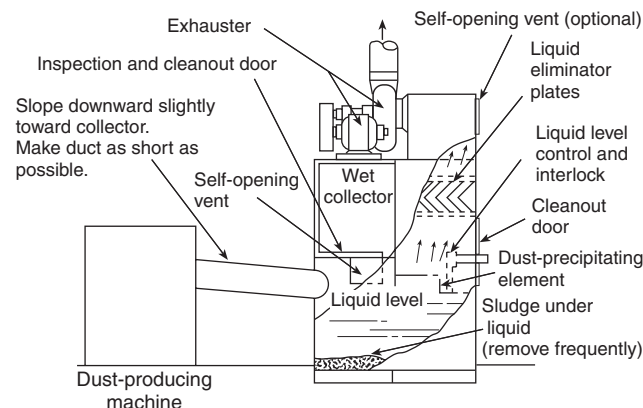


Figure A-5-3.1(a) Typical liquid precipitation separator for fixed dust-producing equipment.

A-5-3.7 Wet zirconium sludge has the potential to generate hydrogen gas. Sealed covers have the potential to confine hazardous accumulations of hydrogen within the container.

A-6 Generation of zirconium scrap from the sponge and melting processes through milling and fabrication is an inherent part of the zirconium 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 zirconium 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 forging, welding, and fabrication shops. Other scrap includes lathe turnings and clippings.

Before recycling, lathe turnings and chips are usually crushed, chopped, degreased, and compacted with a water-soluble detergent. Solid scrap is more difficult to handle. A method of handling fairly large chunks of zirconium 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 zirconium. Reduction of zirconium hydride and some forms of milling are generally used to produce the limited amounts of powder now needed commercially. To reduce oxidation and possible ignition hazards, milling can 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.

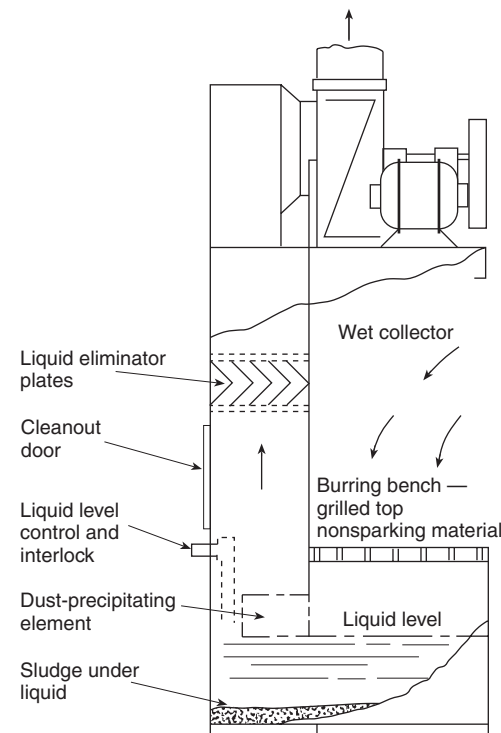


Figure A-5-3.1(b) Typical liquid precipitation separator for portable dust-producing equipment.

