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NFPA 482
Production, Processing, Handling, and Storage of Zirconium
1987 Edition

NFPA

National Fire Protection Association Batterymarch Park, Quincy, MA 02269

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There is a concern that the growing use of synthetic materials may produce more or additional toxic products of combustion in a fire environment. The Board has, therefore, asked all NFPA technical committees to review the documents for which they are responsible to be sure that the documents respond to this current concern. To assist the committees in meeting this request, the Board has appointed an advisory committee to provide specific guidance to the technical committees on questions relating to assessing the hazards of the products of combustion.

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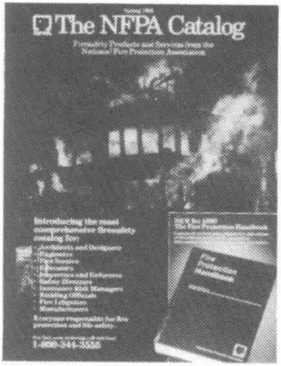

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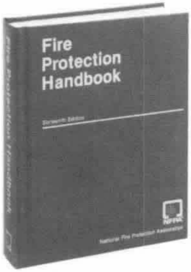

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NFPA 482

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

Zirconium

1987 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 acted on by the National Fire Protection Association, Inc. at its Fall Meeting held November 17-20, 1986, in Denver, Colorado. It was issued by the Standards Council on December 10, 1986, with an effective date of December 30, 1986, and supersedes all previous editions.

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

Origin and Development of NFPA 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 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.

This 1987 edition is a reconfirmation of the 1982 edition.

Committee on Combustible Metals

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This list represents the membership at the time the Committee was balloted on the text of this edition. Since that time, changes in the membership may have occurred.

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Standard for the

Production, Processing, Handling, and Storage of

Zirconium

1987 Edition

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

Supplementary information on zirconium can be found in Appendix B.

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

Chapter 1 General

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

1-2 Purpose. The purpose of this standard is to call attention to the fire and explosion hazards involved in the production, processing, fabrication, and storage of zirconium and to outline requirements and recommendations for fire prevention and protection, as well as safe personnel practices. The information is based on the present state of the art developed through more than 25 years of production and use in nuclear reactors and chemical processing equipment. The purpose of this standard is also to provide management with the necessary information to develop a comprehensive plan for personnel safety, fire and explosion prevention, and fire and explosion protection.

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

Approved. Acceptable to the "authority having jurisdiction."

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

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

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

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

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

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

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

Sponge. A term used to identify the zirconium metal after it has been won from the ore, but before it is melted into an ingot.

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

Zirconium. A metallic element of very low toxicity used primarily in alloy form.

Chapter 2 Sponge Production

2-1 Plant Construction.

2-1.1 Buildings housing reduction furnaces, boring, and sponge crushing facilities, and magnesium refining operations shall be constructed of noncombustible materials. Consideration shall be given to the provision of explosion venting, designed according to information contained in NFPA 68, *Guide for Explosion Venting*, and in the U.S. Bureau of Mines Reports of Investigations 3722, 4835, and 4879.

2-1.2 All buildings shall have adequate ventilation.

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

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

2-2 Processing Equipment.

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

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

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

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

2-3 Storage of Raw Materials.

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

2-3.2* Chlorine containers shall be handled and stored in accordance with recommendations published in *The Chlorine Manual*. (*See Appendix C-1.2.*)

2-3.3 Containers of zirconium tetrachloride ($ZrCl_4$) shall be stored in a cool, well-ventilated, dry location away from areas of acute fire hazard. Containers shall be plainly labeled and tightly sealed until used.

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

2-4 Dust Collection.

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

2-4.2 Bag houses for collection of magnesium chloride dust shall be kept warm and dry.

2-4.3 Collectors shall be emptied daily.

2-4.4 Bag houses shall not be used for collection of zirconium fines.

2-5 Fire Prevention.

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

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

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

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

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

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

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

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

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

2-5.10 Smoking and uncontrolled use of open flames shall be prohibited in all areas where zirconium sponge is bored, crushed, dried, or stored and in all areas where zirconium fines are produced or stored. Areas shall be clearly posted with "No Smoking" signs.

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

2-6* Fire Protection.

