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NATIONAL BUREAU OF STANDARDS REPORT

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EXPLORATORY EXPERIMENTS
WITH
MAGNESIUM FIRES

by
A. F. Robertson & W. H. Bailey

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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ABSTRACT

Experiments are reported which provide a qualitative measure of the burning behavior of a variety of magnesium alloys. Of the alloys tested those prepared by casting exhibited the greatest flammability. It is suggested that heavy sections be used in the fabrication of magnesium tool parts since in this way ignition can be made more difficult. A few experiments were performed which seem to indicate that under certain conditions nitrogen and carbon dioxide in gaseous form may be quite useful for control of such fires. Liquid nitrogen was found to be effective for control of magnesium fires.

INTRODUCTION

The use of magnesium alloys in the fabrication of tools and other devices likely to be required for shipboard use has become increasingly common. This together with the fact that the Navy has for a considerable time avoided the purchase of tools containing magnesium poses problems in the procurement of acceptable ones for marine use. Because of this it has seemed desirable to make a brief review of some of the fire hazard problems associated with the use of magnesium and its alloys. This study has been accomplished by means of both a limited experimental study, and a review of the technical information relating to fire hazards of magnesium alloys. In reporting on this work it has seemed desirable to present the results in two separate papers. The present one is confined to the experimental studies which, while only of an exploratative nature, are considered useful as an indication of the magnitude of the fire hazard problem.

MATERIALS

The materials used in the study were those submitted for this purpose by The Bureau of Ships, U. S. Navy. They were in the form of rough forgings, castings, and machined parts and had been submitted by various manufacturers for examination. These are shown in figure 1. The manufacturers of the various specimens are identified in Table I.

Table II lists the alloy designations corresponding to these specimens, principal alloying elements, and some physical properties. The material contained in this table was taken from information furnished with the specimens as well as that available in reference [1]. For test purposes, specimens were cut from the samples shown.

TEST METHODS

Three types of test were used in this study, one to measure the ease of ignition, another to provide an indication of the ability of the alloy to support combustion and a third to show the possible usefulness of nitrogen and carbon dioxide as fire extinguishing agents. It must be emphasized, however, that all of these studies were exploratative in nature and thus the results obtained should be considered indicative of probable behavior rather than conclusive in nature.

Ignition Behavior

When the study was started it was considered likely that a good correlation could be shown to exist between the length of exposure to a flame ignition source required to produce glow, ignition, or melting of the specimen and its properties including geometry, and thermal characteristics. Accordingly, an apparatus was set up to permit clamping specimens of the thickness involved by 7/16 in. wide and 1-7/8 in. length in a water cooled steel holder. This holder was mounted in such a way that about 3/4-in. of the 1½ in. exposed length could be placed within the flame of a meker burner. The elapsed times between flame exposure and glow, melting, and ignition of the specimen were recorded. In addition the duration of the burning process and length of the specimen protruding from the holder after termination of flaming were noted. The exposure time for each specimen was only that sufficient to achieve ignition after which the specimen was removed from the burner flame. No specimens were exposed for periods greater than one minute. This test method was only used on specimens 1A to D.

Sustained Burning

Because of difficulties, which will be described later, in correlating the ignition test results with theoretical considerations, as well as those resulting from the irregular shapes of many specimens, it seemed undesirable to attempt to prepare specially machined specimens from each of the various alloys furnished for study. Instead, a minimum of three roughly cut specimens as shown in figure 2 were prepared on the band saw from each of the alloys supplied. Qualitative tests were then performed on the ease with which the small end of the specimen could be ignited in a meker burner flame. After ignition the specimen was held in a vertical position with the small burning end down and observations were made on its persistence in burning. If burning was observed to continue, another specimen was tested but this time with the ignited end upwards. The third specimen was then tested in the position considered as possibly evidencing sustained combustion but at the same time presenting considerable difficulty of achieving this condition.

Extinguishment

It was considered desirable to do some work on problems associated with the control of magnesium fires. In most cases small fires involving specimen 5B magnesium alloy AZ91C were used. This material was selected because of its free burning characteristics. The fires were usually formed on an asbestos millboard sheet of one-half inch thickness and about 60-lb/ft^3 density. Since considerable variation occured in the methods of extinguishment studied it seems best to describe these together with the results obtained.

