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**LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO**

**SAFETY CONSIDERATIONS FOR HANDLING PLUTONIUM
URANIUM, THORIUM, THE ALKALI METALS, ZIRCONIUM,
TITANIUM, MAGNESIUM, AND CALCIUM**



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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA LOS ALAMOS NEW MEXICO

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URANIUM, THORIUM, THE ALKALI METALS, ZIRCONIUM,
TITANIUM, MAGNESIUM, AND CALCIUM**

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ABSTRACT

This report compiles from various sources safety considerations for work with the special metals plutonium, uranium, thorium, the alkali group, magnesium, titanium, calcium, and zirconium. General criteria to be observed in handling all of these metals and their alloys are listed, as well as characteristics of individual metals with regard to health hazards, pyrophoricity, explosiveness, and other chemical reactions, in both handling and storage.

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INTRODUCTION

Because of the rather extensive use in this Laboratory of the special metals plutonium, uranium, thorium, the alkali group, zirconium, titanium, magnesium, and calcium, this report compiles safety considerations for such work. Recommended precautions, techniques, and equipment detailed herein are taken from reports of other laboratory workers in this field as well as from experience at Los Alamos.

In evaluating the safe-handling problems connected with all of these metals, there are certain common environmental factors to be reviewed and appraised; in addition, each metal has characteristic unusual hazards. Some of these metals, their alloys, and hydrides are pyrophoric to varying degrees, have explosive characteristics under certain conditions, react with water, etc. In the form of turnings, grindings, and powder, the hazards of these metals greatly increase. Most of their dusts, some oxides, and hydrides are pyrophoric or explosive and require special precautions in handling and storage.

This report itemizes the general criteria to be considered in taking precautions that must be observed in handling any of these metals and their alloys, and also contains sections dealing with individual metals and their unusual hazards.

It should be kept in mind that often safety regulations develop post factum from accidents, and that corrective safe-handling techniques frequently have been devised by arduous experiment. For instance, development of gloveboxes and proper design of gloves for such boxes for work with fissionable materials was a lengthy problem; in addition, an appropriate system for the changing of gloves on boxes which could be accomplished quickly and without spread of contamination had to be developed and perfected.

This compilation is not a procedural guide for work in this field, but is intended to give a general understanding of areas of hazard based primarily on the chemical behavior of these metals.

BASIC PRECAUTIONARY MEASURES

The following general considerations relate to work with these metals in the finely divided form:

1. Consider the physical and chemical properties of the metal in question and the potentialities of the reaction.
2. Make initial trials of any planned reaction on a small scale. Control the reaction rate by addition of the metal in small increments, or by dilution of the reactants.
3. Plan disposal of the reaction residues in advance. Dispose of scrap promptly and do not allow it to accumulate.
4. Eliminate ignition sources if possible. Effort should be made to remove ignition sources from the immediate vicinity of work with these metals in finely divided form. Such items as sparking electrical motors, stirring devices, and light fixtures should be removed from processing equipment.
5. Limit the quantities of these metals in use to the smallest amounts consistent with the work to be performed.
6. With metals that do not react rapidly with water (this excludes the alkali metals such as sodium, sodium-potassium alloys, lithium), store the powders under a cover of water or alcohol; grinding may be accomplished in a water or alcohol suspension.
7. Store metals for future use in the largest particle size available; that is, do not keep large amounts of fine powder in storage. Grind small amounts as needed.
8. Use inert gas atmospheres in working any pyrophoric metal, alloy, or compound. Gases generally used for this purpose are argon, helium, and nitrogen. In certain cases, air can be used with its oxygen content reduced.
9. Carefully check each process in which these metals are used for safety before carrying it out. Particular attention should be given to the venting of any hydrogen formed between the metal and water used as a cover, to the possible formation of pyrophoric oxides of the metal, to the proper maintenance of the inert gas atmosphere, machining speeds, types of machining coolant, etc.

PLUTONIUM¹

The principal properties which make plutonium handling hazardous are: Plutonium is a high order alpha particle emitter. Although gamma rays emitted in conjunction with the alpha particles are of x-ray energy and are not particularly dangerous, an americium daughter is a considerable

gamma ray emitter, and shielding may become important.

Plutonium in the form of chips, turnings, and powder is pyrophoric and when ignition and burning occur, an especially serious spreading of contamination results.