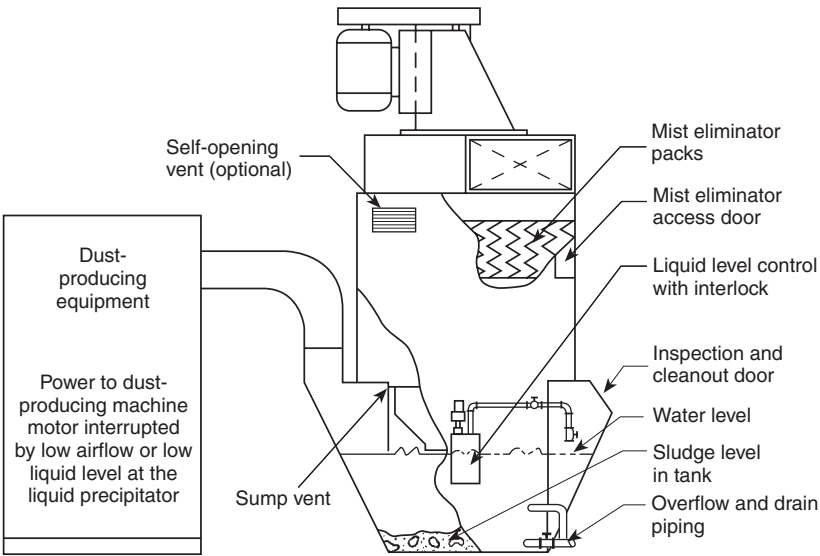


Figure A-5-3.1(c) Typical liquid precipitation separator for fixed dust-producing equipment.

