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SPECTROSCOPIC INVESTIGATION OF METAL COMBUSTION

by

T. A. Brzustowski and I. Glassman

Aeronautical Engineering Laboratory Report No. 58



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Guggenheim Laboratories for the Aerospace Propulsion Sciences
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TABLE OF CONTENTS

	Page
TITLE PAGE	1
TABLE OF CONTENTS	2
ABSTRACT	3
I. INTRODUCTION	5
II. EXPERIMENTAL	5
III. RESULTS	6
A. Magnesium	6
B. Aluminum	7
C. Zirconium	9
D. Discussion	10
IV. COMBUSTION OF METAL PARTICLES IN A HOT OXIDIZING ATMOSPHERE	11
A. Volatile Metal, Small Particle	12
B. Volatile Metal, Large Particle	12
C. Nonvolatile Metal, Nonsoluble Oxide, Large Particle	15
D. Nonvolatile Metal, Nonsoluble Oxide, Small Particle	15
E. Nonvolatile Metal, Soluble Oxide, Small Particle	16
F. Nonvolatile Metal, Soluble Oxide, Large Particle	17
G. High Melting Metal, Volatile Oxide	18
V. CONCLUSIONS	19
REFERENCES	20
TABLES	22
FIGURES	

ABSTRACT

Magnesium ribbons were burned at constant pressure in various oxidizing atmospheres at low pressure levels. The flame spectra show a high level of continuous radiation, atomic lines of Mg, and strong band emission of MgO. Broadening and self-absorption of the Mg resonance line at 2852 Å indicates that magnesium vapor exists in the flame not only at the peak temperature but also at lower temperature levels.

Photographs of magnesium burning at low pressure show the structure of a vapor-phase diffusion flame surrounding the ribbon.

The combustion of Al and Zr foils at constant volume in commercial flashbulbs was studied by time-resolved spectroscopy. The spectra show a high level of continuum radiation. Superimposed on the continuum are atomic lines of the metals and molecular bands of the monoxides.

A double reversal of the Al resonance lines at 3944 and 3961 Å with respect to the continuum indicates that aluminum vapor has a mean temperature lower than the peak flame temperature.

The atomic lines of Zr and the molecular bands of ZrO and AlO appear always in emission indicating that these species exist only near the peak temperature, probably as oxide decomposition products.

The products of combustion of Zr foil of uniform size at constant volume consist primarily of spherical oxide particles in the very broad size range from 15 to 700 microns. Combustion products of Al ignited and burned under the same conditions show only a deposit of oxide smoke of less than 5 microns and a few particles of oxide in the 20 to 200 micron range.

These results indicate that Al foil burned in the vapor phase in the flashbulb environment and that the Zr foil did not.

Al and Mg, with boiling points lower than the boiling points of the respective oxides, satisfy the thermodynamic criterion for vapor-phase burning. Zr probably also satisfies this condition but has not been observed to burn in the vapor phase.

The boiling point criterion now appears to be a necessary but not sufficient condition for vapor-phase burning of metals. Whether this mechanism can actually occur depends also on the rate of heat loss from the flame. The high intensity of continuum radiation observed emphasizes the assertion that radiant heat transfer plays an important role in metal combustion. The intense flame emission is caused primarily by the presence of condensed oxide at the flame temperature.

In an attempt to increase the understanding of metal particle combustion, a scheme is postulated to correlate qualitatively the burning behavior of metals with the physical properties of the metals and their oxides. The suggested scheme is consistent with the observations described here and with those reported by other investigators.

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SPECTROSCOPIC INVESTIGATION OF METAL COMBUSTION¹

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I. INTRODUCTION

This work was carried out in an attempt to increase the understanding of basic metal combustion processes. The experimental observations were made on metals burning under conditions quite different from those occurring in the particle experiments carried out by many investigators. It was hoped that a comparison of observations made under basically different conditions might help separate the effects of the environment from the phenomena related to the characteristic properties of the metals and their oxides.

When the results obtained here and by various investigators were examined, it appeared to be possible to postulate a general description of the burning behavior which was consistent with the observed phenomena.

II. EXPERIMENTAL

Magnesium ribbons were burned in a bell jar of 32 liters volume under nearly constant-pressure conditions. The pressure and composition of the oxidizing atmosphere were controlled. Ribbons 9 cm. long and measuring 0.30 x 0.013 cm. in average cross section (6.5 mgm. per cm. of length) were clamped in electrodes 8 cm. apart and ignited by resistance heating. Quartz windows in the bell jar allowed flame spectra and photographs to be taken. This experiment was carried out in conjunction with an investigation of the production of light in the combustion of magnesium ribbon. The experimental procedure for both is outlined in detail by Brzustowski(1).

Time-resolved spectra of flashbulb combustion were obtained by means of the apparatus described by Rautenberg and Johnson(2). Time resolution is obtained on the spectral plates by having a rotating sector scan the slit of a stigmatic spectrograph. A time resolution of 2.1 milliseconds per millimeter of slit image was used.

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1. The initial phase of the experimental work reported here was carried out by the junior author at the General Electric Company Research Laboratory, Schenectady, New York. This support and the active cooperation of T. H. Rautenberg, Jr., of the General Physics Research Department there, are gratefully acknowledged. Equipment loaned by the General Electric Company has facilitated subsequent work at Princeton. The authors' current work in the field is supported under subcontract from Allegany Ballistics Laboratory, Hercules Powder Company.
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All spectra were photographed on Kodak III F Spectroscopic Plates with a Hilger Medium Quartz prism spectrograph. The F emulsion is sensitive over the wavelength range from 2400 to 6800 Å.