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

2-6.2* For containment and extinguishment of zirconium fires, approved extinguishing agents (*see A-2-6.2*) shall be provided in sufficient quantity and shall be stored in sealed containers. Such agents shall be kept in all areas where zirconium fines and sponge are bored, crushed, dried, blended, or stored. Shovels shall be stored with the agents, if needed for application. All extinguishing agent storage areas shall be clearly identified and easily accessible.

2-6.3* Inert gas (argon or helium) to prevent or extinguish zirconium fires is practical only where the zirconium is handled in an enclosure.

2-6.4* Zirconium fines or sponge shall be segregated by storage in noncombustible drums or tote bins. Burning drums or tote bins shall be moved away from processing equipment and out of buildings as rapidly as possible.

2-6.5* When a fire occurs in processing equipment, material feed to the equipment shall be stopped. The equipment shall be kept in operation, if possible, until all burning material is removed.

2-7 Personnel Safety Precautions.

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

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

2-7.3* Personnel working in chlorine handling or storage areas shall carry respiratory protection at all times. Liquid chlorine shall be handled and stored in accordance with recommendations published in *The Chlorine Manual. (See C-1.2.)*

2-7.4 Personnel involved in reduction furnace tapping, removal of molten magnesium chloride, and magnesium refining shall wear tight above-ankle shoes, flame-retardant clothing, heat-resistant gloves, and face shields. Respirators shall be carried at all times.

2-7.5* Tight above-ankle shoes, flame-retardant clothing, heat-resistant gloves, and face shields shall be worn by all personnel involved in magnesium refining and casting operations. Respirators shall also be carried at all times.

2-7.6* Protective clothing, gloves, and respirators shall be worn by personnel involved in the handling of magnesium chloride. Skin contacted by magnesium chloride shall be promptly washed with water.

2-7.7 Chemical safety goggles or face shields and protective clothing shall be worn by all maintenance personnel when any joint or connection containing a potentially dangerous liquid or gas is being opened.

2-7.8 To prevent potential explosions caused by inadvertently using high pressure compressed air in place of low pressure inert gas, fittings used on compressed air and inert gas line outlets shall not be interchangeable.

2-7.9 Magnesium refining and casting operations shall be protected from rain and all possibilities of water spillage shall be avoided.

2-8 Sponge Storage and Shipping Requirements.

2-8.1 Long-term storage of zirconium sponge shall be in steel drums with tight-fitting clamp-on sealable lids, backfilled with argon. Short-term storage may be in tote bins holding not more than 15,000 lb (67 925 kg).

2-8.2 Dry zirconium fines shall be stored in tightly sealed noncombustible 5-gal (19-L) drums, backfilled with argon.

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

2-8.4* Transportation of zirconium and zirconium fines or powder shall meet all applicable requirements of the U.S. Department of Transportation's Hazardous Materials Regulations.

Chapter 3* Sponge Melting

3-1 Explosion Prevention.

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

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

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

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

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

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

3-1.7 The furnace shall be equipped with:

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

(b) arc voltage and amperage recorders;

(c) electrode position indicators;

(d) furnace pressure sensors and recorders.

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

3-2* Casting.

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

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

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

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

3-3 Fire Prevention.

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

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

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

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

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

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

3-4 Fire Protection.

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

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

3-4.2 Small zirconium fires may be controlled by the use of dry metal powder, flux, or dry salt. (*See A-2-6.2.*) Burning material shall be removed from the equipment and the building as fast as possible.

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

3-5 Personnel Safety Precautions.

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

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

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

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

3-6 Ingot Storage and Shipment.

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

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

Chapter 4* Mill Operations

4-1 Fire Prevention.

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

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

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

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

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

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

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

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

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

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

4-1.11 Swarf shall be packaged in small amounts of 1 gal (3.785 L) or less in work areas. Where containers of fines are stored awaiting final disposal, containers shall contain not more than 15 gal (56.8 L) of material. Container size shall be chosen so that a minimum of free space exists above the level of the contents.

4-2 Fire Protection.

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

4-2.2 All mill buildings shall be provided with portable fire extinguishers according to NFPA 10, *Standard for Portable Fire Extinguishers*. (*See A-3-4.1.*)

4-3 Personnel Safety Precautions.

4-3.1* Personnel operating mill equipment shall wear face shields, gloves, and proper protective clothing.