The toxicity of plutonium is high; it is comparable to radium on a weight basis.

Because plutonium is fissionable, nuclear safety requirements dictate maximum batch sizes and storage limitations.

Health Hazard

A problem of constant concern in handling plutonium is the health hazard created by its radioactivity. It is not the purpose here to discuss this property fully, but it should be pointed out that the chemical properties of plutonium contribute to the problem.

Plutonium oxidizes rapidly in ordinary air, especially if moisture is present. Although the initial oxide layer is usually adherent and protective, nonadherent oxide forms eventually. Because the nonadherent oxide consists of extremely fine particles having high penetrating power, a high level of alpha activity may be built up rapidly in the surrounding atmosphere.

Plutonium metal in finely divided form and plutonium hydride are pyrophoric, and certain plutonium alloys appear to be more pyrophoric than the pure metal, particularly after they have undergone partial oxidation. Plutonium hydride is considered more pyrophoric than any of the other hazardous metal powders and hydrides. Spontaneous ignition can cause a serious spreading of contamination.

Protective Equipment

In general, equipment used for plutonium is housed in gloveboxes which are air-tight and maintained at a slightly negative pressure, so that any leakage is not into the laboratory. Procedures which involve the formation of fine particles of the metal, such as grinding, machining, or the operations of powder metallurgy, are preferably performed in an inert atmosphere, which is usually argon or helium of high purity.

Low water content is a most important consideration. Moisture is an impurity of major concern in plutonium glovebox work. It has been reported that the presence of even a small amount of oxygen in an inert atmosphere of a glovebox inhibits reaction with moisture, presumably by the formation of an oxide film which acts as a barrier. However, when the oxygen is essentially absent, there is evidence that moisture reacts with the plutonium

to form an extremely reactive hydride which will catch fire on subsequent exposure to an oxidizing atmosphere such as air. Operations involving melting may be carried out in an inert atmosphere or a vacuum.

The use of gloveboxes under slight negative pressure for the handling of plutonium has necessitated the design and use of complicated handling systems using remote or semi-remote control techniques and automatic features.

Plutonium handling areas require extensive ventilation systems equipped with efficient filtering arrangements for removing radioactive dusts from the exhaust air. Not only does the maintenance of such systems require constant vigilance, but special techniques are used for changing and disposal of filters, in some cases including the recovery of the metal dust from the filter media. Even the disposal of water used in cleaning floors can be a problem.

The high monetary value of plutonium, coupled with its extreme radioactivity, have brought about the development of chemical and metallurgical handling techniques never previously required for any metal. A discussion of these techniques, even in brief form, would fill several volumes. If only the special analytical chemical procedures that have been developed were covered, a discussion becomes very lengthy. Several handbooks have been written covering just radiation monitoring procedures for handling work with plutonium.

Since gloveboxes fitted with laminated safety glass or plastic windows are normally used for plutonium handling, some protection is afforded workers by these enclosures. However, the wearing of disposable clothing (consisting of coveralls, laboratory coats or smocks, caps, shoe covers, and surgical rubber gloves) is normally required to prevent transfer of active material out of the laboratory. Under some conditions, and especially when transferring the metal or its compounds or alloys to or from gloveboxes, respiratory protection is required. Special laundry installations are required for washing such protective clothing and equipment.

Fire Control

Because of the possible serious spread of contamination in event of a fire in a building in which plutonium is handled or stored, it is recommended that all precautions practical be taken to prevent fires. The use of fire-resistant construction, metal furniture and equipment, fire detection and alarm systems, fire walls, fire doors, and emergency procedures, including possible evacuation, should be considered.

Control of a fire involving plutonium is discussed in the next section

on Uranium and Thorium since the procedure is the same for all three metals.

Storage

The critical mass of plutonium tends to be smaller than for most other fissionable materials and therefore specifications for quantities of metal assembled in storage should be rigidly followed.

URANIUM AND THORIUM^{2, 3}

Potential hazards in work with uranium and thorium are similar to those of plutonium -- radioactivity, toxicity, explosion, and fire.

Health Hazard

Uranium-235 and especially uranium-233 require the same sort of handling techniques as listed for plutonium. Normal uranium and depleted uranium may be handled without elaborate precautions for the most part, except that the finely divided metals, as well as the hydrides, are pyrophoric. Uranium hydride is a fine fluffy powder as it is formed, and is spontaneously flammable at room temperature.

