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METHODS OF CONTROLLING AND EXTINGUISHING TITANIUM FIRES

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INTRODUCTION

This note summarizes information available in the DMIC files prior to April, 1964, as well as that which was obtained in the period of April 17 to June 12, 1964, in a DMIC survey on the general subject of the fire hazards associated with massive pieces of titanium metal.

Historically, it is pertinent to note that, in the early 1950's, extensive studies were made of the fire and explosive hazards associated with the preparation and handling of titanium sponge, powder, scrap and ingots and with the preparation of titanium mill products. These resulted in the preparation and adoption of Standard No. 481 for the production, processing, handling, and storage of titanium by the National Fire Protection Association (NFPA).[1]*

The purpose of this note is simply to summarize the methods and materials which have been developed to date for the control and extinguishment of fires involving titanium metal. The problems of controlling and extinguishing titanium fires are greatly compounded by the extremely high affinity of titanium for oxygen and nitrogen, and the fact that the oxides of titanium are readily soluble in the molten metal. Thus, heated titanium can readily reduce many of the compounds or liquids normally used as extinguishing agents, and the absence of a protective oxide film results in the presence of a continuously reactive surface on the molten metal.

Fire Control

As pointed out by NFPA,[1] the most effective means of fire control is fire prevention. Thus, where titanium is present in readily combustible form (i.e., powder or turnings), the adoption of the most effective fire-preventive measures available is regarded as imperative. The hazards involved and appropriate protective measures are discussed at length in Reference 1.

Control of small fires in titanium powder can usually be effected by separating the burning metal and ringing the burning portion with a suitable dry powder (see below) and allowing the separated material to burn itself out. The desirability of storing finely divided forms of titanium in as small-sized portions as possible is obvious.

Fire Extinguishment

The recent DMIC survey indicated that no studies of methods or materials for extinguishing titanium fires have been performed since 1957. Details on many of these early titanium fire-extinguishing studies are lacking. On the basis of a review of this early information, DMIC concurs with the following observations offered by the NFPA:[1]

"Reports of investigators are not in agreement on the possibility of extinguishing a titanium fire. While some simply state that a titanium fire cannot be extinguished, others call attention to experiences that apparently indicate the effectiveness of certain types of extinguishers on small fires and report some encouragement in connection with the development of both dry and liquid extinguishers for use on combustible metal fires."

Nonetheless, there is general agreement that certain classes of extinguishers are <u>not</u> effective on titanium fires. These include CO_2[1,2,3,4] and foam[1,3] extinguishers and carbon tetrachloride.[1,3,4]

Aside from carbon tetrachloride, very little information on the use of other halogenated extinguishing agents for titanium fires was obtained. This was somewhat surprising, since these agents are known to be highly effective in aircraft engine fire-extinguishing systems.[5] DMIC did note, with interest, that one of the recommendations carried forth in a recent research program[6] concerning halogenated fire-extinguishing agents was that the effects of certain of these agents on titanium alloys should be investigated.

Some positive information along these lines was obtained in an experiment performed by the Douglas Aircraft Company, Inc.[7] which utilized the DC-8 Firex agent, a proprietary fluid which is believed to consist essentially of bromotrifluoromethane. In this case, ignition of a Ti-6Al-4V sheet was achieved by heating it with an oxyacetylene torch to its melting temperature. The fire was then propagated by blowing compressed air parallel to the burning surface. "The addition of the DC-8 Firex agent to the compressed air had no visual effect on the burn rate. The titanium would burn as long as the air and Firex were blown parallel to the surface. Once burning has started and the compressed air blast is stopped, Firex only will continue the burning for approximately 5 seconds. The fire is immediately self-extinguishing when only an air blast is used and removed." This suggests that, under certain conditions, bromotrifluoromethane will support the combustion of titanium.

The following account is given of those extinguishing agents which have been recommended and/or are being used to control and/or extinguish titanium fires.

Proprietary Extinguishing Agents

<u>Met-L-X Powder</u>. This is a dry powder composed of a sodium chloride base with additives including tricalcium phosphate and metal stearates. It is produced and distributed by the Ansul Chemical Company, Marinette, Wisconsin. The powder is noncombustible and may be stored in sealed containers, or extinguishers, and is not subject to decomposition or change in properties.[5]

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* References are listed at the end of this note.

"The technique used to extinguish a metal fire is to open the nozzle of the extinguisher fully and cautiously apply a thin layer of agent over the burning mass from a safe distance to prevent blowing the burning metal into other areas. Once control is established, the nozzle valve is used to throttle the stream to produce a soft heavy flow. The metal can then be completely and safely covered from close range with a heavy layer. The heat of the fire causes the powder to cake, forming a crust which excludes air and results in extinguishment."(5) One additional virtue of the powder is its ability to cling to hot vertical surfaces.

