The Report of the Committee on Combustible Metals is presented in 2 parts.


Part I has been submitted to letter ballot of the Committee on Combustible Metals which consists of 7 voting members; of whom 6 voted affirmatively and 1 abstained (Mr. Lawrence).

Mr. Lawrence abstained based on his inability to participate at the meeting at which the complete revision was developed.


Part II has been submitted to letter ballot of the Committee on Combustible Metals which consists of 7 voting members; of whom 6 voted affirmatively and 1 abstained (Mr. Lawrence).

Mr. Lawrence abstained based on his inability to participate at the meeting at which the complete revision was developed.
Chapter 1 General

1-1 Scope.

1-1.1 This standard shall apply to the processing, handling, and storage of magnesium at magnesium foundries, processing plants, and commercial storage facilities.

1-1.2 This standard shall not apply to the primary production of magnesium.

1-1.3 This standard shall not apply to the production of magnesium powders. (See NFPA 651, Standard for the Manufacture of Aluminum and Magnesium Powder.)

1-2 Purpose. The purpose of this standard is to call attention to the fire and explosion hazards in the storage, handling, and processing of magnesium or magnesium alloys marketed under different trade names but commonly referred to as magnesium, and to emphasize the measures that can be taken to control such hazards. The requirements of this standard are based on conclusions drawn from available reports and data on magnesium fire tests and actual fire experience. (See Appendix E for Supplementary Information on Magnesium.)

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, the authority having jurisdiction may base acceptance on compliance with NFPA or other appropriate standards. In the absence of such standards, the authority having jurisdiction may base acceptance on compliance with NFPA or other appropriate standards. In the absence of such standards, the authority having jurisdiction may base acceptance on compliance with NFPA or other appropriate standards. In the absence of such standards, the authority having jurisdiction may base acceptance on compliance with NFPA or other appropriate standards.

Authority Having Jurisdiction. 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."

Fire-Resistive. Meeting the requirements for Type I or Type II construction, as described in NFPA 220, Standard on Types of Building Construction.

Part I

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: This 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.

Magnesium. Refers to either pure metal or alloys having the generally recognized properties of magnesium, marketed under different trade names and designations.

Noncombustible. In the form used and under the conditions anticipated, will not ignite, burn, support combustion, or release flammable vapors when subjected to fire or heat (Materials reported as noncombustible, when tested in accordance with the Standard Method of Test for Noncombustibility of Elementary Materials, ASTM E-136, shall be considered noncombustible materials.)

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

Chapter 2 Magnesium Mill and Foundry Operations

2-1 Melting and Casting Operations.

2-1.1* Buildings of noncombustible construction with high roofs and adequate ventilation shall be considered for melting and casting operations. Floors of buildings shall be noncombustible. Melt rooms shall have easy and adequate access to facilitate fire control.

2-1.2* All metal added to melting pots shall be thoroughly dried. Floors around melting operations shall be of hard-burned or vitreous paving block, cast iron plate, or steel plate, laid in concrete and kept clean and free of moisture. Fuel supply lines to melting pots shall have remote fuel shut-offs.

2-1.3 Furnace settings shall be kept dry and free of iron scale. Safety runoff containers shall be provided for all melting pots and crucibles. Melting pots and crucibles shall be inspected regularly. Pots and crucibles that show evidence of possible failure or that allow molten metal to contact concrete or iron scale shall be discarded.

2-1.4 Ladles, skimmers, and sludge pans shall be thoroughly dried and preheated before pouring. Permanent molds shall also be purged with sulfur dioxide gas prior to use and between pourings.

2-1.5 Operators in melting and casting areas shall wear flame-resistant clothing, high foundry shoes, and adequate face protection.

2-2 Rough Finishing of Castings.

2-2.1* Provisions shall be made for proper removal of dust produced at grinders and for immediate quenching of sparks produced by such equipment.

2-2.2 Cuttings and swarf from saws shall be swept up at regular intervals to prevent excessive accumulations in work areas.

2-2.3 Good housekeeping shall be maintained.

2-2.4 Electrical equipment and wiring, including motors, shall be approved for use in Class II, Group E, atmospheres and shall be installed in accordance with Article 502 of NFPA 70, NATIONAL ELECTRICAL CODE*. 

2-2.5 Work benches and other equipment shall be noncombustible.

2-2.6 Operators in finishing areas shall wear caps and hard finished or flame-resistant outer clothing without pockets or cuffs.
2-3* Heat Treating.

2-3.1 A standard procedure for checking the uniformity of temperatures at various points within heat treating furnaces shall be established. Furnaces shall be tested prior to use and at regular intervals during use to locate undesirable hot spots.

2-3.2 Furnaces shall be properly and tightly constructed. Gas- or oil-fired furnaces shall be provided with combustion safety controls.

2-3.3 All furnaces shall have two sets of temperature controls operating independently: one to maintain the desired operating temperature; the other, to operate as a high temperature limit control, shall cut off fuel or power to the heat treating furnace at a temperature slightly above the desired operating temperature.

2-3.3.1 To further retard ignition of magnesium, a dilute sulfur dioxide or carbon dioxide atmosphere may be provided in furnaces operating above 750°F (399°C).

2-3.4 Magnesium parts to be put in a heat treating furnace shall be carefully freed of magnesium turnings, chips, and sawdust.

2-3.5 Magnesium billets, castings, and wrought products shall not be placed in a heat treating furnace with wood spacers or pallets.

2-3.6* Aluminum parts, sheets, or separators shall not be included in a furnace load of magnesium.

2-3.7 There shall be strict adherence to the heat treating temperature cycle recommended by the alloy manufacturer.

2-3.8 Molten salt baths containing nitrates or nitrites shall not be used for heat treating magnesium alloys. Special salt fluxes may be safely used for dip-brazing of magnesium.

2-3.9 The possibility of accidental immersion of magnesium alloys in salt baths used for aluminum is ever present in areas where both metals are being processed. Every effort shall be made to keep these metals segregated and easily identified.

Chapter 3 Machining and Fabrication of Magnesium

3.1 Machining.

3.1.1 Cutting tools shall not be allowed to ride on the metal without cutting, as the frictional heat may ignite any fine metal that is scraped off. For the same reason, the tool shall be backed off as soon as the cut is finished. Cutting tools shall be kept sharp and ground with sufficient clearance to prevent rubbing on the end and sides of the tool.

3-1.2* When drilling deep holes (depth greater than five times the drill diameter) in magnesium, high helix drills (450) shall be used to prevent packing of the chips produced.

3-1.3 Adequate relief on tools used in grooving and parting operations shall be maintained, since the tool tends to rub the sides of the groove as it cuts. Side relief shall be 50; end relief shall be between 100 and 200.