There has been a change in thinking on thorium in recent months, and it is now felt that thorium should be handled like more active alpha emitters. This is due to the fact that as thorium ages, dangerous daughter products grow in the metal and its radioactive hazard correspondingly increases.

Thorium hydride is also pyrophoric, and if finely divided may ignite at room temperature. Compacts of these hydrides, however, lose their pyrophoricity and may be handled with comparative ease.

Hazards of Powder Form

The handling of special metal powders such as thorium requires special technique because of the low temperature of ignition. Thorium is shipped dry in special containers filled with helium or argon. This is necessary to eliminate the possibility of accidental oxidation or even combustion during transportation or storage. Great care should be exercised in transferring this metal powder from the container into other vessels. The dry metal powder should not be poured through the air in a continuous stream. The friction of the particles falling through the air or against the

edge of a glass vessel may be sufficient to produce electrostatic sparks and ignite the powder.

Fire Control

Small fires involving plutonium, uranium, or thorium may be controlled with dry powdered graphite or G-1 powder, by the technique of excluding air from the burning metal with the powder. Water should be prohibited from direct fighting of such metal fires, and should be used only for salvage and control operations on supplementary fires that may be started from the heat of the burning metals. Water only adds to the intensity of the metal fire, and greatly increases the contamination-cleanup required after a fire. In some cases it may be desirable to control such a fire with graphite or G-1 powder and allow it to burn itself out. It is recommended that Fire Department personnel for such metal handling areas be thoroughly acquainted with proper fire fighting procedures, and with the locations of the processing equipment, buildings, etc.

It is desirable that in event of a fire involving plutonium, uranium, or thorium that a senior technical person be called for consultation with the Fire Department personnel.

THE ALKALI METALS (Sodium, Potassium, Lithium, Rubidium, Cesium)^{4, 6}

The principal hazards which may be encountered in the handling of the alkali metals are:

Explosions or fires resulting from contact with water, chlorinated hydrocarbons, or other reactive agents.

Fires resulting from their exposure to moist air.

Personal injury from direct contact with hot alkali metals.

Caustic soda burns from the residues from a metal-water reaction.

Storage

The precautions to be followed in storing any of the alkali metals are similar. The important thing is that the area must be dry, because hydrogen gas explosions may result from the contact of the metals with water. Automatic sprinkler systems or water or steam pipes should be eliminated, if possible, from the room. Sufficient heat should be provided to prevent condensation of the moisture in the room, should the temperature change. In any event, a designated alkali metal storage area should be provided. The

area may be a separate room, an area in a large room, or simply a steel box such as that used for the storage of paints or flammables; appropriate labeling should be provided.

On the laboratory bench, the alkali metals may be stored in friction-top metal cans under a layer of water-free hydrocarbons or mineral oil. Glass containers should be avoided where possible, and if used, should be placed inside metal containers to contain the spillage if the glass should break.

Protective Clothing

The degree of protective clothing required in handling the alkali metals depends on the quantity of metal to which a worker is exposed, and on the temperature of the metal. In large volume systems of high-temperature heat transfer, a maximum of protection is required. Aprons, leggings, head coverings, gloves, and face protection may be needed. All clothing, including gloves, should be loose fitting and easily removed. It is desirable that coveralls be flame-proofed.

Blanketing Gases

Nitrogen, which may be used for blanketing molten sodium, should have a moisture content of less than 1 mg per cubic foot. Lithium, however, reacts with nitrogen, forming the characteristic black nitride coating; thus, argon or helium must be used as blanketing gases. The black nitride, Li_3N , increases the viscosity of molten lithium appreciably, so that particular care must be taken to keep nitrogen out of liquid lithium circulating systems.

Sodium, potassium, and alloys of these two metals form explosive mixtures with chlorinated hydrocarbons and with solid carbon dioxide. The work of H. Staudinger describes such systems.⁷ The sensitivity to shock of sodium-potassium alloy-carbon tetrachloride mixtures is 150 to 200 times greater than that of mercury fulminate.

Potassium readily forms the superoxide, KO_2 , which may undergo vigorous reaction with oil, for example, and therefore should be stored under water-free hydrocarbons.