The National Fire Protection Association notes that Met-L-X extinguishers have been "used successfully where...titanium presents a serious hazard".(5) Also, two of the titanium producers have used this powder successfully on titanium fires.(8,9) The experiences at Harvey Aluminum have included ingot fires, initiated by thermite reactions, which were extinguished with Met-L-X.

In October, 1956, the Ansul Chemical Company performed a number of field tests(10) to compare the fire-extinguishing effectiveness of Met-L-X with that of trimethoxyboroxine (TMB).* Both extinguishing agents were used, under similar conditions, to extinguish fires in titanium powder, sponge, and dry and oily turnings. The results of these tests indicated that "TMB was more effective on titanium fires when limiting the amount of agent used to the contents of one extinguisher. The coating built up by TMB appeared to hold up better under the intense heat of titanium fires than the Met-L-X coating did." As another means of comparison, the amount of unburned metal remaining after the application of these extinguishing agents is given as follows:

Form of Titanium	Unburned Metal Remaining, % Met-L-X	Unburned Metal Remaining, % TMB
Powder	30	60-75
Sponge	5-10	60
Dry turnings	Traces	50
Oily turnings	Traces	60

"Pyrene" G-1 Powder.** This powder consists of screened graphitized foundry coke containing an organic phosphate. It is made by Chemical Concentrates, Fort Washington, Pennsylvania, and is distributed by The Fyr-Fyter Company, Dayton, Ohio. The powder is noncombustible and can be stored in cardboard tubes or metal pails for long periods of time without deterioration or caking.(5)

"The powder is applied by being spread evenly over the surface of the fire...to a depth sufficient to smother the fire (as little as a 1/8-inch layer... may be enough). Larger chunks of metal require additional powder to cover the burning areas. Where burning metal is on a combustible surface, the fire should first be covered with powder, then a 1- or 2-inch layer of powder spread out nearby and the burning metal shoveled onto this layer, with more powder added as needed."

* Described later.

** The other trade name variations of this powder, "M-1 Powder" and "Metal Fyr Powder" are also available from the same distributor of the "Pyrene" G-1 Powder.

The National Fire Protection Association indicates that "G-1 powder has proven effective as an extinguishing agent for fires in titanium".(5) Also, one of the titanium producers has recommended this material as being quite effective.(11)

Trimethoxyboroxine. (TMB). This is colorless, syrupy liquid composed principally of the cyclic compound having the formula $(CH_3O)_3B \cdot B_2O_3$. The chemical is produced by the Callery Chemical Company, Pittsburgh, Pennsylvania, and the extinguishers utilizing the material have been produced by the Ansul Chemical Company, Marinette, Wisconsin. The TMB extinguishers were developed originally by the U. S. Navy(12) in cooperation with the Ansul Chemical Company for extinguishing magnesium fires.

The TMB supplied for fire-fighting uses "may contain some" methyl alcohol through hydrolysis,and Navy specifications(13) require a purity (expressed as boric oxide content) of at least 58 per cent by weight. The liquid has a flash point (closed cup) of 57-64 F and is classed as flammable for shipping purposes.(5) It is considered as a nontoxic liquid as it does not give off toxic vapors and "can easily be removed from the skin without undue harmful effects".(13) The liquid rapidly increases in viscosity at low temperatures and must be stored above 32 F for fully successful operation of the extinguisher.(13) It hydrolyzes readily to form boric acid and water and contact with moist air or other water sources must be avoided to prevent this hydrolysis.

"Typical application of TMB to a metal fire yields a heat flash due to the breakdown of the chemical compound and ignition of the methanol. The white metal fire is rapidly extinguished, and the secondary greenish flame is of short duration. A molten boric oxide coating on the hot metal prevents contact with air. A stream of water may be used to cool the mass as soon as the metal flames are no longer visible. This should be done cautiously to avoid rupture of the coating. The fumes from the application of TMB are nontoxic. Indoor application...is not recommended due to the large volume of boric oxide smoke produced."(5) (Additional details on the techniques developed for the use of TMB in fighting magnesium fires are given in References 12 and 13.)