3-1.4 Flashing of chips during machining may be minimized by any of the following methods:

(a) Keep surface speed below 300 ft per minute (91.4 m/min) or above 2000 ft per minute (609.6 m/min).

(b) Increase feed rate to 0.008 to 0.010 in. per revolution (0.2 to 0.25 mm per revolution).

(c) Control relative humidity in the machining area to 45 percent or lower.

(d) Use an alloy containing 3 percent or less aluminum and 1 percent or less zinc.

(e) Use high aluminum (9 percent) + high zinc (2 - 3 percent) magnesium alloy in the solution heat treated condition (T4).

(f) Use carbide tools.

(g) Apply a coolant.

3-1.5* If lubrication is needed, as in tapping or extremely fine grooving, a high flash point neutral mineral oil shall be used. Water, water-soluble oils, and oils containing more than 0.2 percent fatty acids shall not be used, as they may generate flammable hydrogen gas.

3-1.6 Where compressed air is used as a coolant, special precautions shall be taken to keep the air dry.

3-1.7 All machines shall be provided with a pan or tray to catch chips or turnings. The pan or tray shall be installed so that it can be readily withdrawn from the machine in case of fire. It shall be readily accessible for chip removal and for application of extinguishing agent to control a fire.

3-1.7.1 In case of a fire in the chips, the pan or tray shall be immediately withdrawn from the machine, but it shall not be picked up or carried away until the fire has been extinguished.

3-2 Grinding, Buffing, and Wire Brushing.

3-2.1 Dust Collection.

3-2.1.1* Dust shall be collected by means of suitable hoods or enclosures at each operation. Hoods and enclosures shall be connected to a liquid precipitation separator in such a way that the dust will be converted to sludge without contact, in the dry state, with any high speed moving parts. (See Figures 3-2.1 (a) and (b) for examples of liquid precipitation separators.)

3-2.1.2 Connecting ducts or suction tubes shall be completely grounded and as short as possible, with no unnecessary bends. Ducts shall be carefully fabricated and assembled, with a smooth interior and with internal lap joints pointing in the direction of air flow. Ducts shall have no unused capped side outlets, pockets, or other dead-end spaces which might allow an accumulation of dust. (See NFPA 91, Standard for the Installation of Blower and Exhaust Systems.)

3-2.1.3 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.

3-2.1.4 Not more than four portable dust-producing machines in a single enclosure or stand may be served by a single separator.

3-2.1.5 The power supply to dust-producing machines shall be interlocked with the motor driving the exhaust blower and the liquid level controller of the liquid precipitation separator in such a way that improper functioning of the dust collection system will shut down the machine it serves. A time delay switch or equivalent device shall be provided on the dust-producing machine to prevent starting of its motor drive until the liquid precipitation separator is in complete operation and several air changes have swept out any residual hydrogen.

Figure 3-2.1 (a) Typical Liquid Precipitation Separator For a Fixed Grinding Unit.

NOTE: This drawing is schematic and intended only to indicate some of the features which are incorporated in the design of a separator. The volume of all dust-laden air spaces is as small as possible.
3-2.2 Cleaning.

3-2.2.1 Systematic cleaning of the entire grinding area, including roof members, pipes, conduits, etc. shall be carried out daily or as often as conditions warrant.

3-2.2.2 Cleaning shall be done by means of soft brushes and nonsparking scoops and containers or by means of a fixed suction pipe and outlet vacuum cleaning system.

3-2.2.3 If a fixed vacuum cleaning system is used, it shall meet the following requirements:

(a) The dust separator shall be of the liquid precipitation type.

(b) The suction system shall be of standard mild steel pipe, with standard recessed drainage fittings.

(c) A check valve shall be installed at each outlet.

(d) Implements and hoses shall be completely grounded.

(e) A rupture diaphragm shall be installed in the piping at its point of connection to the inlet of the separator so that a possible explosion in the piping may be safely vented to atmosphere.

3-2.3 Electrical Equipment.

3-2.3.1 Electric motors, lighting fixtures, control equipment, and wiring within proximity of or attached to dust-producing machines, including those used in connection with separator equipment, shall be approved for use in Class II, Group E atmospheres and shall be installed in accordance with Article 502 of NFPA 70, NATIONAL ELECTRICAL CODE.

3-2.3.2 All electrical equipment shall be inspected and cleaned periodically.

3-2.3.3 Where flashlights or storage battery lamps are used, they shall be approved for the intended use.

3-2.4 Grounding of Equipment. All equipment shall be securely grounded by permanent ground wires to prevent accumulation of static electricity. (See NFPA 77, Recommended Practice on Static Electricity.)

3-2.5 Safety Precautions.

3-2.5.1 Operators' clothing shall be easily removable and shall be kept clean and free from dust. Any smooth clothing, from which dust can be readily brushed off, may be worn. Clothing shall be made without pockets or cuffs and shall have nonferrous snap fasteners. Fabrics used in such clothing shall be flame resistant. Woolen, silk, or fuzzy outer clothing and shoes with exposed steel parts shall be prohibited.

3-2.5.2 Machinery and equipment described in 3-2.1 shall not be used for processing ferrous metals until the entire grinder and dust collecting system are thoroughly cleaned. The grinding wheel or belt shall be replaced prior to work on other metals.

3-2.5.3 No open flames or electric or gas cutting or welding equipment shall be permitted in the section of the building where magnesium dust is produced or handled while dust-producing equipment is in operation. When cutting or welding equipment is used in such areas, all machinery in the area shall be shut down and the area shall be thoroughly cleaned to remove all accumulations of magnesium dust. All internal sections of grinding equipment, ducts, and dust collectors shall be completely free of moist or dry magnesium dust and any hydrogen shall be flushed out.

3-2.5.4 Special precautions are necessary to prevent ignitions while dressing wheels used for grinding magnesium castings. Hot metal thrown off by the dressing tool may ignite dust or magnesium deposits in the hood or duct. If it is not feasible to move the wheels to a safer location for dressing, the hoods shall be thoroughly cleaned or removed entirely before dressing operations are started and all deposits of dust on and around the wheel shall be removed before, during and after dressing.

3-2.5.5 Nonsparking tools shall be used when making repairs or adjustments around grinding wheels, hoods, or collector units where magnesium dust may be present.

3-2.5.6 Dust collection equipment shall not have filters or other obstructions that will allow accumulation of dust.

3-2.5.7 Sludge pits shall be arranged so that they are well ventilated at all times.

3-2.5.8 When grinding chrome-pickled magnesium surfaces, special precautions shall be taken to prevent accumulations of dust or formation of explosive concentrations of dust and air within range of sparks which may be produced.

3-3 Drawing, Spinning, and Stamping.

