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NATIONAL BUREAU OF STANDARDS REPORT

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A SURVEY OF SOME MAGNESIUM FIRE PROBLEMS

by
A. F. Robertson



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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U. S. DEPARTMENT OF COMMERCE
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A SURVEY OF SOME MAGNESIUM FIRE PROBLEMS

ABSTRACT

At normal pressures magnesium appears to burn in the vapor phase resulting from vaporization of the metal at temperatures below that observed during combustion. Although the heat of combustion is quite comparable to that of wood, the reaction temperature is much higher.

The high temperature existing during such fires can result in flash dissociation of water applied to them. The resulting flareup of the fire and apparent explosion may scatter the molten metal, spreading the fire.

Ignition of magnesium may be controlled by consideration of the relative geometry of the metal and the ignition source, the objective being to dissipate heat more rapidly than the rate of its supply. The use of an anodic coating is suggested as likely to result in greatly increased periods between fire exposure and ignition.

Techniques for extinguishment of magnesium fires appear to have been based largely on the formation of a protecting blanket around the burning magnesium with concurrent cooling and possibly formation of secondary fires. Experiments performed with small fires suggest the possible use of CO₂ or N₂ for control purposes. The heat of reaction of magnesium with these gases amounts to about 60 and 25 percent, respectively, of that for the straight oxidation process. This together with the fact that reaction temperatures are greatly reduced should, under certain conditions, permit their effective use in limiting temperatures experienced with magnesium fires. Liquid nitrogen, when properly applied, provides an effective extinguishing agent.

Physical Properties

Magnesium is a light, white tough metal which tarnishes with an oxide film on exposure to air. It is one-third lighter than aluminum and in its alloys has been widely used in aircraft construction. Recently it has been introduced for fabrication of portable power tools and other implements. Pure magnesium has a specific gravity of 1.74 at 68°F, melts at 1202°F (650°C) and boils at 2043°F (1117°C) and atmospheric pressure [17]. As a solid, it exhibits a vapor pressure of 0.01 atmosphere [2] at a temperature of 1126°F (608°C). In the liquid form the vapor pressure is reported [3] as 5 mm at 1207°F (653°C) and 100 mm at 1618°F (881°C).



Reactivity

Its affinity for oxygen is so great that heavy metal parts, when once ignited, burn with great vigor and may be difficult to extinguish. In the finely ground form it may burn with explosive violence. Its combustion in air is accompanied with liberation of an intense white light. This radiation from burning magnesium may be considered more as an indication of the high temperature at which the oxidation reaction takes place than as an indication of high heat of combustion. This latter is about 10,650 BTU/lb^[4] and thus is of the same order of magnitude as for many other combustibles. The temperatures developed during combustion of magnesium at atmospheric pressure are reported as being usually between the boiling point of the metal 2025°F (1107°C) and the melting temperature of the oxide 5072°F (2800°C)^[4].

Because magnesium boils at a temperature below that developed during its combustion, a flame of considerable size is usually developed. The dazzling white light accompanying this flame is probably largely a result of the high temperature and the resulting emission from thermally excited oxide particles.

Ignition

The ignition of magnesium, as of other combustibles, becomes possible only when, among other requirements, the rate of heat generation exceeds that of heat loss. Thus, with commonly available ignition sources, the physical form of the metal will influence the ease with which it may be ignited. Finely divided material is readily ignited with only small ignition sources while heavy magnesium objects usually require large area ignition sources. The high thermal conductivity of the alloys and pure magnesium ^[5] 320 to 1092 BTU in/hr°F ft² (0.11 to 0.376 cal/cm°C sec) assists in the dissipation of heat from ignition sources which are small compared to the size of the metal part being heated.

Fassell, et al ^[6] have studied the self-ignition behavior of over 100 magnesium alloys. They report ignition temperatures in the range of 864 to 1200°F (462 - 649°C). Their measurements were made on small cylindrical specimens heated within an oven. In performing the experiments, the temperature of the specimen at a time just prior to that at which its rate of temperature change rapidly increased, was taken as the ignition temperature. This technique would be expected to and indeed appears to have resulted in temperatures slightly higher than those measured by Setchkin ^[7] in which specimens were exposed for prolonged periods at essentially constant temperature. During such tests, it would be expected that the surface to volume ratio of the metal specimen would be an important variable affecting the ignition

temperature observed. It seems quite likely that under suitable conditions the ignition of powdered magnesium stored in bulk form could take place at ambient temperatures much below those reported above [8]. Reynolds and Williams have proposed [9] that the self-ignition behavior of magnesium and other metals is closely related to the low temperature oxidation corrosion of the metal.