RESULTS

The results of the various experimental studies are presented below:

Ignition Behavior

Table III presents the data obtained during these studies. It will be observed that differences in behavior between the various alloys are not very great. There seems, however, to be some evidence that the cast alloys are somewhat easier to ignite and more vigorous in their burning characteristics than the extruded alloys. Figure 3 presents the data for each of four alloys in diagrammatic form. No attempt was made to verify the extrapolations shown in this figure as dotted lines.

Sustained Burning

Attempts to correlate time to ignition with theoretical considerations were without success probably largely because of the limiting assumptions necessary for simple analysis. Because of this, in addition to previously mentioned considerations, it seemed impractical to perform similar ignition studies on all of the alloys submitted for inspection. As a result, simplified qualitative tests were used for the remainder of the specimens.

These studies of sustained burning were performed manually. The specimen being held by a large pair of forceps. The results of the observations are summarized in Table II. In general, it appeared that the cast alloys again showed easier ignition and a greater tendency toward sustained burning than the other materials studied. Some specimens of alloy AZ91C were observed to continue burning when the ignited end of the specimen was held vertically upwards. On the other hand, alloy AZ31B gave evidence of being the most difficult of the magnesium alloys to ignite. None of the alloys in which aluminum was the major alloying element were ignited during these tests. Each of these however, melted after prolonged heating.

During these tests it was observed that in many cases the specimen could be more rapidly ignited if it was periodically removed from the heating flame. It was also observed that a burning specimen when introduced into the gas flame seemed to cool off and the brilliant magnesium fire seemed to diminish. Because of this it was considered desirable to perform a few experiments on the use of gases for control of such fires.

Extinguishment

The literature seems quite clear in its advice against the use of nitrogen or carbon dioxide for control of magnesium fires, references 2 and 3. However, theoretical considerations indicate that the heat of reaction in these materials is but 25 and 60 percent, respectively, of that observed when magnesium burns in air. It was considered likely that mention of the occurrence of explosions when these gases were applied resulted from mechanical agitation of the fire resulting from vigorous application techniques. Accordingly, experiments were first performed with carbon dioxide snow. A small amount of snow was dumped on an open magnesium fire. No violent reaction and little effect on the fire was observed until the snow was raked into the fire. This resulted in sputtering and spreading of the fire. Snow and gaseous carbon dioxide were then dumped into a bucket. A magnesium fire was started and lowered into the bucket. As the burning metal entered the carbon dioxide atmosphere the flaming oxidation reaction immediately stopped. The molten metal was observed to cool off but continued to glow with a dull red color. In addition to magnesium oxide, free carbon, and perhaps some carbon monoxide was formed.

This reaction in carbon dioxide still took place at a temperature high enough to cause the magnesium to burn from the molten form, however, no flame was observed and the reaction temperature was greatly reduced.

In using nitrogen on the experimental fires, initial studies were made by fitting a carbon-dioxide fire extinguisher horn to a nitrogen supply. When gas was delivered at low velocities from this horn and directed towards a small magnesium fire it was found to be possible to extinguish the flame. The fire rekindled however on removal of the N_2 supply. It was apparent that some other arrangement to permit application gas from all directions around the fire would provide more rapid and complete control. No attempt was made to develop a portable applicator of this type although it seemed likely to be easily accomplished. Instead, a small open topped drum was fitted with a window and nitrogen supply, burning magnesium was then placed within the drum, the cover closed and nitrogen admitted. The fire was promptly brought under control. The reaction which continued for a while with formation of the nitride eventually was terminated due to heat losses. Metallic magnesium was recovered from this fire.

Two further experiments were performed with small magnesium fires. The first consisted of starting a fire on the asbestos millboard and then placing a closed container over this fire holding it down tightly to the millboard. The fire was gradually extinguished and the reaction ceased. A second experiment consisted of the formation of secondary fires around burning magnesium thus reducing the oxygen supply. This was done in two ways. First, sawdust was dumped on a magnesium fire. There was an immediate flareup of the dispersed dust but after this the dust burned slowly from around the fire zone. The magnesium fire was observed to cool off and the brilliant flame disappeared; this condition continued as long as the wood fire continued around the magnesium core. The second experiment involved placement of dry newspapers over the magnesium fire. There was some delay in igniting and burning through these and similar delay in control of the magnesium fire. However, the intensity of the fire was greatly reduced after the paper fire got well under way.