3-3.1 Reliable means to prevent overheating shall be provided when heating magnesium for drawing or spinning.

3-3.2 Clippings and trimmings shall be collected at frequent intervals and placed in clean, dry, steel or other noncombustible containers. Fine particles shall be handled according to the requirements of Section 4-2.

Chapter 4 Handling and Disposal of Scrap

4-1 Disposal of Sludge from Separators.

4-1.1 Sludge from separators and vacuum cleaning system precipitators shall be removed daily as often as conditions warrant.

4-1.2 Covered, vented metal containers, preferably holding not more than 50 lbs (22.7 kg) each, shall be used to transport sludge for disposal.

4-1.3 Sludge shall be disposed of in one of the following methods:

4-1.3.1 Sludge may be mixed with sand in a ratio of 5 parts sand to 1 part sludge and then shall be discarded in a protected dump.

4-1.3.2 Sludge may be dumped in an open pit. The pit shall be fenced or guarded from public access.

4-2 Disposal of Chips, Turnings, and Swarf.

4-2.1 Chips, turnings, and other fines shall be removed from the pans under machines and from any other places where they collect at such frequency as may be needed to prevent accumulation of any large amount. Each pan shall be cleaned at the end of each day's work.

4-2.2 Magnesium fines shall be placed in covered, plainly labeled, clean, dry, steel or other noncombustible containers and removed to a detached scrap storage building or to a special scrap storage room of fire-resistant construction for subsequent salvage.

4-2.3 Magnesium fines which are not being salvaged shall be disposed of by burning in thin layers at a safe location where surrounding combustible material will not be ignited.

4-2.4 Magnesium fines which are to be recovered shall be kept free of all foreign matter other than neutral mineral oils.

4-2.5 If magnesium fines have been wet with coolants other than neutral mineral oils, they shall be handled with special care and stored outdoors.

4-2.6 Magnesium chips or turnings wet or damp with water present a definite fire and explosion hazard when attempts are made to melt or process them in foundry operations. If such chips or
turnings are included with scrap to be remelted, special precautions shall be taken to ensure that the mixture is free of moisture or water-oil emulsion.

4-3 Disposal of Clippings and Castings.

4-3.1 Solid magnesium scrap such as clippings and castings can be readily salvaged by secondary smelters. Such scrap shall not be contaminated with combustible materials as a fire in wood, heavy cardboard, or flammable liquids could ignite thin sections of the solid metal.

4-3.2 Care shall be taken to see that no pieces of scrap that are moist are thrown into a salavage pot containing molten metal. The scrap shall be preheated prior to melting to prevent a metal-water explosion.

Chapter 5 Storage of Magnesium

5-1 Storage of Pigs, Ingots, and Billets.

5-1.1 Good storage arrangement is important. The size of piles shall be limited and aisle widths shall be based on the height of the piles, in accordance with 5-1.2 and 5-1.3.

5-1.2 Yard (Outdoor) Storage.

5-1.2.1 Magnesium ingots shall be carefully piled on firm and approximately level areas to prevent tilting or toppling. Storage areas and yard pavements shall be well drained. The storage area shall be kept free of grass, weeds, and accumulations of combustible materials.

5-1.2.2 Combustible flooring or supports shall not be used under piles of ingots.

5-1.2.3 The quantity of magnesium stored in any pile shall be kept to a minimum, but in no case shall the amount exceed 1,000,000 lbs. (453,600 kg).

5-1.2.4 Aisle widths shall not be less than one half the height of the piles, but in no case shall they be less than 10 ft (3.05 m).

5-1.2.5 Readily combustible material shall not be stored within a distance equal to the height of the piles plus 10 ft (3.05 m) from any pile of magnesium ingots.

5-1.2.6 An open space, equal to the height of the piles plus 10 ft (3.05 m) shall be provided between the stored magnesium ingots and adjoining property lines where combustible materials or buildings are exposed or where the adjacent occupancy may provide fire exposure to the magnesium.

5-1.2.7 Trash shall not be burned near the storage area.

5-1.3 Indoor Storage.

5-1.3.1 Storage shall be in buildings of noncombustible construction.

5-1.3.2 Floors shall be of noncombustible construction and shall be well-drained to prevent accumulations of water in puddles.

5-1.3.3 Supports used under piles of magnesium ingots shall be noncombustible.

5-1.3.4 Storage of magnesium ingots shall be on the first or ground floor. There shall be no basement or depression below the magnesium storage area into which water or molten metal may flow or fall during a fire.

5-1.3.5 The quantity of magnesium ingots stored in any one pile shall be kept to a minimum, but in no case shall the amount exceed 500,000 lbs (226,800 kg).

5-1.3.6 Aisle widths shall comply with 5-1.2.4.

5-1.3.7 There shall be no combustible material stored in the same building with magnesium.

5-2 Storage of Heavy Castings.

5-2.1 Buildings used for the storage of magnesium castings shall be noncombustible, with particular attention given to construction and maintenance of floors.

Exception: Storage may be in buildings of combustible construction if the buildings are fully protected by an automatic sprinkler system.

5-2.2 There shall be no basement or depression below the magnesium storage area into which water or molten metal may flow or fall during a fire.
5-5.4 Aluminum sheets shall not be stored in piles of magnesium.

5-6.1 Storage of Magnesium Chips.

5-6.1 Buildings shall be of noncombustible construction.

5-6.2 All other combustible materials shall be excluded from the area used for storage of magnesium chips.

5-6.3 The amount of magnesium chips to be held in storage shall be determined in each individual case, based on use, value, and probable loss.

5-7 Storage of Scrap Magnesium Fires.

5-7.1 This section shall apply to the storage of scrap magnesium in the form of chips, turnings, swarf, or other fine particles.

5-7.2 Magnesium fires shall be kept well separated from other combustible materials. They shall be kept in covered steel or other noncombustible containers and shall be kept in such manner or locations that they will not become wet.

5-7.3 Storage in quantities greater than 50 cu ft (1.4 m³) (six 55-gallon drums) shall be kept separate from other occupancies by fire-resistant construction without window openings or by an open space of at least 50 ft (15.2 m). Such buildings shall have explosion vents designed according to information contained in NFPA 88, Guide for Explosion Venting.

5-7.4 Magnesium is melted, machined, fabricated, or stored, particularly if combustible solids, flammable liquids, or flammable gases are present.

5-8 Storage of Solid Scrap.

5-8.1 Solid magnesium scrap, such as clippings and castings, shall be stored in noncombustible bins or containers pending salvage. The storage building shall be of noncombustible construction.

5-8.2 Oilly rags, packing materials, and similar combustibles shall not be permitted in storage bins.

5-8.3 Solid scrap may be shipped loose to secondary smelters.