The National Fire Protection Association notes that TMB has "shown value" in application to fires in titanium.(5) The DMIC survey disclosed that both the Ansul Chemical Company(10) and the Naval Research Laboratory(14) had evaluated this agent in extinguishing titanium test fires. As noted previously, the Ansul Chemical Company tests indicated TMB to be more effective on titanium fires than Met-L-X. No details of the NRL studies were available, nor were any other experiences reported on the use of TMB in extinguishing titanium fires. Nevertheless, the Navy has recommended TMB as an extinguishing agent for titanium fires.(14,15)

Dow 230 Flux. This material consists nominally of the following mixture:

$MgCl_2$	34%	$BaCl_2$	9%
KCl	55%	CaF_2	2%

It is available from the Dow Chemical Company, Midland, Michigan, and is nommally stored in covered steel drums.

The Titanium Metals Corporation of America has reported the successful use of this flux to control titanium fires by applying copious quantities of it to cover and isolate the burning material.(11)

Nonproprietary Extinguishing Agents

Dolomite. The National Fire Protection Association has noted(5) that dolomite can be used to control titanium fires by spreading this powder around the burning area and then adding more powder until the burning pile is completely covered. An early Atomic Energy Commission circular(16) gives essentially the same recommendation.

Graphite. Fine, dry graphite powder has also been recommended to control(5) and extinguish(9) small titanium fires. The technique used is the same as that described above for dolomite.

Inert Gases. Various sources(1,4) have indicated that argon and helium will extinguish titanium fires if they can be applied under conditions which will exclude all air. However, no reports of the use of these gases to actually extinguish titanium fires were available or known to DMIC.

Sand. The Republic Steel Corporation has successfully used fine, dry sand to smother and extinguish fires in titanium turnings.(17)

Water. DMIC fully concurs with the National Fire Protection Association's recommendations(5) that "water must not be used on fires in titanium fines and should be used with caution on other titanium fires". Coarse-spray hose streams have been used effectively on fires in outside piles of titanium machinings.(18) However, violent reactions have been reported in other cases,(4,5) where water was applied to hot or burning metal. Also, an automatic water sprinkler system was not effective in either controlling or extinguishing a warehouse fire which involved titanium sponge stored in galvanized steel drums.(19)

REFERENCES

(1) "Standard for the Production, Processing, Handling and Storage of Titanium", National Fire Protection Association Standard No. 481 (May, 1961). Available from the National Fire Protection Association, 60 Batterymarch Street, Boston 10, Massachusetts, Price $0.60.

(2) Private communication from D. C. Goldberg, Westinghouse Electric Corporation (September 12, 1963).

(3) "Fire Precautions in Handling Titanium", American Machinist, 99 (7), pp 147-148 (March 28, 1955).

(4) Peterseim, F. D., "Hazards and Safety Procedures in the Fabrication and Use of Titanium", Titanium Metallurgical Laboratory Report No. 63, Battelle Memorial Institute (January 25, 1957).

(5) "Fire Protection Handbook", G. H. Tyron, Editor, National Fire Protection Association, Boston, Massachusetts, Twelfth Edition (1962).

(6) Landesman, H., and Basinski, J. E., "Investigation of Fire Extinguishing Agents for Supersonic Transport", National Engineering Science Company, ASD-TDR 63-804 (January, 1964).

(7) "Miscellaneous Experiences on Burning of Titanium", Douglas Aircraft Company, Inc., Materials Research and Process Engineering Laboratory Report Serial No. LR-AD-1531 (June 27, 1962).

(8) Private communication from H. Gilbert, Harvey Aluminum, Inc.,(May 15, 1964).

(9) Private communication from W. L. Finlay, Crucible Steel Company of America (May 19, 1964).

(10) "Primary Evaluation of Trimethoxyboroxine on Metal Fires", Ansul Chemical Company, Technical Services Department (Test Field), 687-750-262-13 (November 12, 1956).

(11) Private communication from W. W. Minkler, Titanium Metals Corporation of America (June 12, 1964).

(13) "Trimethoxyboroxine (TMB) - A New Magnesium Fire Extinguishing Agent for Aircraft Crash Fire Fighting", National Fire Protection Association Committee on Aviation and Airport Fire Protection, Aviation Bulletin No. 193, (October, 1957).

(14) Private communications from Dr. R. L. Tuve, Naval Research Laboratory (May 27 and June 1, 1964).

(15) Private communication from A. B. Guise, Ansul Chemical Company (May 26, 1964).

(16) "Zirconium and Titanium Metal Powders Storage, Handling, and Drying", Chicago Operations Office, Atomic Energy Commission, Accident and Fire Protection Information (December 6, 1954).

(17) Private communication from H. R. Shollenberger, Republic Steel Corporation (May 15, 1964).

(18) Private communication from H. E. Muir, Factory Insurance Association (February 27, 1957)

(19) Private communication from C. Ward, General Services Administration (May 20, 1964).