Protective Equipment

An integral factor in the safe handling of the alkali metals is the proper design of equipment. This involves the maintenance of closed systems,

the proper provision for blanketing gases, and the provision of spray shields at the flanges and pump cells, for example, to prevent spraying of the hot metal in case of a leak. Designing precautions include the pitching of alkali metal lines so that they will drain properly during a shutdown and permit safe dismantling for cleaning and repair. Optimum design for safety may require the provision of a dump tank which is large enough to receive the entire metal charge in the system.

Alkali metals are corrosive to certain construction materials, so care should be taken in selecting materials for piping, vessels, etc. In the laboratory, it is a recognized practice to place beneath individual pieces of equipment metal pans or trays which are capable of containing all the metal within the equipment. Experiments have indicated that holes should be drilled in the steel covers of such trays, giving a maximum open area of about 35% of the total area. Using this design condition, any burning metal which falls onto the tray and through the holes extinguishes itself within the tray. Such an arrangement of pans can be installed underneath a metal gridded floor. The metal grid cover of the pans provides a support for dry extinguishing powders used in fighting or controlling a fire, as without the supporting grid the extinguishing powder would sink below the surface of the metal and do little good.

At Los Alamos, workers in sodium and NaK areas are equipped with the following items of protective clothing: aluminum hard hat, specially fitted with an adjustable full-face shield of fire-resistant plastic, long chrome leather aprons, chrome leather sleeves and leggings, flame-proof cotton twill coveralls, safety glasses, and special heat-resistant leather gloves.

Fire Control

Fighting alkali metal fires simply consists of forming a protective blanket, excluding air, over the metal so that the metal cools below its burning temperature. It should be emphasized that prompt action is vital. In general, the preferred agents for extinguishing sodium and potassium fires are dry sodium carbonate (soda ash), dry sodium chloride, and dry powdered graphite. For lithium fires, dry sodium carbonate (soda ash) and dry sodium chloride are not recommended, however, because lithium liberates free sodium, and the residue is more reactive than the original lithium. Thus, for lithium fires, dry powdered graphite is the recommended agent. The literature indicates that zirconium silicate has been used successfully for this purpose, also, and lithium chloride is an effective extinguishing agent.

ZIRCONIUM AND TITANIUM^{3, 8-14}

The principal hazards of zirconium and titanium are:

Explosion of the finely divided powders.

Fires involving metal turnings or chips, particularly if stored.

Explosions of these metals and their alloys when treated with nitric acid.

Storage and Shipping

Zirconium and titanium metal powders should be shipped and stored wet, no less than 20% moisture by volume.

Because of the hazards of zirconium, it has been recommended that the quantity of powder on hand be kept to the minimum, and in no case should be stored in anything bigger than a can of one-gallon capacity at least 20% wet by volume.

General Handling Procedures

In handling of dry or wet titanium or zirconium, the same precautions commonly employed in handling any finely divided metal powder should be followed. The powder should not be poured or ground in air. It may be ball-milled in suspension in an inert solvent, or ground wet under an inert atmosphere. All metal equipment, vessels, tables, and other metallic objects which come in contact with the metal powder should be grounded.

Mixing, blending, milling, grinding, or other treatment of the dry powder should be carried out only in an inert atmosphere. Personnel working with these powders should be equipped with sturdy face protection and gloves.

The dry powders of zirconium and titanium must be handled with considerably more caution than the moist material. A dust cloud of zirconium powder may ignite spontaneously. The most efficient and economical method of drying the powder is in a vacuum dryer, thirty inches of mercury or better, for two hours at a temperature of 110°C maximum. If this type of equipment is not available, the material may be dried in air in a hood having an adequate exhaust system and at a temperature not exceeding 65°C. Before opening the vacuum dryer or disturbing the material in the air-dry system, the temperature must be brought to room temperature.

Titanium

In tests at the Bureau of Mines Laboratories with titanium powders having a particle size less than 200 mesh, ignitions of dust clouds in air were obtained at temperatures ranging from 330 to 590°C, while ignition of dust layers occurred at 380 to 510°C. In some cases dust clouds ignited at lower temperatures than static layers of the same dust. Coarser particles such as those produced in sawing operations ignite easily and in tests conducted at the Underwriters' Laboratories and reported on Data Cards 511 and 512, ductile titanium in the form of very thin chips and turnings could be ignited with a match. Heavier chips and turnings ignited and burned when heated in the flame of a Bunsen or blast burner. Heavier castings or ingots may give some indication of burning when being cut with an oxyacetylene torch, but when sufficient surface is available to permit radiation cooling below critical temperature, the burning ceases when the torch is removed.