4-3.2* In plants where swarf is commonly disposed of by burning, care shall be exercised in handling of swarf, selection of the burning area, and in the method used for ignition.

4-3.2.1 The maximum quantity of heavy swarf burned at any one time shall be limited to a 4-in. (10-cm) thick layer.

4-3.2.2 Fine swarf (less than 325 mesh or 44 microns) shall be burned in layers not more than 1 in. (2.5 cm) thick.

4-3.3 Ignition shall be remotely initiated.

4-4* Mill Product Storage.

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

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

Chapter 5 Machining and Fabrication

5-1 Machining Operations.

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

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

5-2 Pressing and Forming.

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

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

5-3 Welding.

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

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

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

5-4 Fire Prevention.

5-4.1 Work areas shall be cleaned daily and residue from operations shall be removed to a safe storage or disposal area. Where vacuum cleaners are used, they shall be emptied frequently.

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

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

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

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

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

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

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

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

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

5-5 Fire Protection.

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

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

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

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

5-6 Dust Collection.

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

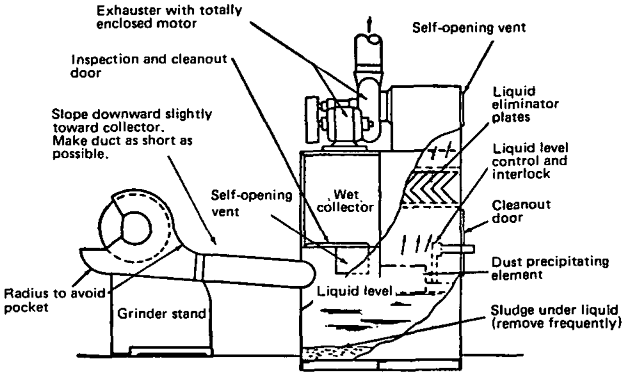

Figure 5-6.1(a) Typical liquid precipitation separator for a fixed grinding unit.

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

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

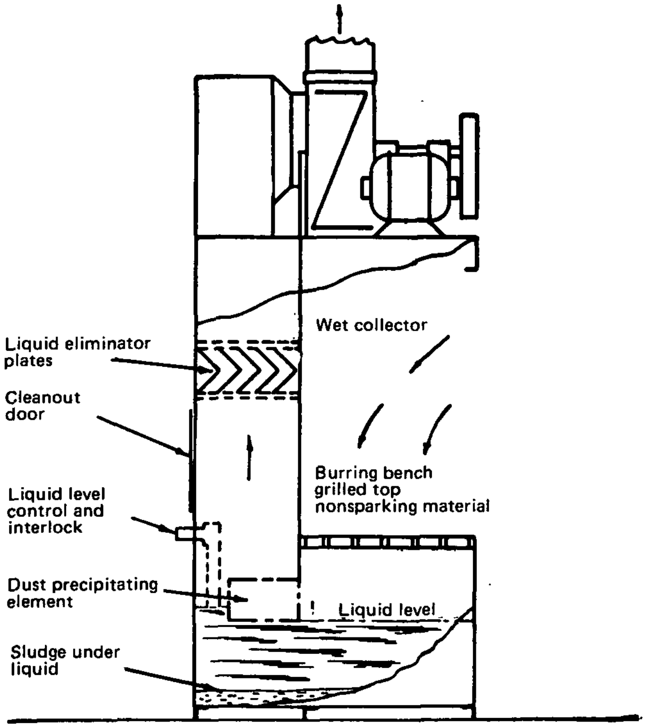

Figure 5-6.1(b) Typical liquid precipitation separator for a portable grinding unit. [*See Note under Figure 5-6.1(a).*]

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

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

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

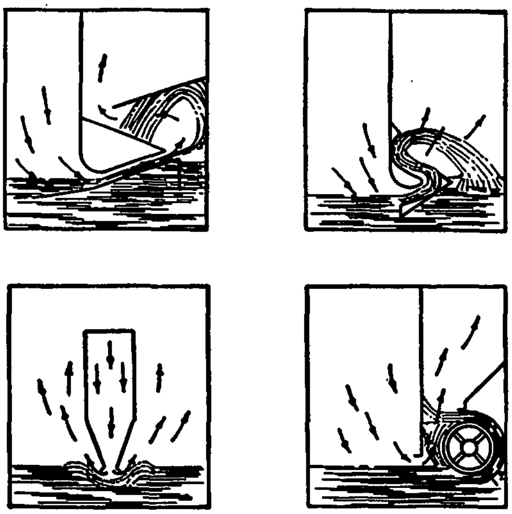

Figure 5-6.1(c) Diagram of four methods of precipitating dust used in precipitators such as those shown in Figures 5-6.1(a) and (b).