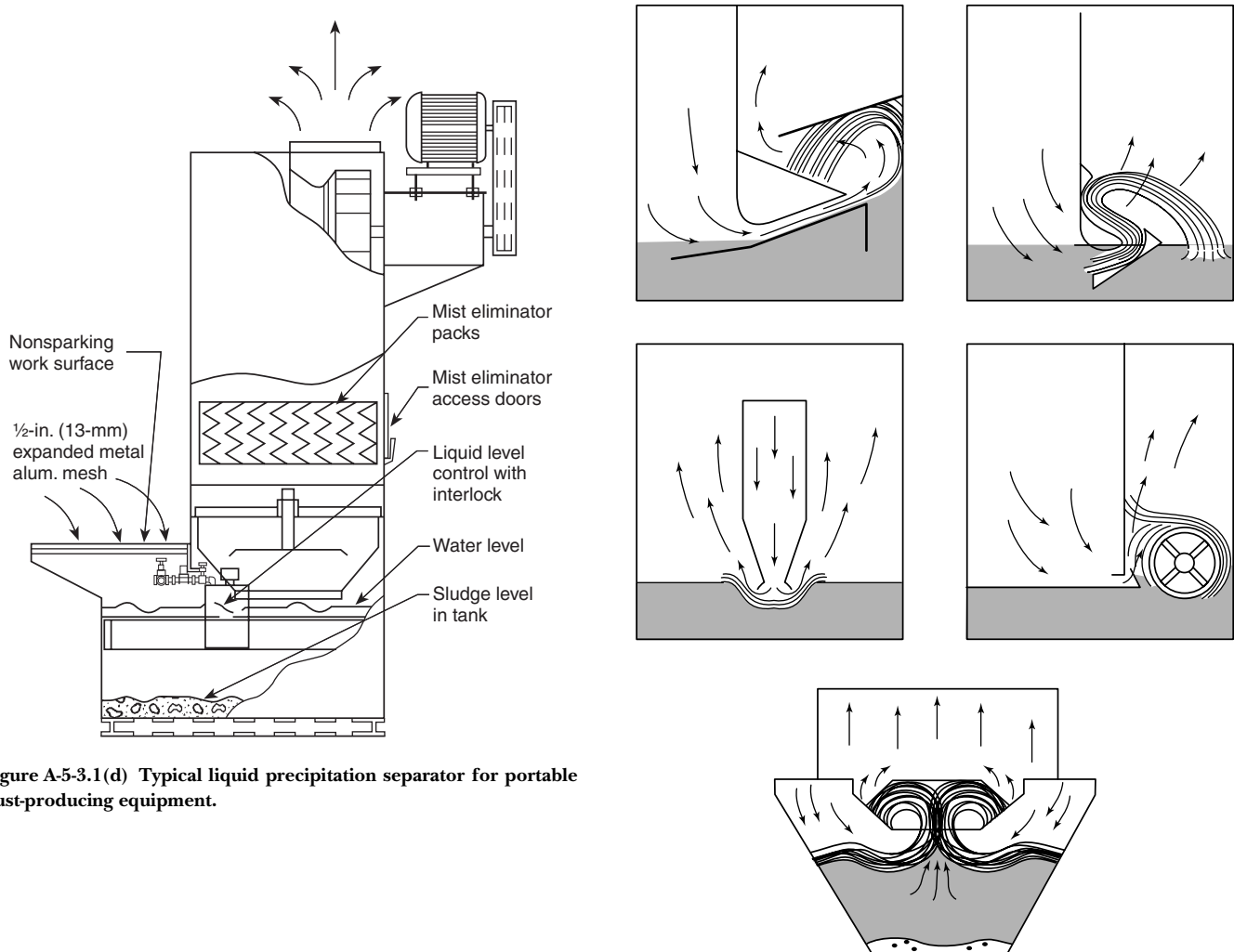


Figure A-5-3.1(d) Typical liquid precipitation separator for portable dust-producing equipment.

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).

Like many other metal powders, zirconium is capable of forming explosive mixtures in air. The ignition temperatures of dust clouds, under laboratory test conditions, range from 626°F to 1094°F (330°C to 590°C). The minimum explosive concentration is 0.045 oz/ft³ (45.1 g/m³). The maximum pressure produced in explosions in a closed bomb at a concentration of 0.5 oz/ft³ (500 g/m³) 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/s to 29,670 kPa/s); the maximum rate of pressure rise ranged from 550 psi/sec to 10,000 psi/sec (3792 kPa/s to over 69,000 kPa/s). The minimum energy of electrical condenser discharge sparks necessary for ignition of a dust cloud was 10 millijoules; for a dust layer, the minimum value was 8 microjoules. Some samples of zirconium powder were ignited by electric sparks in pure carbon dioxide, as well as in air. In some cases, zirconium at elevated temperatures was found to react in nitrogen as well as in carbon dioxide. Zirconium powder is considered a flammable solid.

A-7-1.1 Experience has shown that the tendency for autoignition increases with decreasing particle size of the powder. In particular, in the range of 40 microns and below, the particles exhibit pyrophoric tendencies. This tendency is exacerbated in the presence of moisture.

A-7-1.2 For information on designing deflagration venting, see NFPA 68, *Guide for Venting of Deflagrations*.

A-7-2.2 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 zirconium powders. Design considerations should include the use of deflagration venting, proper dust collection systems, inerting, or a combination of these. The inert gas used should be determined by test to be appropriate for the zirconium powder being handled. Zirconium powder can react exothermically in pure carbon dioxide atmospheres and in pure nitrogen atmospheres.

Tests have shown that, to prevent explosions, the limiting oxygen concentrations for the inert gases argon and helium are 4.0 percent and 5.0 percent, respectively. (See NFPA 69, *Standard on Explosion Prevention Systems*, for further information on limiting oxygen concentrations for safe handling of metal powders.)

This data was obtained from U.S. Bureau of Mines, Report of Investigations 3722, *Inflammability and Explosibility of Metal Powders*, Report of Investigations 4835, *Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium, and Their Hydrides*, and Report of Investigations 6516, *Explosibility of Metal Powders*.

A-8-1.3 For information on cutting and welding practices, see NFPA 51B, *Standard for Fire Prevention in Use of Cutting and Welding Processes*.

A-8-1.4 Molten magnesium and molten magnesium chloride present an extremely dangerous fire and fume hazard, in addition to an explosion hazard, where they come into contact with water or residual moisture.

A-8-1.7 Consideration should be given to the potential ignition sources associated with the operation of cleaning and processing equipment during the cleaning operation.

A-8-1.9 Special attention should be given to the segregation of ordinary trash and the routine collection of sponge, chips, and powder from floor sweepings as a function of housekeeping.

A-8-1.14 For information on static electricity, see NFPA 77, *Recommended Practice on Static Electricity*.

A-8-2 The objectives in fighting zirconium fires are isolation and containment, rather than extinguishment. Water and other liquids have proven ineffective in extinguishing zirconium fires. Streams of water intensify the fire by feeding it oxygen. There is also the possibility of causing a steam or hydrogen explosion, particularly if large amounts of zirconium are involved. The great affinity of high-temperature zirconium for oxygen frees 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.