Combustion can occur in atmospheres other than air. One of the fine powder samples that ignited in air could also be ignited as a layer in pure carbon dioxide at 680°C. At red heat (1300°F) titanium decomposes steam to free hydrogen, and above 1475°F titanium burns readily and vigorously in atmospheres of pure nitrogen.¹²

Attention is called to the extreme importance of continuity of water supply for water-cooled crucibles for melting operations. In this connection, provision should be made for some form of visual and audible signal to alert operators should water circulation fail. Preferably such a signal or alarm circuit should be further extended to automatically interrupt current supply to the crucible in the event of water failure. Precautions should be taken to minimize the possibility of water leakage into the crucible. Electrical field indicators have been used to keep electrodes safely centered, preventing arcing through the crucible walls. Pressure relief devices such as rupture discs should be provided to aid in releasing pressure if a water leak occurs in the system.

According to Kopelman and Compton,¹⁴ all mixing of dry powder should be done in an inert atmosphere. Tests indicate that the maximum values of oxygen allowed when using different inert gases to prevent explosions of titanium dust or powder are:

Carbon Dioxide	0% oxygen
Nitrogen	6% oxygen
Argon	4% oxygen
Helium	8% oxygen

Spontaneous ignition has occurred in fine, oil-covered titanium chips. Such fires, while probably primarily due to the presence of the oil and certain contaminants, are very difficult to control and special precautions should be taken to have all fine scrap and particularly all oil-covered material removed from the processing area as soon as possible.

No spontaneous ignitions of titanium powder have occurred in laboratory tests. Titanium sheets have ignited spontaneously when being removed from a descaling salt bath. Such ignitions have been reportedly due to exothermic reactions which raise the edge of the sheet to the combustion temperature and the hazard can usually be controlled by regulating the bath temperature.

Resistance to corrosion has been stressed as one of the outstanding properties of titanium. Recent experiences have indicated, however, that extreme care should be taken in attempting to use titanium metal or powder in red fuming nitric acid. No difficulty has been reported in using normal strength nitric acid. Although completely satisfactory explanations of these explosions have not been developed as yet, it is believed that the strength of the acid is an important factor and that some pyrophoric material is produced which, when disturbed, releases a large amount of heat that causes rapid oxidation and fusion of the metal.

In an atmosphere of helium and oxygen it was also necessary to have at least 5% oxygen to obtain ignition of dust clouds by electric sparks. In an oxygen-argon atmosphere, 4% oxygen was required. Ignition of dust clouds by electric sparks can be prevented by atmospheres of helium, argon, and nitrogen, but carbon dioxide is ineffective. Dust layers can be ignited in CO₂ and nitrogen, but not in argon or helium.

Zirconium

Zirconium powder, wet with water, is much safer to handle than the dry powder because it is more difficult to ignite. Once ignited, however, the wet powder will burn even more violently than dry powder, partly because the powder will decompose the water and use the oxygen for its own combustion, and partly because the steam formed in the burning mass will scatter the metal. Powder containing about 5% to 10% water is considered to be the most dangerous.

All waste rags, containers, etc., which have been in contact with zirconium powder should be put into separate waste cans filled with water containing a wetting agent, and disposed of as soon as possible.

The major factor to be considered in the safe use of zirconium is its exothermic reaction with a number of other elements and compounds. The

physical state of the material is important in evaluating possible hazards. The greater the ratio of surface area to mass, the greater the explosion hazard.

Dusts of zirconium powder will explode, provided there is a source of ignition and concentration of dust exceeds the lower explosive limit. If the mean particle size is less than about 10 microns, the dust will frequently self-ignite and explode when it is blown or otherwise dispersed in air. There are no data to indicate the exact limiting conditions which are necessary for self-ignition. This would vary with particle size, size distribution, temperature, humidity, and surface character of the particles.