5-9 Storage of Finished Products.

5-9.1 This section shall apply to storage, in warehouses, wholesale facilities, and retail outlets, of magnesium in the form of finished products in which magnesium makes up the major portion of the article on a volumetric basis.

5-9.2 Storage in quantity greater than 50 cu ft (1.4 m³) shall be separated from storage of other materials that are either combustible or in combustible containers by aisles equal in width to not less than the height of the piles of magnesium products.

5-9.3 Magnesium products stored in quantity greater than 1,000 cu ft (28 m³) shall be separated into piles each not larger than 1,000 cu ft (28 m³) with aisles equal in width to not less than the height of the piles.

5-9.4 Where storage in quantity greater than 1,000 cu ft (28 m³) is in building of combustible construction, or the magnesium products are packed in combustible crates or cartons, or there is other combustible storage within 30 ft (9.1 m) of the magnesium, the storage area shall be protected by automatic sprinklers.

Chapter 6 Fire Protection

6-1 General Precautions.

6-1.1 Fire protection shall be provided in all areas where magnesium is handled, machined, fabricated, or stored.

6-1.2 Direct contact of burning magnesium with clothing, shoes, and skin shall be avoided and protected against.

6-2 Extinguishing Powders.

6-2.1 A supply of extinguishing powder approved for use on magnesium fire shall be kept within easy reach of each operator performing a machining, grinding, or other operation on magnesium. The powder shall be kept in suitable containers with easily removable covers and a hand scoop shall be provided at each container for application of the powder. Approved portable extinguishers designed for use with these powders may replace the scoop and container.

6-2.2 The amount of extinguishing powder to be provided will depend on the amount of chips or turnings involved. Where conditions may permit the development of a fire requiring a large quantity of powder, that quantity shall be provided and long-handled shovels provided for its application. Heat-resistant gloves and face guards shall be available for protection of the personnel applying the powder.

6-2.3 Containers of extinguishing powder shall be plainly labeled.

6-2.4 Extinguishing powder shall be applied by making a ring around the fire with the powder and then spreading the powder evenly over the surface of the fire to a depth sufficient to smother it. Care shall be taken to avoid scattering the burning metal. If smoking continues in spots, more powder may be added as required. Where burning magnesium is in contact with a combustible surface, a one or two-inch (25 to 50 mm) layer of powder shall be spread out

6-3 Foundry Flux. The most effective means of extinguishing fires in foundry melting and pouring areas is by application of readily available foundry flux. The flux melts or crusts over the hot metal, excluding air from the burning metal.

6-4 Water.

6-4.1 Small streams of water from portable extinguishers shall not be used on magnesium chip fires since they will violently accelerate the fire. However, a few burning chips may be extinguished by dropping them into a bucket of water.

6-4.2 Water shall not be used on any large chip fire since it is impossible to apply enough cooling capacity to handle the large surface area of the burning metal. However, automatic sprinklers will extinguish the typical shop fire where quantities of chips are limited.

6-4.3 Burning parts such as castings, wrought products, and fabricated parts may be cooled and extinguished with coarse streams of water applied with standard fire hoses. A straight stream scatters the fire, but coarse drops produced by a fixed nozzle operating from a distance or by use of an adjustable nozzle flow over and cool the unburned metal. The hose streams are then worked into the fire where some temporary acceleration takes place, followed by rapid extinguishment as water application is continued.

6-4.4 Water fog shall not be used as it tends to accelerate a magnesium fire rather than cool it.

6-4.5 Application of water to magnesium fires where quantities of molten metal are likely to be present shall be avoided. The steam formation and possible metal-water reactions may be explosive.

6-4.6 With the exercise of care to keep water from reaching molten metal, water spray applied with caution may be used to safely fight fires in combustible material near melting pots.

6-5 Automatic Sprinklers.

6-5.1 Automatic sprinkler protection, installed in accordance with the NFPA 13, Standard for the Installation of Sprinkler Systems, shall be provided where specified by other sections of this standard.

6-5.2 Substantially constructed tight tote boxes (with or without covers) have considerable confining effect on the burning of small magnesium parts within. This confining effect makes the use of such tote boxes of definite value in the control of magnesium fires by sprinklers. Noncombustible tote boxes shall be used. Tote boxes shall not be used as containers for chips or dust.

6-5.3 In general, automatic sprinkler installations, shall be considered for all buildings where magnesium is machined, fabricated, or stored, particularly if combustible solids, flammable liquids, or flammable gases are present.

6-5.4 Foundry operations shall be protected by automatic sprinklers.

6-6 Heat Treating Furnaces.

6-6.1 Magnesium fires in heat treating furnaces shall be controlled with dry extinguishing powders, foundry fluxes, or gases approved for use on such fires.

6-6.2 If powder is used, the burning metal shall, if feasible, be removed from the furnace before application of the powder.

6-6.3 Foundry fluxes may be successfully applied to the burning metal in the furnace.

6-6.4 If an approved gas is to be used, entry ports shall be provided in the furnace at a level near the floor.
A-3-2.1 Water in large volume is normally the precipitating medium. They seldom ignite due to their relatively large heat capacity. When ignited, a water fire may continue to burn and result in ignition of magnesium. Materials to continue to burn and result in ignition of magnesium.

A-2.3.6 Direct contact between aluminum and magnesium at heat treating temperatures promotes diffusion of one metal into the other, resulting in formation of a low-melting, readily ignitable compound. The high temperature flame of the burning compound can ignite the heated magnesium.

A-2-3.8 Certain commonly used molten mixtures of nitrates and nitrites can react explosively with magnesium alloys immersed in the metal. Failure to provide for proper circulation of the heated air in the furnace may result in overheating or higher temperatures in certain zones than that indicated by the thermocouples that operate the temperature control devices. If the BF 3 cylinder shall be opened enough to supply about 2 lbs per minute (0.9 kg/min) depending on the size of the furnace and the number of cylinders used. The furnace circulating fans shall be turned on for about one minute while the BF 3 is flowing into the furnace. The flow of gas shall be maintained until the furnace temperature falls to 700°F (371°C) indicating the fire has been extinguished.

A-3-1.2 Use of the high helix drills prevents frictional heat and high rates of feed, as may be consistent with good workmanship. The resulting chips are thick and relatively free of dust or fine particles of metal. Failure to provide for proper circulation of the heated air in the furnace may result in overheating or higher temperatures in certain zones than that indicated by the thermocouples that operate the temperature control devices. This system at 30 psi (207 kPa) will discharge about 2 lbs per minute (0.9 kg/min).

A-5-2 Heavy castings (25 lbs (11.3 kg) or more) having walls of less than one-quarter in. (6.35 mm) black iron pipe for insertion into the furnace. This system at 30 psi (207 kPa) will discharge about 2 lbs per minute (0.9 kg/min).