All these experiments were, however, performed with very small fires and it seemed, therefore, that at least a few studies should be performed with larger fires prior to reporting on the results observed. Accordingly, a fire involving five pounds of magnesium chips was formed in a tub of four-foot diameter by two feet high. Under the application conditions used, it appeared difficult, if not impossible, to maintain a CO_2 atmosphere in such a tub without the use of a cover. Both N_2 and CO_2 were found to reduce the flaming and reaction temperature of such fires when a cover was used.

However, because of the insulating effect of the asbestos lining and the fact that the size of the fire was so comparable to that of the volume of the tub, these fires were rather slow in cooling off and the usefulness of such control measures seemed of questionable value.

A few experiments were performed on the use of liquefied N_2 for control of such fires. Small scale tests involving up to 1/2 lb of metal were very successful when the N_2 was applied in the form of a heavy spray. One experiment was then performed on a fire involving five lbs of metal turnings. These were burned in the tub previously described. This fire was extinguished with the use of about 1-1/2 quarts of liquid N_2.

DISCUSSION

The ignition and burning experiments seem to indicate significant differences between these properties of alloys in which magnesium forms the principal element. The most pronounced differences seem to be between the cast and extruded form of the alloys, the former exhibiting the most easily ignited form. It is understood that the corrosion behavior of these alloys exhibits quite similar behavior. Reynolds and Williams, reference 4, have shown a correlation to exist between these two behavior characterestics, in this light the observed differences seem reasonable.

The differences shown between the burning behavior of the alloys was undoubtedly influenced to a considerable extent by the testing methods used. It appears likely that all the alloys which were observed to ignite could under suitable conditions burn vigorously. However, it seems unlikely that metals containing aluminum as the principal alloying element present a fire problem even when magnesium is present in the alloy in concentrations of as much as seven percent.

It appears likely that there should be considerable merit, from the standpoint of fire safety, that the thickness of magnesium parts, which could be exposed to an ignition source, be made as heavy as practical. In this way heat losses from the area exposed to the igniter may be large resulting in the necessity of prolonged application of large ignition sources prior to ignition. It is possible that use of the Dow No. 17 anodizing treatment followed by zinc chromate primer plus finish paint applied to magnesium parts could as reported in reference 5, result in a considerable increase in resistance to ignition.

The brief studies of possibilities of control of magnesium fires seem to indicate that the use of nitrogen and carbon dioxide has been neglected apparently as a result of the fact that magnesium reacts with these gases at high temperatures The heat produced

from these reactions is however significantly lower than that resulting from direct oxidation of magnesium. The equilibrium reaction temperatures are also much lower although the metal may still remain in molten form.

Apparently, the normal combustion of magnesium takes place with the formation of solid reaction products which tend to form an insulating layer between the metal and flame. If this layer is moved away the flame is supported on the metal surface and boiling starts as a result of increased heat transfer. Apparently, it is this boiling which scatters the burning metal. Thus it appears that mechanical disturbance of magnesium burning in air is likely to result in spreading of the fire. Reaction of magnesium in an atmosphere of N_2 or CO_2 however appears to take place at temperatures low enough to prevent boiling and thus there appears to be little, if any, evidence of sputtering and spreading of such fires even when mechanically disturbed.

The use of liquid N_2 on magnesium fires appears to have considerable merit. This is especially true when there is a partial enclosure or surround at the base of the fire. The small amount of work done with liquid N_2 indicated need for careful study of application techniques since use of inadequate rates resulted in rekindling of the fire.

CONCLUSIONS

The following conclusions are based on the experiments performed and may not be necessarily applicable to alloys of other types or fires of larger sizes.

1. Alloys containing magnesium as the principal alloying element can, under suitable conditions, be ignited by means of a meker burner flame.

2. Alloys containing aluminum as the primary alloying element and magnesium in quantities as great as seven percent were not found to be ignitable with a meker burner flame.