Because of their unique nature, zirconium fires demand a comprehensive fire protection plan wherever zirconium is processed, handled, used, or stored. This plan should include specific actions in the event of a zirconium fire and should be coordinated with the local facility management, responding fire fighters, and medical personnel.

This plan should recognize the extreme hazards associated with zirconium-water reactions that might occur with sprinkler water. Specific attention should be given to an evacuation plan for personnel in the event of any release of water.

Properly trained personnel who work with zirconium know its hazards. Such personnel are best equipped to extinguish a zirconium fire in its incipient stage. Training should include sufficient information to determine if extinguishment can be accomplished safely and effectively.

A-8-2.2 Automatic sprinkler protection should not be used in buildings used for blending and melting.

A-8-3.4 Water-based extinguishers approved for use on Class A fires should be used only on fires involving ordinary combustibles. Extinguishers approved for Class B fires should be used for fires involving oil, grease, and most flammable liquids. Extinguishers approved for Class C fires should be used for fires involving electrical equipment.

A-8-3.7 Experience has shown that dry sodium chloride is one of the most effective chemicals for containing zirconium sponge or fines fires. 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 also are effective. Covering the fire completely reduces the accessible oxygen supply, thereby slowing the burning rate so that eventual extinguishment is achieved.

A-8-3.9 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 Zirconium

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

B-1 History. Klaproth first reported the discovery of the element zirconium in 1789 during his analysis of the precious stone called jargon. Other chemists confirmed his discovery

and, in 1797, Vauquelin reported on some of its properties and detailed its preparation. At that time, it was called zirconia. Berzelius first isolated the impure metal in 1824, but it was not until 1925 that the ductile metal was produced by van Arkel and deBoer, using their hot-wire reduction process.

A commercial-scale production process for making ductile zirconium was developed at the U.S. Bureau of Mines Laboratories where Dr. Wilhelm Kroll served as consultant and advisor for the process that bears his name.

B-2 Properties.

B-2.1 Zirconium is a silvery-gray metal having a close-packed hexagonal crystal structure at room temperature. At 1584°F (862°C), the crystal structure changes to a body-centered cubic structure. Both structures are very ductile, and the metal is easily machined, rolled, and extruded using conventional equipment and methods.

B-2.2 Some of the chemical and physical properties of zirconium are shown in Table B-2.2:

Table B-2.2 Physical Properties of Zirconium

Atomic number	40
Atomic weight	91.22
Atomic radius	1.60 angstrom units
Specific gravity	6.5
Melting point	3360°F (1850°C)
Boiling point	6475°F (3580°C)
Electronegativity	1.6
Valence	+4 (in most chemical reactions)

B-2.3 Zirconium has a very low capture cross section for thermal neutrons (0.18 barns). Its principal alloys have outstanding resistance to corrosion in water and steam at high temperatures. These properties make zirconium desirable as a cladding material for fuel elements in water-cooled nuclear power reactors. However, it becomes embrittled and loses strength on long-term exposure to air at temperatures above 1004°F (540°C).

B-3 Combustibility and Explosibility.

B-3.1 In laboratory tests, a dust cloud of fine particles of zirconium with an average particle diameter of 3.3 microns ignited spontaneously at 68°F (20°C). Powder having an average particle diameter of 17.9 microns would not ignite under similar circumstances until heated to 662°F (350°C). Similar clouds in carbon dioxide had to be heated to 1020°F (550°C) for ignition to occur. In atmospheres of air and helium, at least 5 percent oxygen had to be present to obtain spark ignition of zirconium dust clouds.

B-3.2 Layers of zirconium powder on hot surfaces ignited at 374°F (190°C) in air; at 1148°F (620°C) in carbon dioxide; and at 1454°F (790°C) in nitrogen.