A-6-1.2 While the flame temperature of burning magnesium is about 2700°F (1482°C), the heat of combustion is only about half that of typical petroleum products. Thus, fire fighting personnel can approach a fire closely during extinguishment, if they are careless.

A-3-1.1 Water in large volume is normally the precipitating medium. While the chance of a flash fire igniting castings is remote, some dust-laden fire is possible when using the proper extinguishing agents during the early stages of the fire. Certain extinguishing agents will accelerate a magnesium fire. These agents include foam, carbon dioxide, halogenated hydrocarbons, dry chemical agents containing mono- or diammonium phosphate. Also, use of water on a magnesium chip fire should be avoided.

A-6-4.3 Well-advanced fires in several hundred pounds of magnesium chips may be extinguished after some delay when in contact with burning magnesium. Certain extinguishing agents will accelerate a magnesium fire. These agents include foam, carbon dioxide, halogenated hydrocarbons, dry chemical agents containing mono- or diammonium phosphate. Also, use of water on a magnesium chip fire should be avoided.

A-5-9.4 The entire building should be protected by automatic sprinklers. Scrape magnesium is usually received by secondary smelters in truck or carload quantities. Solid scrap may be shipped loose, but chips and turnings are packed in multiply oil-proof paper bags or covered steel drums. This scrap is commonly stored outdoors in a paved area and is covered with tarpaulins to avoid contact with water. Such scrap is ordinarily processed promptly so there is no need for a storage building. Since storage is in the open, incipient fires can be readily detected and extinguished.

A-6-4.1 When a fire in a heat treating furnace is discovered, involve a large pool of molten metal on the floor of the furnace, or is in a furnace with excessive air leaks, BF 3 cannot be expected to extinguish the fire completely. However, the gas is valuable in slowing or suppressing the fire until it can be extinguished by other means.

A-2-1.2 Moisture and foreign material are dangerous where molten metal is present. While automatic sprinkler protection is provided, a deflector shield shall be provided over the furnace or the sprinkler heads shall be removed and the ceiling or roof construction shall be modified to be noncombustible.

A-6-6.6 Water may be used to fight fire in combustible material near-by, but shall not be used in fighting fires in furnaces.

A-5-2 Heavy castings (25 lbs (11.3 kg) or more) having walls of less than one-quarter in. (6.4 mm) may be ignited after some delay when in contact with burning magnesium chips or when exposed to fires in ordinary combustible materials.

A-6-1.1 Magnesium fires are easily extinguished if attacked with the proper extinguishing agents during the early stages of the fire. Certain extinguishing agents will accelerate a magnesium fire. These agents include foam, carbon dioxide, halogenated hydrocarbons, dry chemical agents containing mono- or diammonium phosphate. Also, use of water on a magnesium chip fire should be avoided.

A-2.3.2 Such moisture may result from outdoor storage or by collection of condensate during indoor storage.

A-5-1 Magnesium pigs, ingots, and billets are not easily ignited, but they will burn if exposed to fire of sufficient intensity.

A-4-1.3.2 The fire and explosion hazards of the sludge must be kept in mind when this method of disposal is used.

A-4-2.5 Finishes, wet with water, water-soluble oils, and oils containing more than 0.2 percent fatty acids may generate flammable hydrogen gas. Finishes wet with animal or vegetable oils may ignite spontaneously.

A-4-3.2 Such moisture may result from outdoor storage or by collection of condensate during indoor storage.

A-5-3.1 A slow-burning fire in nearby combustible material may develop enough heat to ignite thin-section magnesium, producing a well-ignited magnesium fire before automatic sprinklers operate. Special importance, therefore, attaches to prompt fire detection and alarm service, prompt automatic sprinkler operation, and avoidance of obstructions to sprinkler discharge.
extinguishing, boron trifluoride gives warning through the presence of a white cloud in the air. Contrary to expectations, hydrofluoric acid is not one of the decomposition products.

Boron trifluoride gas (BCl₃) has also been used to suppress magnesium fires in heat treating furnaces. However, the required concentration is about ten times that of boron trifluoride. Also, to assure an adequate and even flow of BCl₃, means must be provided to heat the cylinder to a temperature above 34°F (12.2°C), preferably to 70°F (21°C), a practice not recommended by the suppliers. Also, a special valve and gage is needed to control the gas flow from the cylinder. Flexible 5/8 in. (16 mm) neoprene hose may be used to conduct the gas from the cylinder to the entry port of the furnace. Operations in handling a furnace fire are similar to those described for boron trifluoride.

Appendix B

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

Supplementary Information on Magnesium

B-1 Properties.

Magnesium, a silvery white metal with an atomic weight of 24.32 and specific gravity of 1.74, is sometimes described as the lightest known structural material possessing properties of permanence and stability. The melting point of magnesium is 1202°F (650°C) and the ignition temperature is generally considered to be very close to the melting point but ignitions of magnesium in certain forms may occur at air temperatures below the temperature given as the melting point. Magnesium ribbon and fine magnesium shavings can be ignited under certain conditions at air temperatures as low as 900°F (500°C), and a very finely divided magnesium powder has been ignited at air temperatures below 900°F (482°C).

Commercially pure magnesium may contain traces of aluminum, copper, iron, manganese, nickel and silicon, but these contaminants in typical analyses generally total less than 0.2 percent. Metal marketed under different trade names and commonly referred to as magnesium may be one of a large number of different alloys containing widely different percentages of magnesium, aluminum, zinc and manganese. Some of these alloys may have ignition temperatures considerably lower than that determined for pure magnesium and in some cases it may be necessary to consider the eutectic melting point of certain alloys of these metals which may be as low as 800°F (427°C) because the metal will ignite if it is held at this lower temperature for some time.

B-2 Radioactive Alloys.

There are several magnesium alloys produced which contain thorium. These alloys are used primarily where it is essential that the metal retain good mechanical properties at elevated temperatures, which is a low level radioactive material, is used in these alloys up to a nominal concentration of 3 percent. While it is possible with a sensitive radiation survey meter to detect radiation from such alloys, the level of external gamma radiation is so low that there is no hazard to personnel. The level seldom goes much above one or two millirem per hour at the surface and on small masses is less than one.

The natural decay or daughter products of thorium are locked up in the alloy until such time as the metal is melted, burned or chemically disintegrated. Under fire conditions these decay products are normally within visible fumes and are diluted as the visible fumes disperse into the air. These elements could be inhaled with possible excessive irradiation of the lung tissue and deposition in the bone structure. Maximum permissible air-borne concentrations of such radioactive materials have been set up through the Nuclear Regulatory Commission and are based on continuous exposure for a normal 40-hour work week.