Fine dusts will explode when dispersed in air. Zirconium sponge and turnings, chips or dust from the metal can be rather easily ignited and will burn with an extremely high temperature.* Very little flame results, but the metal gives an incandescent glow while it is burning. If the sponge has been treated so that the oxide film is removed, such as the iodide process of producing crystal bar, contact with air will initiate burning. Turnings and chips from machining operations may start to burn if the machining operation produces sufficiently high temperatures. Once the burning has started, it is very difficult to stop. Owing to the high temperature of burning, the heat may be sufficient to distort a machine tool bed or burn holes through sheet metal.

Flooding of activated sponge with a large volume of water prior to any contact with air will result in inactivation of the surface so that it can be handled with reduced risk. Speed in adding the water is very important; if the sponge is kept wet, it will not self-ignite. If the sponge is stored in water for a considerable length of time, there may be a small evolution of hydrogen, and protection against the ignition of the hydrogen must be realized.

Zirconium machining operations can usually be conducted with the use of a coolant which may be either a cutting oil or an oil-water emulsion. The rate of flow of the coolant must be kept high, and continually observed to prevent stoppage of the flow. Complete immersion of the surface being machined has been used in some cases. Only small amounts of turnings or chips should be allowed to collect on the machine before removal. By removing these in small batches and placing them in covered metal cans, the risk of fire is reduced.

When dust collection equipment is used to carry away dust from any machines or processes, wet collection methods should be used. The system

* Experience at Los Alamos has not confirmed this statement. Small batches of zirconium turnings from the Shops Department have been difficult to ignite.

should be carefully designed with short ducts between hood and dust collector so that there will be little accumulation of materials which might ignite and burn.

Fire Control

Keep water away from burning zirconium and titanium. Do not use CO₂ gas extinguishers on a fire of these metals, as it increases the intensity of the fire.

If dry powder should become ignited, it cannot be extinguished — only controlled. Dolomite (powdered limestone) or dry graphite powder should be spread completely around the burning area with a long handled shovel, and then more extinguishing powder added until the burning pile is completely covered. Keep personnel away from the area until the fire has burned out. Burning powders should be removed from cement floors as soon as possible. Extreme heat from the fire will cause the cement to crack and split with explosive force, spewing hot particles in all directions and causing other fires.

When quantities of turnings are kept to a minimum, it is no trouble to put out a tiny fire with a scoop of powdered graphite. Although small volumes of water should not be applied to burning zirconium, large volumes of water can be successfully used to completely cover the heated zirconium, such as drowning the metal in a tank or barrel of water.

Alloys

Alloys of zirconium with lead or uranium are particularly hazardous. Zirconium and its alloys can react violently with acid solutions used for pickling or dissolving. Fine particles of these alloys are more reactive than massive pieces, although even large sections will burn vigorously if ignited by intense heat. Although much is known of conditions that promote the violent reactions of zirconium, the complete picture is not clear, and not all of the accidents that have occurred have been explained.

Laboratory explosions have occurred when alloys of uranium containing 8, 10, and 20% zirconium were pickled in (1:1) nitric acid. One laboratory has apparently eliminated this hazard by adding about 25 grams of ammonium bifluoride per liter of (1:1) nitric acid.

Serious explosions of metal surfaces are not confined to uranium-zirconium alloys. An article¹⁵ points out that the residue of titanium-manganese alloys after nitric treatment can be exploded by scratching the surface or by heating. "Extreme Precautions" were suggested when

handling any titanium alloys exposed to nitric acid. Emphasis on the need for face and eye protection during such laboratory activities is indicated.

MAGNESIUM¹⁶⁻²⁰

The principal hazard in working with magnesium is fire resulting from the ignition of fine shavings, chips, and dust; the burning of the metal during melting and casting operations; ignition in metal dust exhaust and collecting systems; and ignition during disposal of the waste metal.

If certain safety precautions are not followed, magnesium can be dangerous to work with, but with reasonable care it can be processed as safely as any commercial metal.

Fire Prevention

Magnesium has a melting point slightly in excess of 1200°F, and its ignition temperature is very close to the melting point. Ignition can occur at lower temperatures, depending on the alloy and the size and shape of the piece. Fine shavings can be ignited at 950°F, while finely divided dust may ignite below 900°F. It is obvious, then, that prevention of accidental ignition is essential in any operation involving magnesium. The ease of ignition depends to a large extent upon the size and shape of the material as well as the size and intensity of the ignition source. Magnesium ribbon, shavings, chips, and dust can be ignited by a spark or match flame. Heavier pieces are difficult to ignite because heat is conducted rapidly away from the ignition source.