B-3.3 The minimum explosive concentration for zirconium dust in air was found to be 0.04 oz/ft³ (40.5 g/m³). At concentrations of 1.0 oz/ft³ (1000 g/m³), the maximum explosion pressure was 76 psig to 78 psig (524 kPa gauge to 538 kPa gauge), and the maximum rate of pressure rise ranged from 9500 psi/sec to 10,000 psi/sec (65,500 kPa/s to 69,000 kPa/s). For further information, see U.S. Bureau of Mines Reports of Investigations 3722, *Inflammability and Explosibility of Metal Pow-*

ders, and Report of Investigations 4835, *Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium, and Their Hydrides*.

B-4 Hazards.

B-4.1 Zirconium and its alloys do not present a serious risk where handled in most forms in which they are ultimately used (e.g., tubes, bars, and sheets). However, finely divided chips, turnings, or powder can be easily, sometimes spontaneously, ignited and can burn very rapidly. Although other potential hazards exist during melting, those that have resulted in the most serious and lethal accidents have been associated with the handling of zirconium powders, finely divided scrap, and so-called black reaction residues. For this reason, special precautions should be observed during handling or disposal of these materials.

Several companies have reported that fires have occurred while zirconium bars, plates, and other shapes were being chopped. A number of fires have occurred where hot or burning chips fell into accumulations of moist fines on or under lathes or milling machines. The most violent reactions have occurred where burning chips fell into drums or deep containers partially filled with moist turnings or scrap.

B-4.2 In the molten state, zirconium either dissolves or is contaminated by every known refractory. Slight contamination apparently has little effect on the flammable characteristics of chips, turnings, or powder produced in machining operations. However, such contamination should be avoided because of its effect during acid treatment, in salt baths, or during exposure in nuclear reactors.

B-4.3 At temperatures considerably below its melting point, zirconium or zirconium sponge readily combines with oxygen, nitrogen, carbon dioxide, hydrogen, and water vapor. Surface discoloration can indicate contamination. Contaminated sponge can present an increased combustion hazard.

B-5 Special Hazards.

B-5.1 A cloud of zirconium dust in air presents a serious flash fire hazard, as well as a potential explosion hazard. Accumulations of static dust on horizontal and vertical surfaces (e.g., beams, walls, ledges, ductwork) present the potential for a more serious dust explosion, since such static dust is likely to be thrown into suspension by the disturbance created by the ignition of a dust cloud in the same area. Therefore, the importance of preventing and controlling any dispersions of zirconium dust or powder warrants special emphasis. The provision of inert atmospheres in equipment and storage containers and the use of special cleaning equipment are two methods that aid in preventing explosions. Any dust deposits produced accidentally should be cleaned up promptly and the affected area washed down. All collected dust should be kept in small containers [1 gal (3.8 L) maximum] under water until disposal. Good housekeeping and prevention of ignition sources in areas where zirconium powder is handled are essential.

B-5.2 The burning rate of zirconium chips and turnings increases where water or water-soluble oils are present as a surface coating. The burning rate also increases with increasing pile depth, degree of confinement, and increasing void space in the pile. Chips and turnings less than 0.003 in. (0.08 mm) thick are particularly susceptible to rapid burning. Where all other factors are equal, partially wet material ignites more easily and burns more rapidly than dry material.

B-5.3 Small amounts of water tend to increase the risk of explosion. Additional heat is liberated on formation of the hydrated oxide, thereby increasing the chance of an explosion. Scrap that is fully immersed in water generally does not overheat because the water provides a substantial heat sink. However, with tight-packed, very finely divided zirconium, some risk might still be present.

B-5.4 Explosions can occur while immersing specimens of uranium alloys of 1 percent to 50 percent zirconium in nitric acid or while subsequently handling the clean, dry surface after nitric acid pickling. The formation of such explosive surface coatings can be mitigated by providing fluoride ions in the pickling bath. The fluoride should be in the form of 30 grams of ammonium fluoride per liter of 50 percent nitric acid/50 percent water solution.

B-5.5 There are incipient hazards associated with collected zirconium particulate where it is mixed with ordinary combustibles during cleanup or where it is mixed with laundry. Depending on the particular problems generated, management techniques should be developed to mitigate any hazards to the general public. Any and all zirconium wastes generated should be disposed of in accordance with all federal, state, and local regulations.