B-3 Spot Tests for Magnesium.

In the construction or assembling of certain machinery or equipment, magnesium or one of its alloys having similar properties may have been used for only a few of the component parts and where finished or painted products are being stored or handled it may be difficult to determine what percentage consists of magnesium. Investigation has shown that silver nitrate, vinegar or acetic acid can be used to distinguish between parts composed of magnesium and those composed of aluminum. The portion of metal to be tested is first cleaned of grease, dirt, oxide, etc., by abrading with sandpaper or steel wool. After the test area has been prepared a drop of the test solution is placed on it.

B-3.1 Silver Nitrate Test.

The test solution is prepared by dissolving about 5 grams of silver nitrate (AgNO₃) in one liter of distilled water. A black coloration is immediately produced on magnesium or magnesium alloy. This coloration is essentially reduced silver. No coloration is noted on aluminum and its alloys, or most other metals. Zinc and cadmium will show a similar black coloration but are much heavier.

B-3.2 Vinegar or Acetic Acid Test.

Ordinary vinegar or a weak solution of acetic acid will give a bubbling reaction in contact with magnesium while other common metals are not affected.

B-4 Combustibility and Explosibility.

The ease of ignition of magnesium depends to a large extent upon the size and shape of the material as well as the size or intensity of the source of ignition. In the form of ribbon, shavings or chips with thin feather-like edges or grinding dust a spark or the flame of a match may be sufficient to start the material burning. Heavier pieces such as ingots and thick-wall castings are difficult to ignite because heat is conducted rapidly away from the source of ignition. If the entire piece of metal can be raised to the ignition temperature (about 1200°F (649°C) for pure magnesium) and any of the alloys, self-sustained burning will occur.

The combustibility of magnesium, the ineffectiveness of ordinary types of extinguishing agents on magnesium fires, and the fact that under certain conditions the application of some of these agents intensifies the burning and may release hydrogen to form an explosive gas-air mixture, all combine to create serious fire and explosion hazards.

Magnesium, in its solid form, melts as it burns and may form puddles of molten magnesium which, in the presence of sufficient moisture, may present explosion hazards similar to those associated with other molten metals.

B-5 Extent of Hazard.

Magnesium is widely used in the construction of household appliances, furniture, office equipment, portable tools, luggage, automobiles, buildings, machine parts and engines and structural members of airplanes. As a result of this general usage, the fire hazards associated with this material are of interest to firefighting and fire prevention organizations.

Appendix C

C-1 This portion of the Appendix lists publications referenced within this NFPA document and is considered part of the requirements of the document.

C-1.1 NFPA Publications. The following publications are available from the National Fire Protection Association, Batterymarch Park, Quincy, MA 02269.

NFPA 13-1978, Standard for the Installation of Sprinkler Systems

NFPA 68-1978, Guide for Explosion Venting

NFPA 70-1981, NATIONAL ELECTRICAL CODE

NFPA 77-1977, Recommended Practice on Static Electricity

NFPA 91-1973, Standard for the Installation of Blower and Exhaust Systems

NFPA 220-1979, Standard on Types of Building Construction

NFPA 651-1980, Standard for the Manufacture of Aluminum and Magnesium Powder

C-1.2 Other Publications


C-2 This portion of the Appendix lists publications which are referenced within this NFPA document for information purposes only and thus is not considered part of the requirements of the document.

Lawrence, K.D., et al, New Agents for the Extinguishment of Magnesium Fires, Washington, DC, Dept. of the Navy, Naval Research Laboratory, April, 1976, CEDDO-TR-76-19

Threshold Limit Values for Chemical Substances and Physical Agents in the Workplace Environment, Cincinnati, OH, American Conference of Governmental Industrial Hygienists, 1977
Standard for the Production, Processing, Handling, and Storage of Titanium
NFPA 481-1981

Chapter 1 General

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

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

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

Approved. "Acceptable to the authority having jurisdiction."

NOTE: The National Fire Protection Association does not approve, inspect, or certify any installations, procedures, equipment, or materials; nor does it approve or evaluate testing laboratories. In determining the acceptability of installations or procedures, equipment or materials, the authority having jurisdiction may 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 organization, office or individual responsible for "approving" equipment, an installation, or a procedure.

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

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

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

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

Appendix A.

Appendix B.

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

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

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

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

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

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

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

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

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

2-6* Fire Protection.

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

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

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

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

2-7 Personnel Safety Precautions.

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

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

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

2-7.4* Personnel working in chlorine handling or storage areas shall carry respiratory protection at all times. Liquid chlorine shall be handled and stored in accordance with recommendations published in the Chlorine Manual. (See C-1.-2.)

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

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

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

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

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

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

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

2-8 Sponge Storage and Shipping Requirements.

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

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

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

Chapter 3* Sponge Melting

3-1 Explosion Prevention.

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

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

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

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

3-1.5 A minimum of 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 0 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 which have been wetted. In all cases, ingots shall be thoroughly dried and carefully stored to prevent accumulation of moisture in the molds.

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

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

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

3-3 Fire Protection.

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

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

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

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

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

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

3-4 Fire Protection.

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

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

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

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

3-5 Personnel Safety Precautions.

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

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

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

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

3-6 Ingot Storage and Shipment.

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

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

Chapter 4* Mill Operations

4-1* Fire Prevention.

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

4-1.2 Fuel lines to gas- or oil-fired furnaces or other heating equipment shall be equipped with emergency shutoff valves installed at an accessible location remote from equipment being serviced. All lines and fittings shall be inspected regularly to detect corrosion or mechanical damage that might permit leaks to develop. (See NFPA 86A, 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 Drip Tanks Containing Flammable or Combustible Liquids.

4-1.4 When mobile bins on casters are used to transport oily castings, 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-to 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 nonflammable oil. Oil leaks shall be repaired immediately and leakage kept to a minimum. Cleanliness is required in areas where hot metal is handled or where sparks are produced and bits of scale are continuously being dropped.

4-1.7 No welding or torch cutting shall be 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 filler 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 3-4.)

4-2 Fire Protection.

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

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

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

4-3 Personnel Safety Precautions.

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

4-4 Mill Product Storage.

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

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

Chapter 5 Machining and Fabrication

5-1 Machining Operations.

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

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

5-2 Pressing and Forming.

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

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

5-3 Welding.

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

5-3.2 Welding of small assemblies may be carried out in inert gas filled chambers.
5-3.3 Special shielding devices shall be used for larger assemblies where chambers are impractical.

5-4 Fire Prevention.

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

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

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

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

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

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

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

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

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

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

5-5 Fire Protection.

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

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

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

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

5-6 Dust Collection.