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

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

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

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

5-7 Personnel Safety Precautions.

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

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

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

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

Chapter 6* Scrap Generation, Processing, and Storage

6-1* Fire Prevention and Storage.

6-1.1 Dry zirconium fines shall be kept dry for recycling or burning. Such fines shall be stored under an argon or helium atmosphere in a sealed container.

6-1.2 Fines produced in wet operations shall be kept wet by storing under water or oil until disposal by recycling or burning.

6-1.3 Each container shall be labeled to identify the type of scrap and its source.

6-1.4 Areas used for torch cutting of massive pieces of scrap shall be kept free of combustible materials. Swarf shall be collected daily and removed to a disposal area.

6-1.5* Oily lathe turnings and swarf shall be stored in small covered containers no larger than bucket size in well-ventilated areas or in enclosed outside areas remote from buildings.

6-1.6 "No Smoking" signs shall be posted around all scrap processing and storage areas. Only authorized personnel shall be allowed in these areas.

6-1.7 Open storage of sheet, plate, forgings, or massive pieces of scrap presents no fire problems and shall be permitted.

6-1.8 Fire protection requirements shall be as set forth in Section 2-6.

6-2 Personnel Safety Precautions.

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

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

Chapter 7* Powder Production and Use

7-1 Shipping and Storage.

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

7-1.1.1 Zirconium powder shall be shipped in steel containers that have been filled in a chamber filled with argon, or the container shall be backfilled with argon before sealing. Care shall be taken to not disturb the powder and to keep the argon in the container.

7-1.1.2 The powder containers shall be packed within a similar steel container.

7-1.2 Containers of zirconium powder shall be stored in well-ventilated areas, kept free of combustible material, and protected from damage.

7-2* Handling.

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

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

7-3 Fire Prevention.

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

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

7-3.3* All mixing and blending of dry zirconium powder shall be done in an inert atmosphere of argon or helium. Oxygen content of the inert atmosphere shall be monitored, with alarms set to sound when the oxygen content exceeds 1.0 percent.

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

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

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

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

7-4 Fire Protection.

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

7-4.2 High pressure streams or fog streams of water shall not be used to extinguish fires in zirconium powder. Water may be used with extreme caution where copious amounts may be quickly applied to the powder.

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

7-5 Personnel Safety Precautions.

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

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

Chapter 8 Referenced Publications

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

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

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

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

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

NFPA 70-1987, *National Electrical Code*

NFPA 91-1983, *Standard for the Installation of Blower and Exhaust Systems*

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

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

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

8-1.2 Other Publications.

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

Appendix A

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

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

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

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

A-2-6 Water and other liquids have proven ineffective in extinguishing zirconium 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 zirconium for oxygen will free a considerable amount of hydrogen, which may reach explosive concentrations in confined spaces. Entrapment of water under any burning or hot metal may result in a steam explosion. Where water has been applied in copious quantities by dumping a tankful of water or by using a large heavy stream, fire control is possible. However, fire fighters and production personnel must be trained in such techniques.

A-2-6.1 While automatic sprinklers are desirable for the areas noted, they are specifically not recommended for installation over sponge production areas, crushing, leaching and drying operations, chlorinators, magnesium refining equipment, blending operations, or sponge storage areas.

A-2-6.2 Covering a zirconium fire to reduce or remove the oxygen supply will slow the burning rate so that eventual extinguishment occurs. A few salts or mixtures are effective for this purpose, including commercial dry extinguishing powders approved for use on Class D (combustible metal) fires, dry sodium chloride, and a dry fluxing compound consisting of potassium chloride, magnesium chloride, and calcium fluoride. (CAUTION: Sodium chloride is highly hygroscopic and should be stored in a warm, dry area.)

A-2-6.3 Inert gas is not practical for extinguishment of zirconium fires.

A-2-6.4 Application of dry salt or a dry powder will tend to minimize the fire and contain it, but any container in which a fire occurs will usually become a total loss, along with the material contained.