B-5.6 In the case of certain common metals, such as nickel and iron, zirconium can form eutectic mixtures that exhibit melting points much lower than the individual metals and can result in unexpected meltdown. The condition can be exacerbated by one or more of the materials being in a finely divided form.

B-6 Molten Metal and Water.

B-6.1 As with any other molten metal, a violently destructive explosion can occur if water is present in any mold, pit, or depression into which molten zirconium is poured or spilled. The damage might be the result of a steam explosion, an exothermic chemical reaction, a low-order hydrogen/air explosion, or a combination of these.

B-6.2 Several violent explosions have occurred in titanium melting furnaces using consumable electrodes. The explosions occurred when cooling water accidentally entered the furnace. These explosions are of interest to the zirconium production industry because of the chemical and physical similarities between titanium and zirconium and the fact that the same types of furnaces are used for both metals. These accidents resulted in the formation of a committee of industry representatives that prepared general guidelines for the design of titanium and zirconium melting furnaces. Their recommendations have been published by the Defense Metals Information Center of Battelle Memorial Institute and have been considered in the development of this standard.

B-7 Pickling of Zirconium. Several mineral acids are used in the production of zirconium sponge and mill shapes, including hydrochloric, nitric, sulfuric, and hydrofluoric acids. The acids are used to pickle the surfaces of zirconium ingots, to clean reaction vessels and copper crucibles, and to pickle and clean mill shapes of zirconium and its alloys. Care should be exercised to prevent overheating acid baths during pickling operations to prevent explosions. Acid supplies should be stored remote from production facilities.

B-8 Tests for Zirconium.

B-8.1 Several tests can be used in the identification of zirconium and its alloys. It is important that other metals are separated from zirconium alloys if the zirconium is to be recycled.

B-8.1.1 Spark Test. Titanium, zirconium, and hafnium produce a very brilliant spark when held against a grinding wheel. The white lines traced by the flying sparks end with bursts that produce several brilliant white rays or branches.

B-8.1.2 Glass Test. The softer grades of zirconium, titanium, and hafnium can be identified by rubbing a moistened piece of the metal on a piece of glass. The metal leaves distinctive gray-white marks on the glass.

B-8.1.3 Density Test. Titanium, zirconium, and hafnium can be separated by density measurement. Their densities are 4.54 g/cm³, 6.50 g/cm³, and 13.3 g/cm³, respectively.

B-8.1.4 Spectroscope. The use of a portable metal spectroscope is best for identifying and separating zirconium alloys.

B-9 Zirconium Alloys.

B-9.1 The following nuclear grade zirconium alloys are available:

UNS R60001	99.5 percent Zr; 0.05 percent max. Fe and Cr; 0.005 percent max. H ₂ ; 0.025 percent max. N ₂ ; 0.05 percent max. C; 0.02 percent max. Hf.
UNS R60802	1.2 percent to 1.7 percent Sn; 0.07 percent to 0.2 percent Fe; 0.05 percent to 0.15 percent Cr; 0.03 to 0.08 percent Ni; balance percent Zr.
UNS R60804	1.2 percent to 1.7 percent Sn; 0.18 percent to 0.24 percent Fe; 0.07 percent to 0.13 percent Cr; balance, Zr.
UNS R60901	96 percent Zr; 3 percent Nb; 1 percent Sn.

B-9.2 Non-nuclear grades of the alloys specified in B-9.1 are available and contain up to 4.5 percent hafnium. (See Table B-9.2.)

Table B-9.2 Nuclear and Non-nuclear Zirconium Alloy Grades

Nuclear Grade	Non-nuclear Grade
R60001	701
R60802	702
R60804	704
R60901	705 (tentative)

B-10 Applications.

B-10.1 One of the major uses of zirconium alloys is in the nuclear field where it is used for the cladding of fuel elements of water-cooled power reactors.

B-10.2 Zirconium alloys are used for chemical process equipment and chemistry laboratory equipment. They also are used as filament material for photo flashbulbs.