Spectral lines were identified with the help of tables in the Handbook of Chemistry and Physics(3). Molecular bands were identified mainly from the tabulation by Pearse and Gaydon(4).

The products of combustion of Al in the G.E. M-2 and Zr in the G.E. M-5 flashbulbs were micriphotographed and measured from the photographs.⁴ Both the deposit on the inside of the bulb envelope and the loose products in the bulb were examined in each case.

III. RESULTS

A. Magnesium

The flame of magnesium ribbon widens and becomes less opaque as the pressure is lowered. At 60 mm. Hg the ribbon and the deposits of oxide on its surface are clearly visible through the flame (see Figure 1). The thin bright envelope surrounding the ribbon is the projection of a three-dimensional flame front and the bright striations in the flame front are caused by obstructions on the ribbon surface.

The corresponding flame spectrum is shown as No. 1 in Figure 2. The major light emitter is MgO vapor, and atomic lines of Mg are also visible. Continuum radiation becomes important only in the red.

In particular, the following can be identified in the spectrum: the green system of MgO bands (4900-5007 Å), the ultra-violet (U-V) system of MgO bands (3720-3860 Å, with the strongest bandheads at 3721-3726 Å), and the three triplets of Mg at 3091, 3093, 3097 (weak), 3829, 3832, 3838 Å and 5167, 5173, 5184 Å (strong) all in emission.

Densitometer traces showed also the characteristic broadened and self-absorbed profile of the Mg resonance line at 2852 Å. This profile indicates that Mg vapor exists at varying temperatures in the flame.⁵

As the pressure is increased the continuum radiation becomes significant at shorter wavelengths, indicating that the color temperature of the condensed phase is increasing. However, the U-V bands of MgO always in emission against the continuum background. This emission shows that MgO vapor exists at the highest temperature in the system, the flame temperature. The continuous radiation is given off

4. The microphotographs were made by the Metallography Laboratory of the G. E. Research Laboratory, Schenectady, New York.

5. See Mavrodineanu (5), pages 134-135, for an excellent discussion of this point.

by the oxide when it diffuses away from the flame zone and condenses in the decreasing temperature field.

At the lowest pressure the rate of diffusion of oxide vapor away from the flame is high and the rate of condensation is low, with the result that there is little condensed oxide in the high temperature region. As the pressure is raised the rate of diffusion decreases, the rate of condensation increases, the amount of condensed oxide in the high temperature region becomes greater, and the color temperature of the continuous radiation rises.

In Figure 1 the radiation from the condensed oxide appears as the nebulous glow outside the flame zone.

Densitometer traces of the resonance line contour show further that the mean temperature of the magnesium vapor is also lower than the temperature of MgO vapor. This effect is the result of the temperature gradient between the ribbon and the flame front.

The above photographic and spectroscopic evidence points to the fact that in the constant-pressure experiment at subatmospheric pressure levels, magnesium ribbon burns by the vapor-phase diffusion mechanism discussed by Coffin(6) and Glassman(7,8).

B. Aluminum

The ignition process in the metal-foil flashbulb is purely a thermal one. Hot particles of burning zirconium from the primer impinge on the foil and ignite it locally. Ignition waves then propagate along the surface of the foil strands(9). This process should not be confused with that of igniting a foil by discharging a capacitor through it(2).

1. Time-Resolved Spectrum

The most prominent feature of the time-resolved spectrum of Al foil burning in the M-2 (Figure 7) is the continuum. At the peak of the flash it runs from about 3300 Å to the red limit of plate sensitivity. The 3944 and 3961 Å lines of Al appear in emission early in the flash, reverse at about 5 milliseconds, and appear in absorption until about 16 milliseconds at which time they reverse again. The bands of AlO , with the most prominent bandheads at 4648, 4842, and 5079 Å appear in emission throughout the flash. Other features of the spectrum are the unresolved K doublet at 4044 and 4047 Å and the broadened unresolved Na D lines.

A few milliseconds after the flash begins the band emission is only a small ripple on the continuum background. At peak it is almost indistinguishable. As the flash progresses the brightness temperature of the continuum increases to the peak and then decreases. Near the end of the flash the band emission once again becomes visible against the continuum.

The strong AlO band emission indicates that Al_2O_3 dissociates at the flame temperature. Since the bands of AlO never appear in absorption the monoxide must exist only at the highest temperature in the system.

The densitometer traces of the time-resolved spectrum of the aluminum flash are shown in Figure 7A. The first reversal of the Al lines of 3944 and 3961 Å is clearly shown.

The appearance of the Al lines indicates the existence of Al vapor at various temperatures. In a vapor-phase diffusion burning mechanism Al vapor can appear from two sources. First, it vaporizes from the burning metal at a temperature lower than the flame temperature. Secondly, it is a dissociation product of the oxide at the flame temperature. The average of these temperatures is lower than the peak flame temperature.

The appearance of the time-resolved spectrum can be explained on this basis. At the early stages of the flash the average temperature of the continuous emitters (metal strands, some metal droplets, some condensed oxide) is low. The Al lines therefore appear in emission. As the flash progresses and the cooler metal particles are replaced by the hot condensed oxide the average temperature of the continuous radiators increases. When it exceeds the average temperature of the Al vapor the metal lines appear in absorption against the continuum. In the later stages of the flash the condensed oxide cools faster than the metal vapor and eventually the average temperature of the continuous emitters drops below that of the Al vapor. The Al lines then reverse again and appear in emission.