The standard safe practices for melting and casting metals generally apply to magnesium. Additional precautions required to prevent burning are the use of special fluxes to cover the molten metal and a sulphur dioxide atmosphere in molds. Pots, crucibles, or any ferrous objects that may contact molten magnesium should be kept free of scale and moisture. Iron oxide and molten magnesium, combined, may produce a violent thermite reaction with extreme temperatures.

Sawing and coarse grinding of magnesium may produce sparks capable of igniting fine dust, and it is important that such dust and fine chips be continually removed from the work. Grinding equipment should be designed with exhausts which lead into water-type dust collectors. The exhaust system should be designed with short straight runs to the collector, and points where material may accumulate should be avoided. Such a system should be cleaned regularly and frequently.

Most magnesium machining operations allow for heavy cuts. Friction between tool and metal should be kept at a minimum by taking as heavy cuts as possible and not allowing the tool to ride on the metal without cutting. Fine cuts at high speeds (over 600 fpm) without coolants may ignite cuttings, particularly with improper tooling. Tools should be kept very sharp, and the tool should be backed off as soon as the cut is finished. Equipment used for working magnesium should be grounded, and no open flames or electric or gas welding equipment should be permitted in an area where magnesium dust is produced or handled.

Employees should keep magnesium particles brushed off their clothing. Where magnesium dust is produced, clothing should be flameproofed and be without cuffs or pockets.

Molten magnesium is somewhat different from common molten metals; it reacts chemically, as well as physically, with water. The fluxes which are used to protect molten magnesium against oxidation are hygroscopic; most tools and metal stored in a melt room are covered with a thin layer of flux dust which can pick up moisture from the atmosphere. It is important that all metal, both ingot and scrap, and all tools such as skimmers, ladles, and thermocouple wells should be thoroughly preheated before they are submerged in the molten metal.

Magnesium Dust Disposal. Sludge from dust collectors can be burned in a segregated area at a safe distance from combustible material. The wet sludge should be spread in a layer not more than three or four inches thick. It should be remembered that damp sludge is more flammable than dried sludge, and caution should be exercised in ignition. Magnesium sludge may be rendered chemically inactive and noncombustible by reacting it with a 5% solution of ferrous chloride ($\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$). The reaction takes place with the evolution of hydrogen at such a rate that the magnesium fines are converted in less than twenty-four hours to magnesium hydroxide and magnesium chloride to such an extent that the residue will not burn. Since hydrogen is generated by the reaction, the process should be carried out in an open container in an outdoor location. Open flames and smoking should be prohibited in the immediate vicinity of the process. The amount of ferrous chloride required is about 0.6 pound for each pound of dry weight of magnesium fines.²⁰ While this method of disposal is simple, it should be operated under technical supervision. Several fires have resulted recently when the disposal was left to janitorial personnel.

Fire Control

A supply of extinguishing powder should be kept within easy reach of magnesium operations. G-1 powder is an effective preparation and should

be kept in large containers equipped with hand scoops. To apply the powder, spread evenly over the surface of the fire to a half inch depth without scattering the burning metal. If smoking continues in spots, more powder may be added and stirred in gently to bring it in contact with the fire. If the burning metal is on a combustible surface, the fire should first be covered with powder, then a two inch layer of powder spread out nearby and the burning metal shoveled onto this layer, with more powder added as needed.

Recently, the Dow Chemical Company has conducted experiments to test the effectiveness of boron trichloride as an extinguishing agent for magnesium fires. These tests indicated that magnesium fires in heat-treating furnaces can be effectively extinguished with this agent. Boron trichloride is a corrosive liquid, however, and considerable care must be exercised in using it. On contact with moisture, this material forms HCl gas and boric acid.

CALCIUM

The principal hazard in work with calcium is fire resulting from the ignition of hydrogen formed by the reaction of calcium with water or moisture in the air, and from explosions of fine dust.