5-6.1 Dust shall be collected by means of suitable hoods or enclosures at each dust-producing operation. The hoods or enclosures shall be connected to liquid precipitator 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).)

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

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

Exception: With multi-unit machines, two dust-producing machines may be served by a single separator.
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 operation and several air changes have swept out any residual hydrogen.

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

5-6.6.1 Vacuum cleaning systems shall 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 collected daily. Covered, vented steel containers shall be used to transport collected sludge to a safe storage area or for disposal by mixing with sand (in a ratio of one part sludge to five parts sand) and buried.

5-7 Personnel Safety Precautions.

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

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

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

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

Chapter 6* Scrap Generation, Processing and Storage

6-1 Fire Prevention and Storage.

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

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

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

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

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

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

6-2 Personnel Safety Precautions.

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

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

Chapter 7* Powder Production and Use

7-1 Shipping and Storage.

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

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

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

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

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

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

7-2 Handling.

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

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

7-3 Fire Prevention.

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

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

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

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

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

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

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

7-4 Fire Protection.

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

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

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

7-7 Personnel Safety Precautions.

7-7.1 Personnel handling dry titanium powder shall wear nonsparking shoes and noncombustible or flame retardant clothing without pockets, cuffs, laps, or pleats in which powder may accumulate.

7-7.2 Personnel shall also use goggles or face shields that will provide protection against flash burns.

Appendix A

This Appendix is not a part of the requirements of this NFPA standard.... 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-2-2.2 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-2-4.6 Water and other liquids have proven ineffective in extinguishing titanium sponge fires. Streams of water intensify the fire by feeding oxygen to it. There is also the possibility of causing a steam or hydrogen explosion, particularly if large amounts of sponge are involved. The great affinity of high-temperature titanium for oxygen will free a considerable amount of hydrogen which may reach explosive concentrations in confined spaces. Entrapment of water under any burning or hot metal may result in a steam explosion.
Experience has shown that dry sodium chloride is one of the most effective chemicals for containing titanium sponge or fines fires. Ammonium chloride, a nonmetallic flux compound consisting of potassium chloride, magnesium chloride, and calcium fluoride. Commercial dry fire extinguishers approved for use on combustible metals are also effective in extinguishing the fire. As the fire completely reduces the accessible oxygen supply, thereby slowing the burning rate so that eventual extinguishment is reached.

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

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

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

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

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

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

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

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

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

During the 1950s, several titanium melting furnace explosions occurred when water inadvertently entered the melting crucibles during the melting operation. Three distinct types of explosions were evident: steam explosions produced by water contacting molten metal; chemical reaction between the molten metal and water; evaporation 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 result in the same incident. The explosion hazard is present with any crucible which uses water as the coolant.

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

A-3-2.3 The general process for shape casting of titanium is the "slush-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 castings poured. Vacuum or inert gas is provided to protect the metal from atmospheric contamination. The crucible crucible is made of copper and has water or NaK cooling. Due to the high power levels used, seams in the crucible should not be visible to the electric arc or the molten metal.

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

A-4 Forging remains the most popular method of forming titanium because it is generally simpler and less costly than other forming processes. Gas or electric furnaces with accurate heat controls are used to heat the metal into the proper forging range, which may vary from 1600 to 2300°F (870 to 1260°C). The rate of heat-up and final temperature must be precisely controlled to achieve specific metallurgical and physical properties. Slabs, billets, and bar stock are produced by forging.

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

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

A-4-1.3 When stored in the open for any length of time, the water soluble oils gravitate to the base of the pile. The water evaporates, leaving the oily residue. If exposed to an ignition source, the oil may ignite and create enough heat to ignite the titanium. Sparks from this use of earth-moving equipment have been known to cause ignition, followed by an explosive reaction in piles of turnings.

A-4-1.4 Not all methods of producing metal powder are applicable to titanium. Reduction of titanium hydride and some forms of milling and generally used to produce the ingot metal. The ingot metal required commercially. To reduce oxidation and possible ignition hazards, milling may be performed under water or in an inert atmosphere of helium or argon. Some powders are given a very light copper coating during the manufacturing process.

A-4-1.5 Elliptical or flat faces on a broad area should be avoided during machining. 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, are 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-5-1.2 Improperly designed or dulled tools may produce high temperatures at the interface, causing ignition at the turnings, if an adequate coolant flow is not used.

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

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

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

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

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

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

A-7-1.4 Elliptical or flat faces on a broad area should be avoided during machining.
Like many other metal powders, titanium is capable of forming explosive mixtures in air. The ignition temperatures of dust clouds, under laboratory test conditions, range from 3300°F to 5900°F. The minimum explosive concentration is 0.045 oz per cu ft (0.045 kg per m³) ranging from 46 to 81 psi (317 to 559 kPa). The average density of pressure is 100 psi per sec (370°C per sec 10,000 psi per sec (3890°C per sec) in these tests ranged from 260 to 4300 psi per sec (1274 to 29650 kPa/sec). The maximum rate of pressure rise ranged from 550 to 10,000 psi per sec (3792 to 68,950 kPa/sec). The minimum value was 10 microjoules; for a dust layer, the minimum value was 8 microjoules. Some samples of titanium powder were ignited by electric sparks in pure carbon dioxide, as well as in air. In some cases, titanium at elevated temperatures was found to react in nitrogen as well as in carbon dioxide. Titanium powder is considered a flammable solid. (See NFPA 77, the Manual on Hazardous Material in Industry, April 1980.)

A-7, 2.3 Tests have shown that the maximum oxygen concentrations allowed for different inert gases to prevent explosions are:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Maximum Oxygen Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>0 percent Oxygen</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>6 percent Oxygen</td>
</tr>
<tr>
<td>Argon</td>
<td>4 percent Oxygen</td>
</tr>
<tr>
<td>Helium</td>
<td>8 percent Oxygen</td>
</tr>
</tbody>
</table>

Appendix B

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

Supplementary Information on Titanium

B-1 History.

Titanium was discovered by William Gregor, an English clergyman who was an amateur chemist. The name titanium is derived from the Greek words "Titanos" which means "Titan", referring to the Titans of Greek mythology. Titanium was first produced in the United States in 1910 by Dr. M. A. Hunter of Rensselaer Polytechnic Institute. The basic process for producing titanium was developed by Wilhelm Kroll, a native of Cornwall. His patent was vested in the US Government. The Kroll process was used extensively for producing titanium by the Kroll process was announced.

B-2 Commercial Production.

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

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

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

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

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

B-3 Properties.