2. Combustion Products

An examination of the inside of the M-2 envelope (Figure 3) reveals some white spheres in the range from 20 to 100 microns, many of which are broken. Some are thick-walled and hollow, others seem to contain a metallic nucleus. Most of the combustion products, however, appear in the form of a fairly uniform smoke deposit (the order of 5 microns) on the surface of the envelope. Figure 5 shows that there are no loose combustion products in the body of the bulb. (The photograph shows only the fragments of glass broken when the bulb was pierced.)

The fact that most of the products of combustion appear in the form of a fairly uniform smoke deposit indicates that most of the metal was consumed in a vapor-phase reaction. The product of such a reaction is a vapor which might be expected to condense to give a uniform smoke deposit of oxide.⁶

6. The M-2 is loaded with Al and O_2 at 1000 mm. Hg in proportions which are very close to stoichiometric.

Some aluminum obviously burns by a particle mechanism, as indicated by the presence of the oxide spheres characteristic of Al particle combustion.

The appearance of the time-resolved spectrum discussed above also indicates that combustion of Al by means of a vapor-phase diffusion mechanism is a significant mechanism in this experiment.

C. Zirconium

1. Time-Resolved Spectrum

The time-resolved spectrum of the M-5 flashbulb containing Zr foil⁷ is shown in Figure 3. The major emitter is the continuum which runs from 3000 Å to the red limit of the plate sensitivity at the peak of the flash. Other important features of the spectrum are the lines of Zr at 3601 and 3664 Å, the unresolved Zr lines at 4239, 4240, 4241 and 4242 Å and four systems of ZrO bands: 3682 U-V, Blue, Yellow, and Red. The most prominent bandheads at 3682, 4640, and 5718 are indicated in the figure. All the lines of Zr and all the bands of ZrO appear in emission throughout the duration of the flash. Also prominent in the spectrum are the 3248 and 3274 Cu lines in absorption and the Na D lines.

The appearance of Zr lines and ZrO bands in emission throughout the flash indicates that these species exist only at the peak temperature in the system. They are probably the decomposition products of ZrO_2 . There is no indication here that Zr evaporates from the metal at a temperature significantly lower than the flame temperature.

2. Combustion Products

There is no uniform smoke deposit of the envelope of the M-5 flashbulb (Figure 4). Many white and yellow spheres in the range from 10 to 200 microns can be seen. There is also a scattering of particles smaller than 10 microns. Many white streaks of smoke can be observed emanating from burned spots on the envelope. Some of these streaks are long and sharply defined, others are short and nebulous.

The loose products of combustion found in the M-5 are shown in Figure 6. There are many large, hollow, thin-walled, white and yellow spheres up to 700 microns in diameter. There are many smaller spheres between 150 and 300 microns. Some are yellow, some white, and some metallic grey with a mirror luster. Most of these spheres are hollow and thin-walled. Many of the grey ones are dimpled and punctured. When some of the grey lustrous spheres are broken with a fine needle it is found that they are white or yellow-green inside with only a thin layer of grey metallic substance on

7. The M-5 is loaded with Zr and O_2 , the metal being in excess.

the outside. In addition to the large particles, there is a large number of yellow or metallic-grey spheres in the 20 micron range. It is not known why spheres of two colors appear in the products. A possible explanation may have to do with the existence of two phases of ZrO_2 .

The particles and spheres found in the M-5 are indicative of the various particle-burning mechanisms characteristic of zirconium. An explanation of the mechanism of formation of such particles is postulated below.

The metallic grey surface of many particles can probably be attributed to a condensation of excess Zr vapor, derived from ZrO_2 decomposition, on the oxide particles as they cool.

The sharply-defined streaks found on the bulb envelope are probably condensed jets of oxide vapor indicative of the bursting of hollow spheres. The more diffuse shorter trails are traces of oxide evaporating from the surface of burning particles stuck to the lacquer of the envelope.

The combustion products obtained from the zirconium foil flashlamp indicate that the metal burned primarily by surface combustion of particles. The time-resolved spectrum of the burning process shows no indication of vapor-phase burning.

It is not surprising that metal originally in the form of foil should burn as particles. The formation of liquid droplets of metal from foil is intimately associated with the ignition process. The formation of these droplets depends on the velocity of surface ignition waves, the rate of reaction behind these waves, the surface tension of the liquid metal, and the forces acting on the foil during the ignition process.⁸ Harrison (10) reported that Zr wires burning in a quiescent atmosphere produced liquid droplets which dropped off and burned independently. He found that this effect depended on the oxygen content of the surrounding atmosphere. In the flashbulb the oxidizing atmosphere is anything but uniform as the flash progresses, accordingly, particles are probably formed in a wide range of sizes.

D. Discussion

The spectroscopic observations and the examination of combustion products described above indicate that Al burns mostly in the vapor phase and Zr mostly by surface combustion of particles

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8. Unpublished data obtained by Rautenberg and Johnson give further evidence for vapor-phase burning in Al flashbulbs and particle burning in Zr lamps. Fastax moving pictures of the flash show a nearly homogeneous volume of light in the Al lamp with only some areas brighter than the rest. In the flash of Zr lamps the motion of individual particles, their collisions, and their fragmentation can easily be seen. In both types of lamps there is violent motion on the scale of the bulb during all stages of the flash.

in the constant-volume flashbulb experiment. Spectroscopic and photographic data showed that Mg ribbon burns in the vapor-phase in the constant-pressure experiment.