3. The rapidity of ignition of a magnesium part is a function of the size and type of igniting source as well as the geometry of the part being ignited. In general, it appears desirable to require that parts of magnesium tools which may be exposed to an ignition source have as heavy sections as practicable.

4. Magnesium parts prepared from castings appear to exhibit greater flammability than similar specimens from extruded material.

5. Liquid nitrogen appears to have considerable merit for extinguishment of magnesium fires.

REFERENCES

1. "Magnesium Alloys and Products," Dow Chemical Co., 1955.

2. "NFPA Handbook of Fire Protection," Crosby-Fiske-Forster, Eleventh Edition 1954.

3. "Magnesium," National Board of Fire Underwriters, Special Interest Bulletin No. 178, Sept. 1956.

4. "An investigation of the Ignition Temperatures of Solid Metals," Summary Report, W. C. Reynolds, Department of Mechanical Engineering, Stanford University. It is understood that this report will be published in 1959 by NASA.

5. "Private Communication" Dow Chemical Corp. (see also NBS Report No. 6302)

TABLE I

Manufacturers of Various Specimens

Specimen Number	Manufacturer
1A, 1B, 1C, 1 D	Dow Chemical Co.
2A, 2B, 2C	Thor Power Tool Co.
3A	Chicago Pneumatic Tool Co.
4A	Ingersall-Rand Co.
5A, 5B, 5C	Mall Tool Co.
6A, 6B	Cleco Div.,Reed Roller Bit Co.

TABLE II

Properties of Alloys Tested

Alloy Designation				Principal Alloying Elements									Physical Prop'ties			Form of Prep.	Burn. Behavior*			Spec. Symb. No.
ASTM	Dow	Mill.	Other	Al	Cu	Fe	Mg	Mn	Ni	Si	Zn	Zr	ρ gm/cm³	k cal/cm°C sec	Melting Temp. °F		Ing'tion	Ign. up	end down	
AZ63A	H			5.3-6.7	<0.10		Bal	0.15	<0.01	<0.3	2.5-3.5		1.82	0.15	1135	Cast	2	-	2	1A,6B
AZ91C	AZ91C			8.1-9.3	<0.10		Bal	0.13	<0.01	<0.3	0.4-1.0		1.81	0.17	1120	Cast	2	1	2	1D,5B
AZ31B	FS 1			2.5-3.5	<0.05	<0.005	Bal	0.20	<0.005	<0.3	1.0		1.77	0.19	1160	Extruded	1	-	1	1B
ZK60A							Bal				4.8-6.5	0.45	1.83	0.28	1175	Extruded	1	-	2	1C
SC 7				83.			<0.1				0.55	5.7				Cast	-	-	-	5C
		10935		92.0			7.0									Cast	-	-	-	5A
			A	Bal	3-4.5		<0.1	<0.5	<0.5	8.5-9.5	<1.0					Cast	-	-	-	2A
			B	Bal	2.5-3.5	<0.8	<0.1	<0.5	<0.3	5.5-6.5	<1.0					Cast	-	-	-	2B
			C	Bal			0.3			7.0						Cast	-	-	-	2C
			365	Bal	<0.2	<0.5	0.2-0.4	<0.3		6.5-7.5	<0.3					Cast	-	-	-	3A
			355	Bal			0.4-0.6									Cast	-	-	-	4A
			356-T6	Bal	<0.2	<0.5	0.2-0.4	<0.1		6.5-7.5	<0.2					Cast	-	-	-	6A

* The following symbols are used to designate burning characteristics:

- Did not ignite (burn)
1 Was ignited (burned) with some difficulty
2 Relatively easily ignited (burned)

TABLE III

Ignition Behavior of Magnesium Alloys
(average of two observations)