Titanium is a silver-grey light metal, about 60 percent heavier than aluminum, but only 56 percent as heavy as alloy steel. Its atomic weight is 47.94, specific gravity is 4.5, and melting point is 3140°F (1727°C). Titanium-based alloys are stronger than aluminum alloys and most alloy steels and have excellent ductility. They are superior to all the usual engineering metals and alloys in strength-weight ratio. Their fatigue resistance (ability to resist repeated flexures) is above that of heat-treated alloy steels and far greater than that of nonferrous metals. Titanium alloys are harder than aluminum and almost as hard as the high alloy steels. Surface hardness comparable to nitrided steel is obtainable.

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

Titanium-based alloys may be subject to cracking during hot-forming operations if they are in contact with halide salts. Manufactures' recommendations should be sought if applications are considered where high strength alloys are expected to be in contact with halide salts at temperatures above 1000°F (593°C) and may become embrittled after extended exposure to air at temperatures above 800°F (427°C).

Normal compositions of some widely used titanium alloys are:

- Titanium 90 percent, Aluminum 6 percent, Vanadium 4 percent
- Titanium 92.5 percent, Aluminum 5 percent, Tin 2.5 percent
- Titanium 90 percent, Aluminum 8 percent, Molybdenum 1 percent, Vanadium 1 percent
- Titanium 86 percent, Aluminum 6 percent, Vanadium 6 percent, Tin 2 percent
- Titanium 92 percent, Manganese 8 percent

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

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

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

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

B-4 Tests for Titanium.

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

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

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

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

B-5 Applications.

While titanium has many uses, production is still largely consumed by commercial and military aircraft production for use in jet engines, aircraft frames, and other uses. Other uses include armor plate, electrical components, pontoon, cables, structural braces, fire walls, personnel helmets and protective vests.

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

Specially prepared, very finely divided titanium powders find limited application in powder metallurgy and other relatively small scale uses.
B-6 Combustibility and Explosibility.

In tests conducted by the U.S. Bureau of Mines with titanium powder or dust of less than 200 mesh, ignition of dust clouds in air was obtained at temperatures from 380°C to 500°C. Ignition of dust layers occurred at temperatures from 380°C to 510°C. In some cases, dust clouds ignited at lower temperatures than those deemed safe by the Bureau of Mines. (See Report of Investigations 43722 and 4385, listed in Appendix C-2.) Titanium fines, nominally under 48 mesh, a by-product of sponge production and handling, and coarse particles, such as dust from sawing and grinding operations, can be ignited by a spark.

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

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

Titanium can burn in atmospheres other than air. For example, one titanium powder sample which ignited in air as a cloud at 480°C and as a layer at 47°C also ignited as a layer in pure carbon dioxide at 680°C. At red heat, about 760°C, titanium will decompose steam to free hydrogen and oxygen. Above 800°C, titanium burns readily and vigorously in atmospheres of pure nitrogen.

When titanium will burn in the presence of dry chlorine or oxygen at room temperature, the oxygen concentration and only occurs with oxygen concentration above 35 percent at pressures over 350 psig (2445 kPa) when a fresh surface is created. The actual hazard in air is much less than that for aluminum.

B-7 Special Hazards.

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

Low melting eutectics may form when titanium or its alloys are in contact with metals such as iron, nickel, or copper at high temperatures. Phase diagrams for titanium, such as those in Volume 8 of the ASME Metals Handbook, should be consulted in such potential situations.

Titanium engages in thermite-type reactions with iron oxides. Caution should be exercised in introducing titanium into process environments not previously investigated, since titanium may react and, in some cases, become pyrophoric.

B-8 Spontaneous Combustion.

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

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

Like any other metal in the high temperature molten state, titanium can cause a violently destructive explosion if water is present in any mold, pit, or depression into which the molten metal is poured or spilled. Under such circumstances, severe fuming nitric acid. While no problems have been reported with fines collected in cyclones, on occasion, ignites due mostly to the presence of oil and certain contaminants, are oil-coated titanium chips and swarf. Such fires, while probably with titanium and red fuming nitric acid. These incidents have care should be taken when using titanium metal or powder in red explosively with some hazardous materials. For example, extreme reaction, or a low order hydrogen-air explosion.

In the 1950s, several violent explosions occurred in consumable electrode furnaces when water entered the furnace because of a crucible failure. The failures resulted from loss of cooling water flow and severe arc-through. A committee of industry representatives then prepared a set of general recommendations on design of melting furnaces to improve process safety. Their recommendations, given consideration in this standard, have been published by the Defense Metals Information Center of Battelle Memorial Institute. (See Section C-2, General Recommendations on Design Features for Titanium and Zirconium Production Melting Furnaces.)

B-9 Process Description.

Current titanium production processes involve reduction of titanium tetrachloride to titanium metal. The titanium tetrachloride (TiCl4) is made from rutile ore (approximately 95 percent titanium dioxide) by high temperature reaction with chlorine in the presence of a reducing agent, usually carbon. They are two basic commercial methods for the production of titanium: the Kroll-Bureau of Mines process, which uses magnesium as the reducing agent, and the Sodium process, which uses liquid sodium as the reducing agent.

Batterymarch Park, Quincy, MA 02269:

C-1-1 NFPA Publications. The following publications are available from the National Fire Protection Association, Batterymarch Park, Quincy, MA 02269:

NFPA 10-1978, Standard for Portable Fire Extinguishers

NFPA 13-1980, Standard for the Installation of Sprinkler Systems

NFPA 24-1979, Standard for Dip Tanks Containing Flammable or Combustible Liquids

NFPA 48-1981, Standard for the Processing, Handling, and Storage of Magnesium

NFPA 70-1981, NATIONAL ELECTRICAL CODE

NFPA 91-1973, Standard for the Installation of Blower and Exhaust Systems

NFPA 101-1981, LIFE SAFETY CODE

NFPA 220-1979, Standard on Types of Building Construction
NFPA 551-1980, Standard for the Manufacture of Aluminum and Magnesium Powder

C-1-2 Other Publications.

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

C-2 This portion of the Appendix lists publications which are referenced in this NFPA document for information purposes only, and thus is not considered part of the requirements of the document.

C-2-1 NFPA Publications. The following publications are available from the National Fire Protection Association, Battery March Park, Quincy, MA 02269:

- NFPA 49-1975, Hazardous Chemicals Data
- NFPA 68-1978, Guide for Explosion Venting
- NFPA 69-1978, Standard on Explosion Prevention Systems
- NFPA 77-1977, Recommended Practice on Static Electricity
- NFPA 86A-1977, Standard for Ovens and Furnaces
- NFPA 491M-1975, Manual on Hazardous Chemical Reactions

C-2-2 Other Publications.

- Chemical Engineering Progress, November, 1954, Powell, R.L., pp. 578-581
- General Recommendations on Design Features for Titanium and Zirconium Production Melting Furnaces, Columbus, OH, Defense Metals Information Center, Battelle Memorial Institute