Al, Mg, and probably Zr also, satisfy the thermodynamic criterion for vapor-phase burning described by Glassman (8).⁹ Their boiling points are lower than the boiling temperatures of their oxides, which are limiting values of the respective flame temperatures. As a result, it now seems clear that the boiling point criterion is a necessary but not a sufficient condition for vapor-phase combustion. Whether a metal actually burns in the vapor-phase depends also on the rate of heat loss from the flame.¹⁰

The high level of continuous radiation observed both in the constant-volume and in the constant-pressure experiments indicates that flame emissivities are, in general, high and that radiant heat transfer plays an important part in metal combustion processes. The molecular and atomic radiation, although intense, is responsible for much less energy transfer than the continuum emitted by condensed oxide species at the flame temperature.

IV. COMBUSTION OF METAL PARTICLES IN A HOT OXIDIZING ATMOSPHERE

An attempt will now be made to correlate the observed behavior of metal particles burning in a hot oxidizing gas with the physical properties of the metals and their oxides and the results described in the first part of this report. It is hoped that this correlation will lead to a better understanding of the important processes occurring when a metal particle burns and to a fuller appreciation of the interactions between these processes and the environment provided for them. The ultimate result which can be hoped for is a degree of understanding of the pertinent physical phenomena sufficient to allow the propulsion engineer to control the combustion of metal particles in a rocket motor.

The metals discussed are Li, Na, K, Mg, Ca, Al, Be, Si, Ti, Zr, and B. They are divided into the volatile and nonvolatile, and the nonvolatile are further divided into three classes according to the properties of their oxides.

Table I shows the melting and boiling points of the volatile metals Li, Na, K, Mg, and Ca and of their oxides. Several significant conclusions can be drawn directly from this table.

1. All of these metals have a vapor pressure of about 1 mm Hg or more at 1000 K. Their boiling points are much lower than

9. The thermodynamic data given in Reference 8 have been modified by more recent information.

10. This consideration is obvious when it is realized that the oxide boiling point is only an upper limit on the flame temperature.

TABLE I
VOLATILE METALS

Metal	Metal M.P. K	Metal B.P. K	Oxide	Oxide M.P. K	Oxide B.P. K	$\frac{V_{\text{oxide}}}{V_{\text{metal}}}$
Li	454	1620	Li_2O	1700	3200	0.58 (12)
Na	371	1156	Na_2O	1190	1550 subl.	0.55 (12)
K	337 (13)	1052 (13)	K_2O	800 (12)	1750 (12)	0.45 (12)
Mg	923	1381	MgO	3075 (12)	3350 (12)	0.81 (12)
Ca	1123 (13)	1693 (13)	CaO	2873 (13)	3800 (13)	0.64 (12)

TABLE II

NONVOLATILE METALS

Metal	Metal M.P. K	Metal B.P. K	Oxide	Oxide M.P. K	Oxide B.P. K	$\frac{V_{\text{oxide}}}{V_{\text{metal}}}$
INSOLUBLE OXIDE						
Al	932	2740	Al_2O_3	2318	3800 (12)	1.45 (18)
Be	1556	2750	BeO	2823	4123	1.68 (18)
Si	1685	3582	SiO_2	1883	3000	
SOLUBLE OXIDE						
Ti	1950	3550	TiO_2	2128	4100	1.73 (18)
Zr	2125	4650	ZrO_2	2960	5200	1.45 (18)
VOLATILE OXIDE						
B	2300	3950	B_2O_3	723	2520 (12)	

The numbers in brackets are the references from which the data were taken. Unmarked values are taken from Reference 11.

diffuse away from the surface. It burns near the oxide surface in a slow diffusion flame. Heat from the reaction is transferred back to the metal droplet and the metal temperature continues to rise. Eventually the metal within the thickening oxide shell may reach its boiling point, becomes slightly superheated, and burst the oxide shell. The original droplet, or what remains of it, breaks up into a number of small, very hot droplets which proceed to burn by the diffusion mechanism already described for small particles.

The boiling temperatures of the volatile metals are not very high, in the sense that radiant heat losses from the particle are still not too important at the boiling point. It is not expected, therefore, that an increased concentration of large particles would accelerate the slow diffusion burning over the oxide layer. However, a marked effect can be expected from the presence of small particles. The important process is the radiant heat exchange between the large particles and the small particles which reach their high flame temperature very quickly.

According to the observations of Wood (14) magnesium particles in the 80 micron range behave as large particles in the gases given off from a burning solid propellant.

One additional effect has to be included in this scheme. Any gas dissolved in the metal effectively decreases its boiling temperature, in that the partial pressure of released gas adds to the vapor pressure of the metal. As a result, the fragmentation of large particles occurs at a lower temperature, hence sooner.

The above mechanism explains the appearance of streak photographs obtained by Gordon (15) and others. In a time exposure of the combustion of magnesium powder suspended in oxygen and ejected through a pilot flame there are some bright spots close to the outlet of the burner tube, some long nebulous streaks, and some more bright nebulous spots where the streaks suddenly end. The initial bright spots are the diffusion flames of the small particles in the powder, the long nebulous streaks correspond to the diffusion flames over the oxide layer covering the larger particles, and the final bright spots are the fast diffusion flames of the hot droplets formed in the fragmentation of large particles.