Fire Prevention

As with other combustibles, there is little that can be done to prevent the combustion of magnesium and its alloys when exposed to heat or fire in the presence of oxygen. Means can, however, be devised to reduce the ease with which ignition can occur. The relatively high thermal conductivity of these metals can result in high heat losses from the portion of a specimen which may be exposed to an ignition source. Thus when exposed in sheet form to a given ignition source, the ease of ignition will be related in an inverse manner to the thickness of the material.

Another factor influencing the combustion behavior of magnesium is the ability of the oxide film, formed on the metal surface when exposed to high temperatures, to support and contain the molten metal. Here again, thin sheets of magnesium are more susceptible to sustained combustion than are heavy ones. Work done at Underwriters' Laboratories [10] has resulted in the recommendation that a minimum thickness of 0.080 in. be required for magnesium sheet material proposed as enclosure for electrical appliances. If, however, the magnesium is in the form of a rod there is evidence that considerably heavier sections may support combustion when burned in the inverted position.

Another method which has been proposed for delaying ignition of magnesium parts involves the use [11] of a special anodizing process followed by zinc chromate primer and paint finish. Six inch square sheets of 0.1 in. thickness when so treated showed delays to ignition, after application of a torch flame, of more than thirty times those observed with similar but untreated specimens. This treatment appears to form a tough but flexible envelope which contains the molten magnesium. Methods such as these seem definitely worthwhile from the standpoint of fire safety, but seem unlikely to result in prevention of all such fires.

Fires - Extinguishment

During combustion of magnesium and many of its alloys, the high temperatures involved results in melting and boiling of a portion of the metallic fuel. Because of this and its low specific gravity, it seems probable that when a water stream or that of any other liquified or solidified gas is directed at the fire, the molten metal is spread about exposing it to air and immediate violent burning. The hot magnesium may cause dissociation of water vapor with which it comes in contact releasing hydrogen as a decomposition product. It is possible that, under suitable conditions, (including those of limited water supply) recombination of this hydrogen with oxygen from the ambient atmosphere can result in serious explosions.

At elevated temperatures the reactivity of magnesium is so great that nitrogen and carbon dioxide are decomposed and combine with the metal. The reaction with these usually inert gases is a comparatively mild one and normally proceeds at lower temperatures than the oxidation reaction. Experiments with small magnesium fires indicate that, under certain conditions, the reduction of reaction temperature and heat release may warrant their use where complete flooding is practical. Thus experiments with small magnesium fires showed that the brilliant flame was immediately extinguished when burning magnesium was immersed in an atmosphere of CO_2 . The molten magnesium was observed to cool but continue to react with the formation of the oxide, carbon, and possibly also carbon monoxide. Theoretical considerations indicate that this reaction is accompanied with a release of heat on the order 60 percent of that for the reaction in air. Similar experiments involving the flooding of a compartment, within which magnesium was burning, with N_2 resulted in rapid reduction and disappearance of the flame followed by cooling of the molten metal. For small fires the continuing reaction with formation of the nitride proceeded so slowly that the reaction was in some cases terminated. The heat release during this reaction, when maintained, has been estimated to be on the order of 25 percent of that for the reaction in air. The behavior of magnesium in such atmospheres together with a cooling and smothering effect seems to form the basis of operation of combustible materials which have been suggested [12] for control of magnesium fires. These include graphite, powdered pitch and heavy mineral oil. Other materials such as powdered volcanic ash, flux, dry sand and sodium chloride [12] are probably effective primarily to the degree with which they reduce the access of oxygen to the burning metal and act, as heat sinks, to assist in cooling the molten mass.

Experiments recently performed with liquid N_2 indicate that when properly applied to magnesium fires it is highly effective for their extinguishment. Fires involving as much as five pounds of magnesium turnings as formed in a four-foot metal tub were completely extinguished with less than a gallon of liquid nitrogen.

Recently, several new extinguishing agents have been proposed for use on magnesium fires. Trimethoxyboroxine has been used for this purpose by the Navy 137. Work done for the Air Force has resulted in the proposal that tricresyl phosphate or a 9-17 percent mixture of boric acid in trethylene glycol 147 be used for such fires. Each of these, when applied, results in the development of secondary fires which apparently have the merit of removing oxygen from the atmosphere surrounding the burning magnesium. In addition, these materials are said to form a flux coating around the molten mass thus largely excluding oxygen and permitting the metal to cool below the ignition temperature.

The usefulness of N_2 , CO_2 for control of magnesium fires appears to have been overlooked. The reason for this is probably the fact that such gases can only be counted on reducing the heat of the reaction and do not necessarily prevent its completion. These gases do, however, reduce the temperature of the burning magnesium and permit its safe attack with other extinguishing agents which may be used to smother or cool the burning metal to temperatures below the kindling point. The use of liquified N_2 as an extinguishing agent for such fires apparently has not been considered.

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U. S. DEPARTMENT OF COMMERCE

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THE NATIONAL BUREAU OF STANDARDS

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