A-2-6.5 Keeping the equipment in operation until all burning material is removed actually reduces damage to the equipment. Small amounts of burning material can be handled with a shovel to facilitate removal.

A-2-7.1 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 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 zirconium tetrachloride must be wiped immediately and then flushed with a large amount of water. Eyes splashed with zirconium tetrachloride must also be flushed with copious amounts of water.

A-2-7.3 Chlorine gas is highly irritating to the eyes and respiratory tract. Canister-type gas masks are only effective to a maximum concentration of 1000 ppm.

A-2-7.5 Molten magnesium presents a potentially dangerous fire and fume hazard, in addition to an explosion hazard, if contacted with water.

A-2-7.6 Magnesium chloride dust can be highly irritating to the skin, especially if perspiration is present. Also, magnesium chloride will readily absorb moisture to create a slipping hazard.

A-2-8.4 At present, there are no special requirements set by the U.S. Department of Transportation for shipment of sponge. However, it is common practice to ship sponge in 55-gal (208-L) metal drums with tightly sealed, clamp-on lids, backfilled with argon.

A-3 Unlike other metals that 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, must be melted in special water-cooled copper crucibles under a moderately high vacuum or an inert gas blanket of dry argon or helium.

During the 1950s, several titanium melting furnace explosions occurred when water inadvertently entered the melting crucibles during the melting operation. A similar hazard exists with zirconium. Three distinct types of explosions were evident: steam explosions produced by water contacting molten metal; chemical reactions between the molten metal and water; explosions 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 both consumable and nonconsumable electrode furnaces, which use water as the coolant.

A-3-2 The general process for shape casting of zirconium is the "skull-casting" process in which 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 cooling. Due to the high power levels used, seams in the crucible should not be visible to the electric arc or the molten metal.

A-3-4.1.1 Water-base extinguishers suitable for use on Class A fires should only be used on fires in ordinary combustibles. Extinguishers suitable for Class B fires are recommended for fires involving oil, grease, and most flammable liquids. Extinguishers suitable for Class C fires should be used for fires in electrical equipment.

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

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

Large rounds of zirconium are produced by lathe turning or by grinding forges. A considerable amount of zirconium 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. 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; thin wall tubing is usually formed from extruded stock by tube reducing equipment.

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

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

A-4-3.1 The wearing of hard hats, safety glasses or goggles, and safety shoes is recommended.

A-4-3.2 Zirconium swarf has been known to explode shortly after ignition, spreading fire to the mobile bin or transporting vehicle and a fairly large surrounding area.

A-4-4 No special regulations apply to storage or shipment of zirconium mill products. Packing and handling procedures are the same as for the more common ferrous and nonferrous metals. Automatic sprinkler protection is recommended for warehouses containing mill products packed in wood crates or paper casings.

A-5-1.2 The use of forced dry air as a coolant results in less contamination to chips and has resulted in fewer fire incidents. While water-soluble cutting oils facilitate rapid removal of chips, they complicate recycling and disposal processes with respect to fire and explosion hazards.

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

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 forge, welding, and fabrication shops. Other scrap includes lathe turnings and sheet clippings. Swarf is produced by sawing and grinding operations.

If scrap is to be accumulated for recycling, care must be taken to segregate the scrap by grade. Finely divided swarf is normally sufficiently contaminated that the zirconium cannot be recovered economically.

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 complete the preparation for recycling. Another method of handling fairly large chunks of scrap is to weld them to the sides of consumable electrodes prior to melting.

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

A-6-1 The storage of zirconium fines has resulted in some spectacular fires and explosions with resulting injury and death to personnel working in the storage area. Often, the cause has been loss of the liquid used to cover the fines. A monitoring program is therefore recommended to ensure that the liquid is not lost by leakage or evaporation.

A-6-1.5 When stored in the open for any length of time, the water-soluble oils gravitate to the base of the pile. The water evaporates, leaving the oily residue. If exposed to an ignition source, the oil may ignite and create enough heat to ignite the zirconium. Sparks from the blades of earth-moving equipment have been known to cause ignition, followed by an explosive reaction in piles of turnings. Where possible, it is recommended that swarf and other fines be burned to the stable oxide before disposal, storage, or shipment.