Table II shows the melting and boiling points of the nonvolatile metals Al, Be, Si, Ti, Zr, and B and of their oxides. Wherever possible the data are taken from the JANAF Thermochemical Data (11) for consistency. Since the following discussion depends significantly on the relative values of the metal and oxide boiling points, it must be pointed out that there is disagreement in the literature on some of these values.¹¹

11. A very limited survey of literature yielded five values for the boiling point of Zr: 3850 K (19), 4650 K (11), 5020 K (13), 5170 K (12), and 5270 K (16); two values for the boiling point of ZrO_2 : 4570 K (12, 13, 17) and 5200 K (11); two values for the

Table II shows that for Ti and Zr the oxide boiling point exceeds the metal boiling point and that in the case of Si the metal boiling point is the larger.¹¹ It is possible to find values in the literature which give exactly the opposite relations between the metal and oxide boiling points of these three metals. This uncertainty must be recognized in the discussion of burning mechanisms which follows from Table II.

The following observations can be made from Table II.

1. The metals are classed according to the properties of the oxides which characterize the burning mechanism. The oxides of Al, Be, Si, are protective materials which adhere well to the metal surface. It is expected that an oxide layer on the surface of these metals largely inhibits oxidation over a wide temperature range.

Both Ti and Zr show the ability to form a solid solution of oxide in the metal. There is no distinct interface between the oxide and the metal. Oxygen can diffuse through the oxide at a low but finite rate. As a result of this property combustion can take place even if the metal is covered with a layer of solid oxide (10).

The oxide of boron melts at a low temperature and has a relatively low boiling point. It is therefore expected that diffusion of metal and oxygen through liquid oxide and, at higher temperatures, the evaporation of oxide and diffusion of oxide vapor away from the surface may be significant in the combustion process.

The volume ratios of the oxides of Al, Be, Ti, and Zr are all larger than unity but not so large that the oxide coating might be expected to blister and peel off the metal surface.

2. The oxides of Al, Be, Ti, and Zr boil at temperatures exceeding the boiling points of the respective metals. The oxides of Si and B boil at temperatures lower than the metal boiling points. The criterion for vapor-phase burning indicates that Al, Be, Ti, and Zr can burn in diffusion flames and that Si and B cannot.

Heat transfer considerations indicate further that Ti and Zr should not be expected to burn in the vapor-phase except under nearly adiabatic conditions. Because the boiling temperatures

boiling point of Ti : 3550 K (11,12,13) and 3808 K (16); one boiling point at 4100 K and one decomposition temperature at 2500 K for TiO_2 . In addition (12) considers the product of combustion of Ti to be Ti_2O_3 with the boiling point at 3270 K. Three values were found for the boiling point of Si : 2753 K (16), 2870 K (13), and 3582 K (11); two values were found for the decomposition temperature of SiO_2 : 2500 K (12) and 3220 K (17); a single value of the boiling point at 3000 K was given in (11).

of these two metals are very high, the radiant heat loss from a burning particle may never allow the diffusion flame to develop.

Figure 10 shows the scheme postulated to explain the observed burning behavior of Al, Be, and Si.

C. Nonvolatile Metal, Nonsoluble Oxide, Large Particle

The rate of heat transfer from the surrounding gas to a large particle is low enough so that a layer of oxide has time to build up on the surface before the particle melts. This layer greatly inhibits further oxidation, so that for all intents and purposes ignition does not take place. Indications are that in the combustion gases given off from the surface of a burning solid propellant aluminum particles larger than about 80 microns behave in this way (4).

D. Nonvolatile Metal, Nonsoluble Oxide, Small Particle

If the metal particle is small enough several interesting phenomena are possible. The rate of heat transfer to the particle is high and melting occurs before appreciable surface oxidation has taken place. Some metal and oxygen can diffuse through the oxide layer and a slow surface combustion results. The net rate of heat loss from the surface of the oxide layer determines the surface temperature which, in turn, determines the burning mechanism.

i. When the surface temperature cannot rise above the melting point of the oxide the solid shell thickens and further oxidation is inhibited. This case is similar to that occurring for the large particles.

ii. Once the surface temperature reaches the melting point of the oxide, diffusion through the liquid oxide layer becomes the rate-limiting step. It is faster than diffusion through the solid. A surface combustion now takes place with some oxide evaporating from the surface and heat being fed back to the droplet. The liquid oxide layer can follow the change in size of the metal droplet, therefore the particle diminishes. Eventually all that remains is a droplet of oxide. If the particle is quenched before all the metal is consumed it appears as a thick-walled shell of oxide surrounding a small sphere of metal.

iib. It is postulated that an interesting effect possibly can occur if some gas is dissolved in the metal.¹² Coming out of solution this residual gas can blow the liquid oxide shell into the form of a thin-walled spherical bubble. Oxygen can still diffuse through the shell. The remaining metal inside the hollow sphere is consumed by surface combustion, therefore, it is possible that all the metal might eventually be consumed. The only product remaining then is a hollow, thin-walled sphere of oxide.