B-10.3 In zirconium processing and production plants, zirconium is used for critical parts where corrosion resistance and minimal contamination are of extreme importance. Some typ-

ical applications include raffinate storage vessels, venturi scrubbers, pollution control piping and ducts, fan housings and blades, heat exchanger shells and tubes, and other equipment exposed to chloride attack.

B-10.4 Zirconium is an efficient gettering agent for removing hydrogen, oxygen, nitrogen, and carbon dioxide from vacuum tubes. Where alloyed with titanium at a ratio of 66 percent Zr to 34 percent Ti, zirconium gettering efficiency is increased.

B-10.5 In powder form, zirconium is used as an ingredient in lighter flints and in the pyrotechnic component of safety flares.

B-10.6 Zirconium sheet is formed into special crucibles used for sodium peroxide fusions conducted in analytical chemistry laboratories.

B-11 Production.

B-11.1 Zircon-bearing sand is found throughout the world, including the United States. The most abundant mineral containing zirconium is zircon; the second is baddeleyite (ZrO_2). Only zircon is used currently for the production of zirconium.

B-11.2 The element hafnium is associated with zirconium in each of the two ores. In zircon, it is present in the ratio of one part hafnium to 49 parts zirconium. Most of this hafnium is removed by liquid-liquid extraction in glass columns before the zirconium can be used for nuclear grade alloys.

B-11.3 The production of zirconium begins with the manufacture of zirconium tetrachloride (ZrCl_4) by high-temperature reaction with chlorine (Cl_2) in the presence of a reducing agent, usually carbon. The zirconium tetrachloride is made into zirconium sponge by means of the Kroll process.

B-11.4 In the Kroll process, zirconium tetrachloride vapor is fed to a steel reaction chamber containing molten magnesium. The reduction is carried out under an inert atmosphere of dry argon or helium at 1292°F to 1652°F (700°C to 900°C), with magnesium chloride formed as a by-product. Any residual magnesium chloride or magnesium is vacuum-distilled from the reaction chamber, leaving behind a porous form of zirconium called "sponge."

The reactor is cooled to 122°F (50°C) and the sponge treated with air for a short period to reduce the possibility of igniting the sponge. The reactor then is evacuated, backfilled with inert gas, and cooled to 68°F (20°C). The sponge then is removed, crushed, and sized.

B-11.5 An electrolytic process for producing zirconium is currently under development. In this process, zirconium tetrachloride is fed to a fused salt bath containing sodium chloride and other materials. The zirconium produced is a crystalline form of the metal that then is crushed and leached.

B-11.6 Zirconium ingot is produced by arc-melting a consumable electrode of compacted sponge (or sponge and alloy) in a cooled copper crucible. The molten metal is protected by a vacuum or an inert atmosphere.

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

NFPA 69, *Standard on Explosion Prevention Systems*, 1992 edition.

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

NFPA 86, *Standard for Ovens and Furnaces*, 1995 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 AMCA Publication. Air Movement and Control Association, 30 West University Drive, Arlington Heights, IL 60004.

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

C-1.2.2 Battelle Memorial Institute Publications. Battelle Memorial Institute, Defense Metals Information Center, Columbus, OH.

General Recommendations of Design Features for Titanium and Zirconium Production-Melting Furnaces, 1961.

C-1.2.3 Chlorine Institute Publication. The Chlorine Institute, Inc., 2001 L Street NW, No. 506, Washington, DC 20036.

The Chlorine Manual, 5th edition, 1986.

C-1.2.4 U.S. Bureau of Mines Publications. U.S. Bureau of Mines, Cochran's Mill Road, Pittsburgh, PA 15236-0070.

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

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

RI 6516, *Explosibility of Metal Powders*, M. Jacobsen, A. R. Cooper, and J. Nagy, 1964.

C-1.2.5 U.S. Government Publication. U.S. Government Printing Office, Superintendent of Documents, Washington, DC 20402.

Title 29, *Code of Federal Regulations*, Part 1910.146.

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