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 required commercially. (Ordinary methods of grinding produce an excessively oxidized product unsuitable for certain purposes.) To reduce oxidation and possible ignition hazards, the operation is always conducted in a chamber having an inert atmosphere of argon. The atmosphere is monitored for oxygen, with an alarm sounded when oxygen content exceeds 1.0 percent. The powder is sealed in metal containers in the chamber. Subsequent removal of the powder, pressing, and sintering is also done in an argon-filled chamber or under vacuum.

Like many other metal powders, zirconium is capable of forming explosive mixtures in air. The ignition temperature of dust clouds, under laboratory test conditions with various samples, was 20°C. The minimum explosive concentration was 0.10 oz/ft^3 (0.10 kg/m^3). In tests where energy was applied, powder exploded at concentrations of 0.04 oz/ft^3 (40.5 g/m^3) and 15 millijoules of energy. Maximum pressure produced in explosions in a closed bomb at a concentration of 0.5 oz/ft^3 (0.5 kg/m^3) ranged from 47 to 66 psi (324 to 455 kPa) . The average rate of pressure rise in these tests ranged from 2350 to 3900 psi/sec (16,203 to 26,890 kPa/sec); the maximum rate of pressure rise ranged from 760 to over 7500 psi/sec (5,240 to over 51,712 kPa/sec). The minimum energy of electrical condenser discharge sparks required for ignition of a dust cloud was 5.0 millijoules; for a dust layer, the minimum value was 0.064 microjoules. Some samples of zirconium powder were ignited by electric sparks in pure carbon dioxide, as well as in air. In some cases, zirconium was found to react at elevated temperatures in nitrogen as well as in carbon dioxide.

A-7-2 The hazards of zirconium powder in powder metallurgy are similar to those associated with other combustible metal powders. The fire risk tends to increase with decreasing particle size. The fire risk may also be affected by the type of surface coating on the particles.

A-7-3.3 Tests reported in U.S. Bureau of Mines Reports of Investigations 3722 and 4835 indicate that the maximum oxygen concentrations allowed for different inert gases are:

Carbon Dioxide	0 percent oxygen
Nitrogen	4.5 percent oxygen
Argon	4.0 percent oxygen
Helium	5.0 percent oxygen

Appendix B Supplementary Information on Zirconium

This Appendix is not a part of the requirements of this NFPA document, but is included for information 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 862°C, the crystal structure changes to body-centered cubic. 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 as follows:

Atomic Number	40
Atomic Weight	91.22
Atomic Radius	1.60 angstrom units
Specific Gravity	6.5
Melting Point	1850°C
Boiling Point	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, Zircaloy 2, 3, and 4, 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 540°C.

B-3 Combustibility and Explosibility.

B-3.1 In laboratory tests, a dust cloud of fine particles of zirconium (average particle diameter of 3.3 microns) ignited spontaneously at 20°C. Powder having an average particle diameter of 17.9 microns would not ignite under similar circumstances until heated to 350°C. Similar clouds in carbon dioxide had to be heated to 650°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 190°C in air; at 620°C in carbon dioxide; and at 790°C in nitrogen.

B-3.3 The minimum explosive concentration for zirconium dust in air was found to be 0.04 oz/ft^3 (40.5 g/m^3). At concentrations of 1.0 oz/ft^3 (1013 g/m^3), maximum explosion pressure was 76 to 78 psig (524 to 538 kPa) and maximum rate of pressure rise ranged from 9500 to 10,000 psi/sec (65,500 to 68,950 kPa/sec). For further information, see U.S. Bureau of Mines Reports of Investigations 3722 and 4835.

B-4 Hazards.

B-4.1 Zirconium and its alloys do not present serious risk when handled in most forms in which they are ultimately used, i.e., tubes, bars, and sheets. However, finely divided chips, turnings, or powder may be easily—sometimes spontaneously—ignited and may 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 must 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 when hot or burning chips fell into accumulations of moist fines on or under lathes or milling machines. The most violent reactions have occurred when 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 contaminations should be avoided because of effects during acid treatment, in salt baths, or in radioactivity from materials exposed in nuclear reactors.

B-4.3 At temperatures considerably below its melting point, zirconium readily combines with oxygen, nitrogen, carbon dioxide, hydrogen, and water vapor. Freshly exposed surfaces of the metal tend to quickly form an adherent oxide coating evidenced by surface discoloration.