12. The role of dissolved gases in this process was suggested by Gordon, who first found evidence of it (Personal Communication, October 1960).

iii. If the surrounding atmosphere is hot enough and the residence time in it long enough, it is possible that the metal within the liquid oxide shell may reach its boiling point. It then becomes slightly superheated and bursts the shell. The hot metal droplets released in this fragmentation can burn by the vapor-phase diffusion mechanism previously described for the small particles of volatile metals.¹³ This mechanism is not possible in the case of Si because the flame temperature, limited to the boiling point of the oxide, cannot exceed the metal boiling point.

The above mechanisms account for the oxide spheres found by Fassell. They also explain the observations of Wood (14) that aluminum particles burned with sharply-defined streaks ending in a flash with abrupt extinction. The long streaks correspond to the surface burning limited by diffusion through liquid oxide. The flash represents the fragmentation of the original particle and the subsequent very fast diffusion burning of the fragments.

From Gordon's observations (15) it may be estimated that aluminum particles of about 50 microns exhibit this behavior in a 2800 K oxidizing gas.

The concentration effect observed by Gordon is also explained by the above scheme. He finds that increasing the concentration of metal particles increases the number of particles that fragment and decreases the lengths of the sharply-defined streaks. He correctly attributes this to the radiant heat exchange with the surrounding particles. The radiation from the surrounding particles decreases the net heat flow away from the surface of a particle and allows the surface temperature and the metal temperature to rise.

Figure 11 shows the burning mechanism postulated for Ti and Zr particles.

E. Nonvolatile Metal, Soluble Oxide, Small Particle

A small particle melts before any appreciable oxide layer can form on the surface. The droplet then burns by a slow surface reaction limited by the diffusion of oxygen and metal through the

-
13. Gordon (15) shows a streak photograph of Al powder ignited by a long, closed premixed hydrogen-oxygen flame. Fragmentation occurs as the particles leave the luminous zone of the pilot flame. The streaks observed after fragmentation are long and sharply defined. The scheme postulated above is consistent with this observation. The fragmentation results from the passage of the particles through the pilot flame, but occurs when the particles have passed out of the flame and into a zone of lower temperature. The fragments therefore cool quickly and then burn by the surface mechanism characterized by the liquid oxide shell.

oxide. As in the case of aluminum, the rate of heat loss from the surface and the resultant surface temperature are of great importance.

i. If the rate of heat loss from the surface is such that the oxide does not reach its melting point, the slow burning mechanism continues, its rate being limited by the diffusion of metal and oxygen through solid oxide. The droplet shrinks and the oxide shell thickens. If this slow process is allowed to continue long enough all the metal is consumed and the final product is a thick-walled sphere of oxide of roughly the same size as the original particle.

ii. If the surface temperature of the particle can reach the oxide melting point, the shell melts and adheres to the liquid droplet. A surface-burning mechanism now becomes operative with diffusion of oxygen and metal through the liquid oxide as its rate-limiting step. Oxide evaporates from the surface and the particle decreases in size. The ultimate product is a solid sphere of oxide smaller than the original particle.

iib. Here also, as in the case of Al, Be, and Si, gases dissolved in the metal can lead to the formation of thin-walled bubbles. If the residence time in the high temperature surroundings is long enough, all the metal within the bubble is consumed and only a hollow shell remains.

iii. If the temperature of the metal droplet within the liquid oxide shell reaches the boiling point, then the shell bursts and the droplets formed burn by a vapor-phase diffusion mechanism. Because of the radiant heat losses at the very high temperatures involved, it is very unlikely that this phenomenon will ever be observed when Ti or Zr particles burn in combustion gases. It is possible that a very high concentration of small metal particles might produce this behavior when introduced into a very hot pilot flame.

F. Nonvolatile Metal, Soluble Oxide, Large Particle

There is another, much more easily observed, fragmentation mechanism of Ti and Zr particles. It arises when a large particle of the metal is burned in hot surroundings or a small particle is introduced into a low-temperature oxidizing environment. A layer of oxide builds up on the surface before the particle can melt. The oxides of Ti and Zr form a solid solution with the metals and allow appreciable interdiffusion of oxygen and metal through the solid layer. This diffusion process results in a slow surface burning which feeds heat back to the solid metal. Eventually the metal may reach its melting temperature.

Since there is no distinct interface between the metal and its oxide, melting shatters the brittle oxide shell and the particle fragments into small droplets probably still attached to bits of oxide. These droplets then proceed to burn by one of the mechanisms described for the small particles.

The latter mechanism explains the observations of Gordon (15) that Ti and Zr produce long sharply-defined streaks which end in stars with long sharply-defined rays. It also accounts for Brzustowski's observation of the combustion of a mixture of Zr powder and $KClO_4$ set off in open air (9). The first two burning mechanisms postulated above for small particles of Ti and Zr account for the products of combustion of Zr described earlier in this report.

G. High Melting Metal, Volatile Oxide

Figure 12 illustrates the burning mechanism postulated for boron particles on the basis of Talley's results (21) with rods of elemental boron. There is no size effect here, nor any mechanism by which fragmentation can occur. The metal is solid except at the highest burning temperatures. The state of the oxide depends on the convective heat exchange with the surrounding atmosphere and on the net radiant heat loss from the surface.

1. If the heat loss rate is such that the oxide is below its melting point the burning rate is limited by the very slow process of oxygen diffusion through solid oxide. The oxide layer thickens and the burning rate increases little, if at all. Under these conditions the residence time required for complete combustion of metal inside the rocket is probably much greater than the actual residence time of gases in the motor.