Handling and Storage

In contrast to magnesium, calcium is much more reactive with water. This fact is the key to handling it in a safe manner. Calcium is usually shipped in metal drums under an argon atmosphere, with the metal in lump or shot form. Calcium can be ground in the normal manner, but care should be taken in handling fine dust. The ground metal should be stored in small containers under an argon atmosphere. All operations with calcium should be directed toward keeping moisture out of contact with the metal. It is, of course, more active with water when it is in a finely divided state.

Fire Control

Calcium fires should be controlled with powdered graphite or G-1 powder in much the same manner as for zirconium fires.

REFERENCES

1. A. S. Coffinberry and M. B. Waldon, "The Physical Metallurgy of Plutonium," in Finniston and Howe, editors, Progress in Nuclear Energy, Series V, Vol. 1, p. 355, Pergamon Press, Ltd., London, 1956.
2. R. C. Goertz et al., "Safe Handling of Radioactive-Pyrophoric Materials," Argonne National Laboratory Report ANL-5509, December 1955.
3. Bureau of Mines Report of Investigation 3722, Inflammability and Explosibility of Metal Powders, October 1943; and Report of Investigation 4835, Explosive Characteristics of Titanium, Zirconium, Uranium, and their Hydrides, December 1951.
4. Marshall Sittig, "Safe Handling of Alkali Metals," Ind. Eng. Chem. 48, No. 2, 227 (1956). Portions used by permission of the American Chemical Society, copyright owner.
5. Richard N. Lyon, editor-in-chief, Liquid-Metals Handbook, Atomic Energy Commission and Department of the Navy, Washington, D.C., June 1952; Carey B. Jackson, editor-in-chief, Liquid-Metals Handbook, Sodium (NaK) Supplement, Atomic Energy Commission and Department of the Navy, Washington, D. C., July 1, 1955.
6. H. N. Gilbert, "Some Unique Properties of Sodium and Potassium," Chem. Eng. News 26, No. 36, 2604 (1948). Portions used by permission of the American Chemical Society, copyright owner.
7. H. Staudinger, Z. Elektrochem., 31, 549 (1925).
8. Horace T. Reno, "Zirconium and Hafnium," from Mineral Facts and Problems, Bureau of Mines Bulletin No. 556, U. S. Department of the Interior, n.d.
9. Accident and Fire Information Bulletins, United States Atomic Energy Commission, Washington, D. C.
10. E. C. Barns, "Industrial Hygiene and Safety of Zirconium and Its Alloys," Technical Bulletin No. 3, Westinghouse Electric Corporation, Atomic Power Division, United States Atomic Energy Commission, Washington, D. C., April 15, 1955.
11. Properties of Zirconium Metal, Zirconium Metals Corporation of America, 1952.

12. Standards for Fire and Explosion Prevention and Protection During the Production, Processing, Handling and Storage of Titanium (Tentative), 1957 Advance Reports to the Sixty-First Annual Meeting, May 20-24, 1957, National Fire Protection Association, Boston 10, Massachusetts. This standard has not been finally adopted by N. F. P. A.
13. W. B. Harris, "Health and Safety in Powder Metal Handling," New York Operations Office Report NYOO-4896, April 1957.
14. B. Kopelman and V. B. Compton, "Spontaneous Combustion of Metal Powders," Metal Progr., 63, 77 (1953).
15. "Titanium Alloy Corroded by Nitric Acid Can Detonate," Safety Forum Section, Chem. Engr. News, Aug. 10, 1953, p. 3320.
16. Neil Flammer, "Safe Handling Practices with Magnesium," Modern Metals, IX, No. 9, 35 (1953). Portions used by permission of Modern Metals, copyright owner.
17. F. P. Strieter and H. A. Schertel, "Safe Handling of Magnesium in Foundry Operations," paper presented at Conference on Safety, Health and Air Pollution at the University of Illinois, February 17-19, 1953, The Dow Chemical Company, Midland, Michigan, n.d. Portions used by permission of American Foundrymen's Society, copyright owner.
18. "Extinguishing Magnesium Fires in Heat Treating Furnaces with Boron Trichloride," Technical Memo No. 17a, The Dow Chemical Co., Midland, Michigan, n.d.
19. "Storage, Handling and Processing of Magnesium," Pamphlet No. 48, National Fire Protection Association, 1954.
20. "Machining Magnesium," The Dow Chemical Co., Midland, Michigan, 1954.