Thickness	Alloy	Elapsed time from Exposure to Glow	Melt	Fire	Fireout	Length of Specimen Consumed
in.		min	min	min	min	in.
1/32	AZ91C*	0.18	0.23	0.30	1.02	1
	AZ63A*	0.18	0.22	0.29	1.04	1
	ZK60A	0.20	0.28	0.33	0.89	11/16
	AZ31B	0.17	0.22	0.35	0.98	13/16
1/16	AZ91C*	0.25	0.32	0.41	1.37	13/16
	AZ63A*	0.25	0.32	0.46	1.25	7/8
	ZK60A	0.29	0.38	0.49	1.22	3/8
	AZ31B	0.28	0.40	0.53	1.46	5/8
1/8	AZ91C*	0.33	0.51	0.68	1.91	11/16
	AZ63A*	0.36	0.54	0.76	1.40	1/4
	ZK60A	0.42	0.75	-	-	0
	AZ31B	0.36	0.64	-	-	0
1/4	AZ91C*	0.49	-	-	-	0
	AZ63A*	0.53	-	-	-	0
	ZK60A	0.64	-	-	-	0
	AZ31B	0.64	-	-	-	0

* Castings

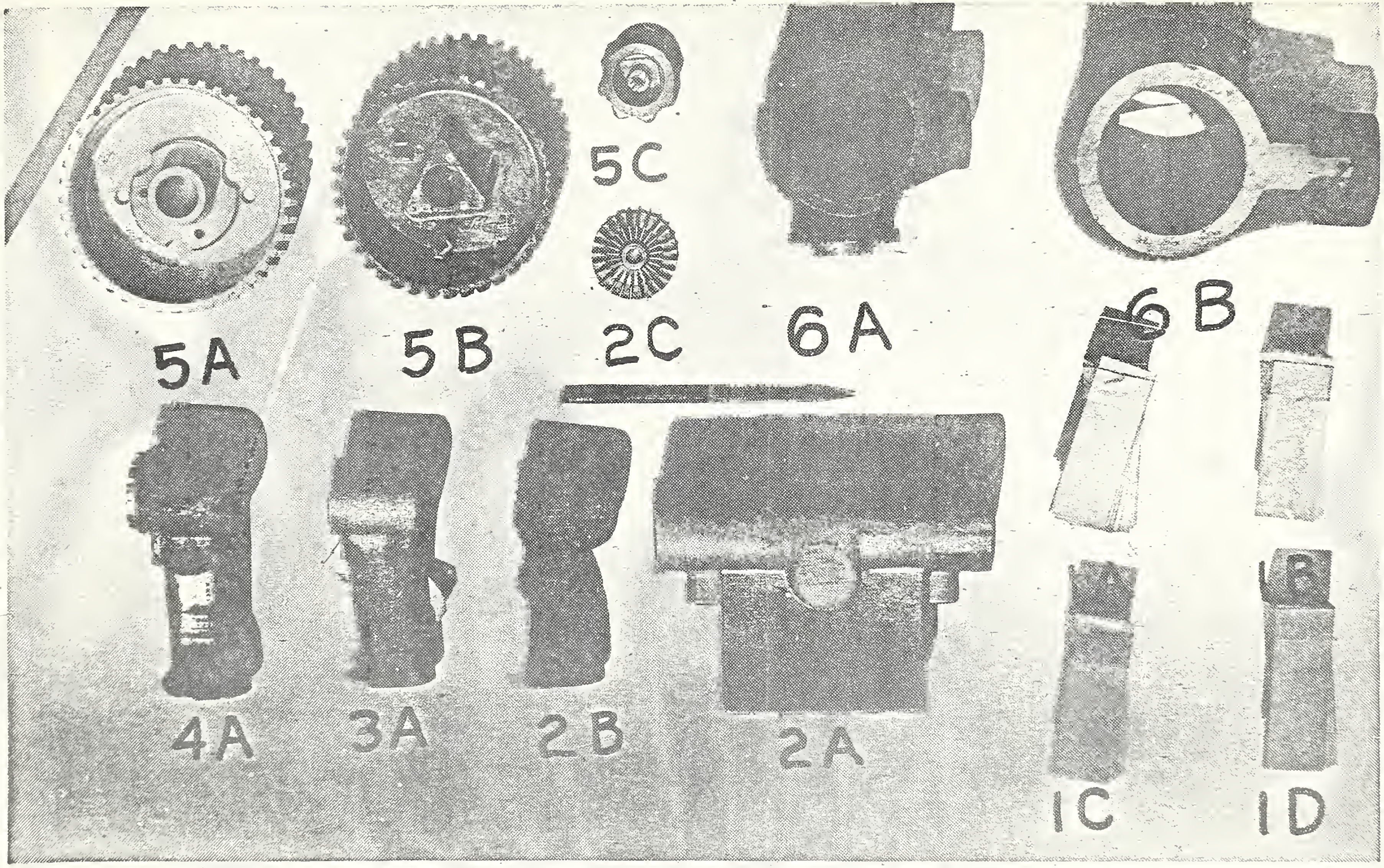

Fig. 1. Specimens used in present investigation

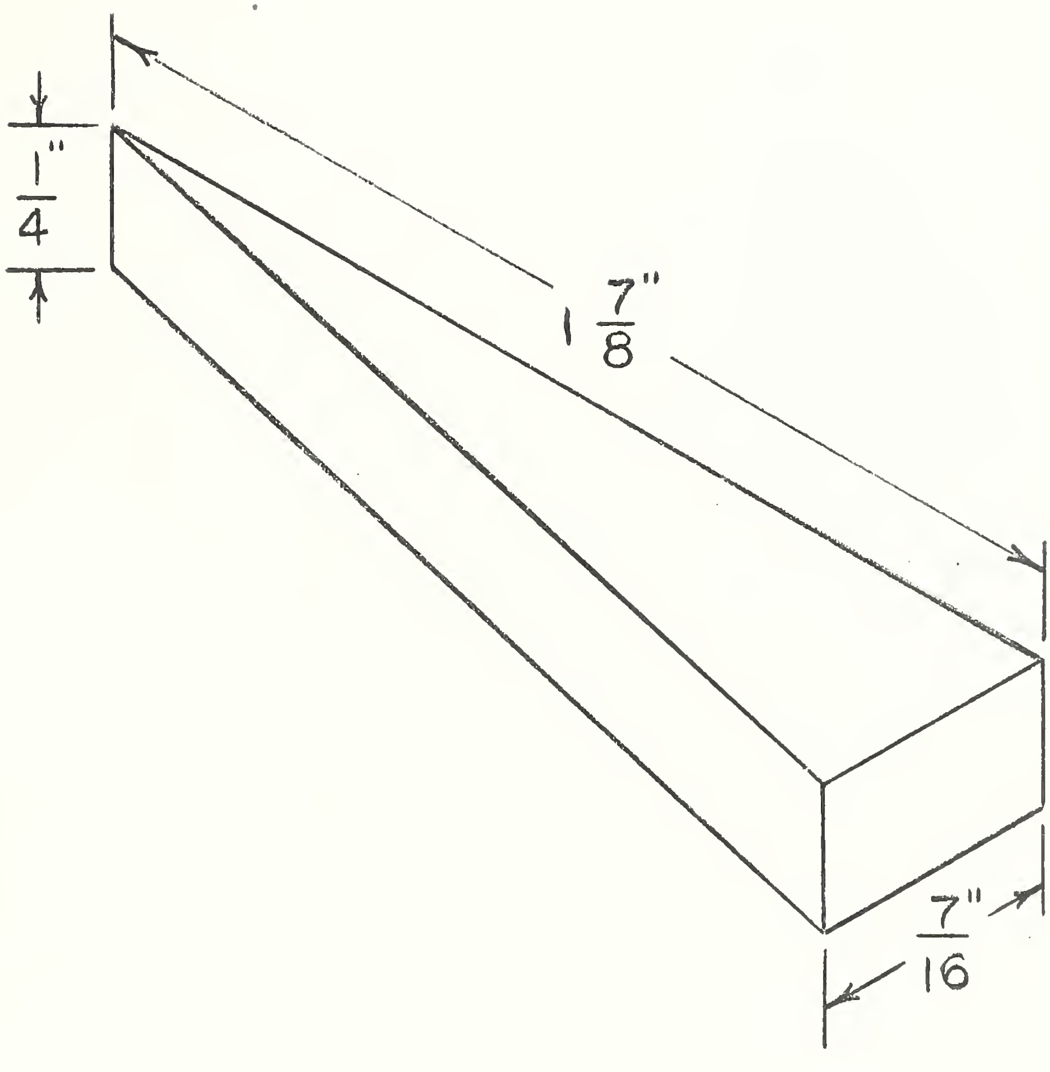

FIG. 2

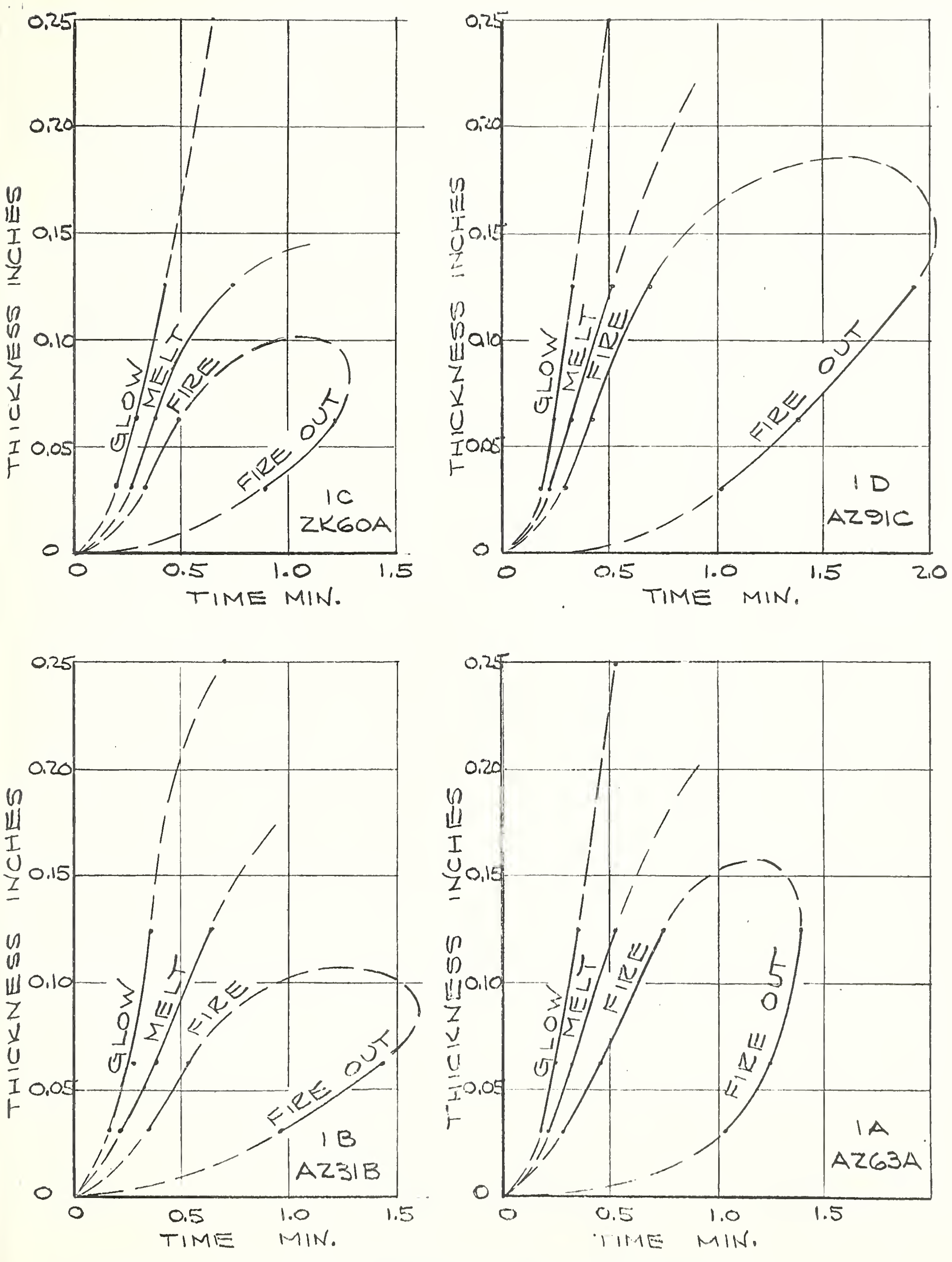

FIG. 3 IGNITION BEHAVIOUR—MAGNESIUM

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