2. If the heat loss rate is such that the oxide melts, the burning rate is limited by the diffusion of oxygen through the liquid oxide layer. At the lower end of the liquid oxide temperature range the oxide layer thickens because of the low evaporation rate. At the upper end of this range the rate of evaporation of oxide is probably great enough so that the particle decreases in size.

3. If the liquid oxide can reach its boiling point the burning rate may become limited, not by the thickening of the liquid film, but by the rate of diffusion of oxide vapor and dissociation products away from the surface of the particle. Which of these is the limiting process depends on the heat available to evaporate the oxide from the surface which, in turn, depends on the rate of heat exchange with the surroundings.

It should be pointed out that the description of burning mechanisms of boron particles postulated above can hope to be realistic only in the absence of water vapor. Traces of water accelerate the evaporation of the oxide by forming the very volatile metaboric acid HBO_2 . The result is a tendency to reduce the thickness of the oxide film with an attendant cooling effect on the particle.

V. CONCLUSIONS

Spectroscopic experiments establish the fact that Al and Mg can burn in the vapor phase. Further it appears that the vapor-phase burning criterion put forth earlier (8) must now be modified to include the rate of heat loss in which radiation plays the greatest part.

One can correlate the observed behavior of metal particles in a hot oxidizing gas with the physical properties of the metals and their oxides and the results stated above.

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TABLE I
VOLATILE METALS

Metal	Metal M.P. K	Metal B.P. K	Oxide	Oxide M.P. K	Oxide B.P. K	$\frac{V_{\text{oxide}}}{V_{\text{metal}}}$
Li	454	1620	Li_2O	1700	3200	0.58 (12)
Na	371	1156	Na_2O	1190	1550 subl.	0.55 (12)
K	337 (13)	1052 (13)	K_2O	800 (12)	1750 (12)	0.45 (12)
Mg	923	1381	MgO	3075 (12)	3350 (12)	0.81 (12)
Ca	1123 (13)	1693 (13)	CaO	2873 (13)	3800 (13)	0.64 (12)

TABLE II
NONVOLATILE METALS

Metal	Metal M.P. K	Metal B.P. K	Oxide	Oxide M.P. K	Oxide B.P. K	$\frac{V_{\text{oxide}}}{V_{\text{metal}}}$
INSOLUBLE OXIDE						
Al	932	2740	Al_2O_3	2318	3800 (12)	1.45 (18)
Be	1556	2750	BeO	2823	4123	1.68 (18)
Si	1685	3582	SiO_2	1883	3000	
SOLUBLE OXIDE						
Ti	1950	3550	TiO_2	2128	4100	1.73 (18)
Zr	2125	4650	ZrO_2	2960	5200	1.45 (18)
VOLATILE OXIDE						
B	2300	3950	B_2O_3	723	2520 (12)	

The numbers in brackets are the references from which the data were taken. Unmarked values are taken from Reference 11.



FIGURE 1. COMBUSTION OF MAGNESIUM RIBBON IN AIR AT 60 mm. Hg.
SHOWING A VAPOR-PHASE DIFFUSION FLAME.