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 (beams, walls, ledges, ductwork, etc.) present the potential for a more serious dust explosion since such static dust will likely be thrown into suspension by the disturbance created by 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. Provision of inert atmospheres in equipment and storage containers and the use of special cleaning equipment are two methods which aid in preventing explosions. Any dust deposits produced accidentally should be promptly cleaned up 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. Needless to say, 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 when 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. (0.8 mm) thick are particularly susceptible to rapid burning. Other factors being 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, thus increasing the chance of an explosion. Scrap that is fully immersed in water will generally not overheat because the water provides a substantial heat sink. However, with tight-packed, very finely divided zirconium, it would seem that some risk might still be present.

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

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 may be the result of a steam explosion, an exothermic chemical reaction, a low-order hydrogen/air explosion, or by a combination of these.

B-6.2 In the 1950s, several violent explosions occurred in titanium melting furnaces using consumable electrodes. The explosions occurred when cooling water accidentally entered the furnace. These explosions are of interest to zirconium production because of the chemical and physical similarity between titanium and zirconium and the fact that the same 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. The acids are used to pickle the surfaces of magnesium ingots, to clean reaction vessels and copper crucibles, and for pickling and cleaning 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 will assist in the identification of zirconium and its alloys. It is important that other metals be 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 will leave distinctive grey-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, 6.50, and 13.3 g/cm^3, respectively.

B-8.1.4 Spectroscope. A portable metal spectroscope will better serve the purpose for identifying and separating zirconium alloys.

B-9 Zirconium Alloys.

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

ASTM 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.
ASTM R60802 Zircaloy 2	— 1.2 to 1.7 percent Sn; 0.07 to 0.2 percent Fe; 0.05 to 0.15 percent Cr; 0.03 to 0.08 percent Ni; balance Zr.
ASTM R60804 Zircaloy 4	— 1.2 to 1.7 percent Sn; 0.18 to 0.24 percent Fe; 0.07 to 0.13 percent Cr; balance Zr.
ASTM R60901 Creep Resistant	— 96 percent Zr; 3 percent Nb; 1 percent Sn.

B-9.2 Non-nuclear grades of the above alloys are available, designated as follows and having up to 4.5 percent hafnium:

Nuclear Grade	Non-Nuclear Grade
R60001	701
R60802	702
R60804	704
R60901	705 (tent.)

B-10 Applications.

B-10.1 By far the largest use of zirconium alloys is in the nuclear field where it is used for the cladding on fuel elements of water-cooled power reactors.

B-10.2 Zirconium alloys are used for chemical process equipment and chemistry laboratory equipment. They are also 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 typical 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 scavenging hydrogen, oxygen, nitrogen, and carbon dioxide from vacuum tubes. When alloyed with titanium at a ratio of 66 percent Zr to 34 percent Ti, its 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 Zirconium-bearing ores are found throughout the world, including the United States. The most abundant mineral containing zirconium is zircon; second is baddeleyite (ZrO_2). At present, only zircon is used for production of zirconium.

B-11.2 Associated with zirconium in each of the two ores is the element hafnium. In zircon, it is present in the ratio of one part hafnium to 49 parts zirconium. Most of this hafnium must be 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 via 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 700 to 900°C, with magnesium chloride formed as a byproduct. The molten magnesium chloride and excess magnesium are drained off. 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 50°C and the sponge treated with air for a short period to reduce the possibility of igniting the sponge. The reactor is then evacuated, backfilled with inert gas, and cooled to 20°C. The sponge is then 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 is then 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 vacuum or an inert atmosphere.

Appendix C Referenced Publications

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

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

NFPA 49-1975, *Hazardous Chemicals Data*

NFPA 68-1978, *Guide for Explosion Venting*

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

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

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

C-1.2 Other Publications.

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

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

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

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

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SUBMITTING PROPOSALS ON NFPA TECHNICAL COMMITTEE DOCUMENTS

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

INSTRUCTIONS

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

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

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

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

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

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

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

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

(a) identification of the submitter and his affiliation (Committee, organization, company) where appropriate, and
(b) identification of the document, paragraph of the document to which the proposal is directed, and
(c) a statement of the problem and substantiation for the proposal, and
(d) proposed text of proposal, including the wording to be added, revised (and how revised), or deleted.