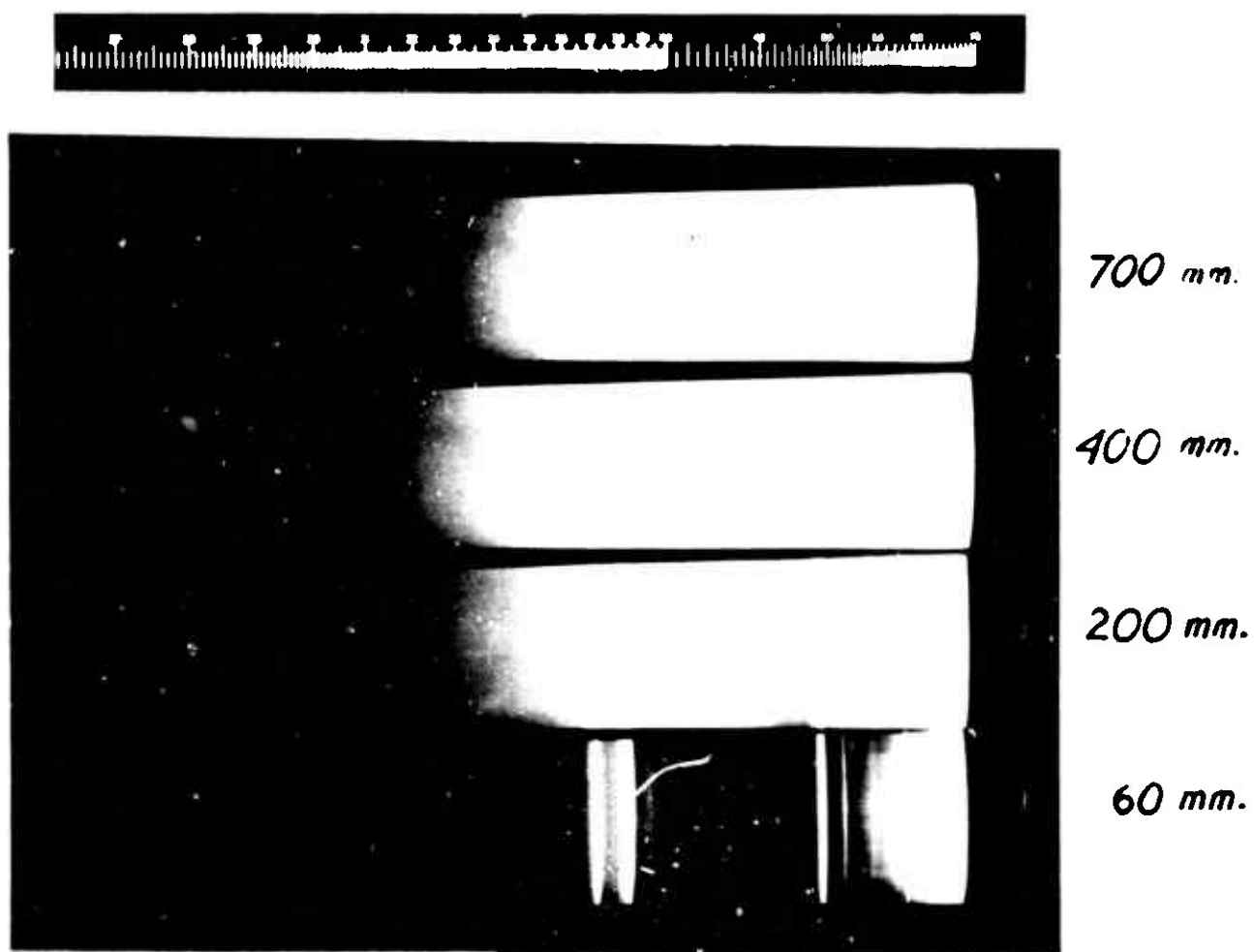


FIGURE 2. FLAME SPECTRA OF MAGNESIUM RIBBON BURNING IN AIR AT VARIOUS PRESSURES. (WAVELENGTH SCALE IN UNITS OF 100 Å.)

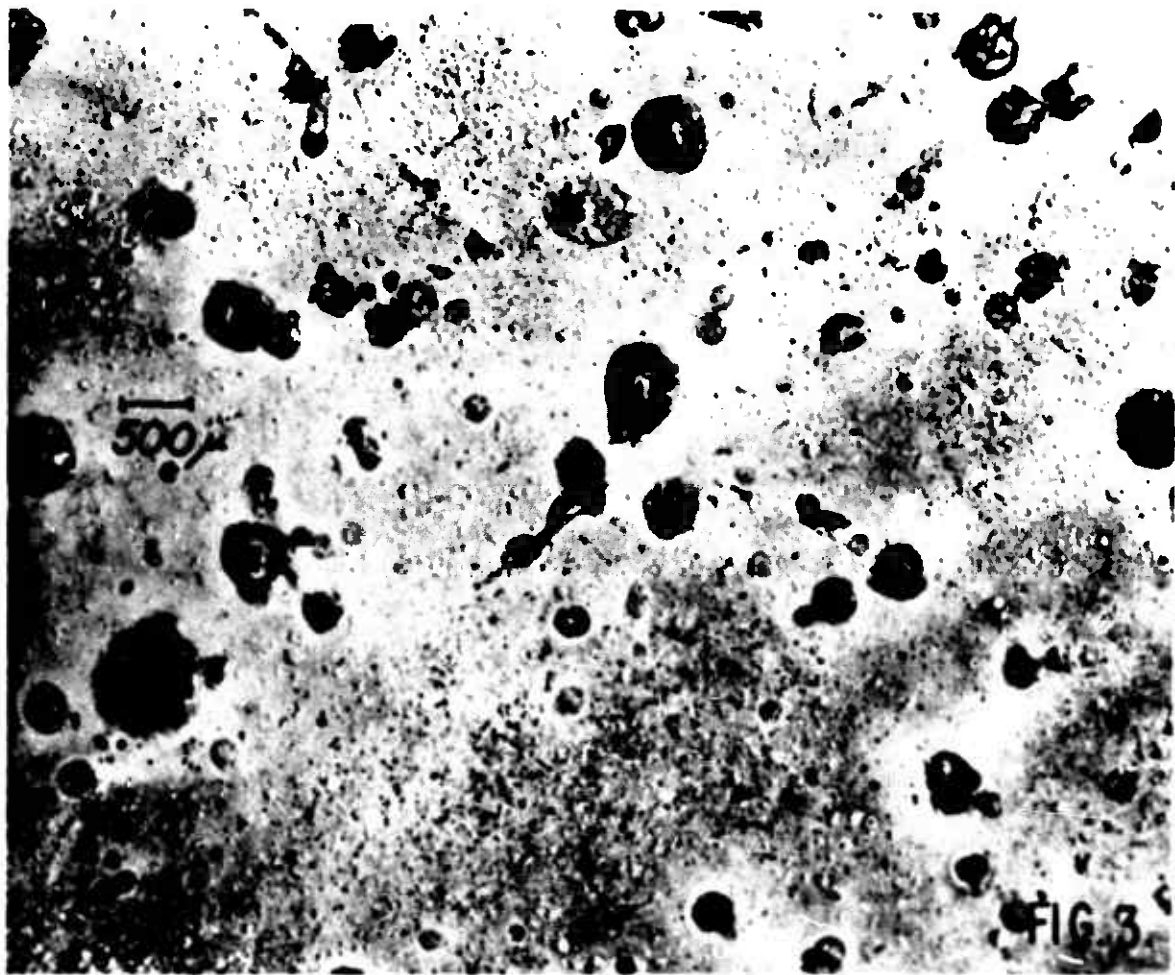


FIGURE 3. COMBUSTION PRODUCTS OF ALUMINUM FOIL ON M-2 ENVELOPE.

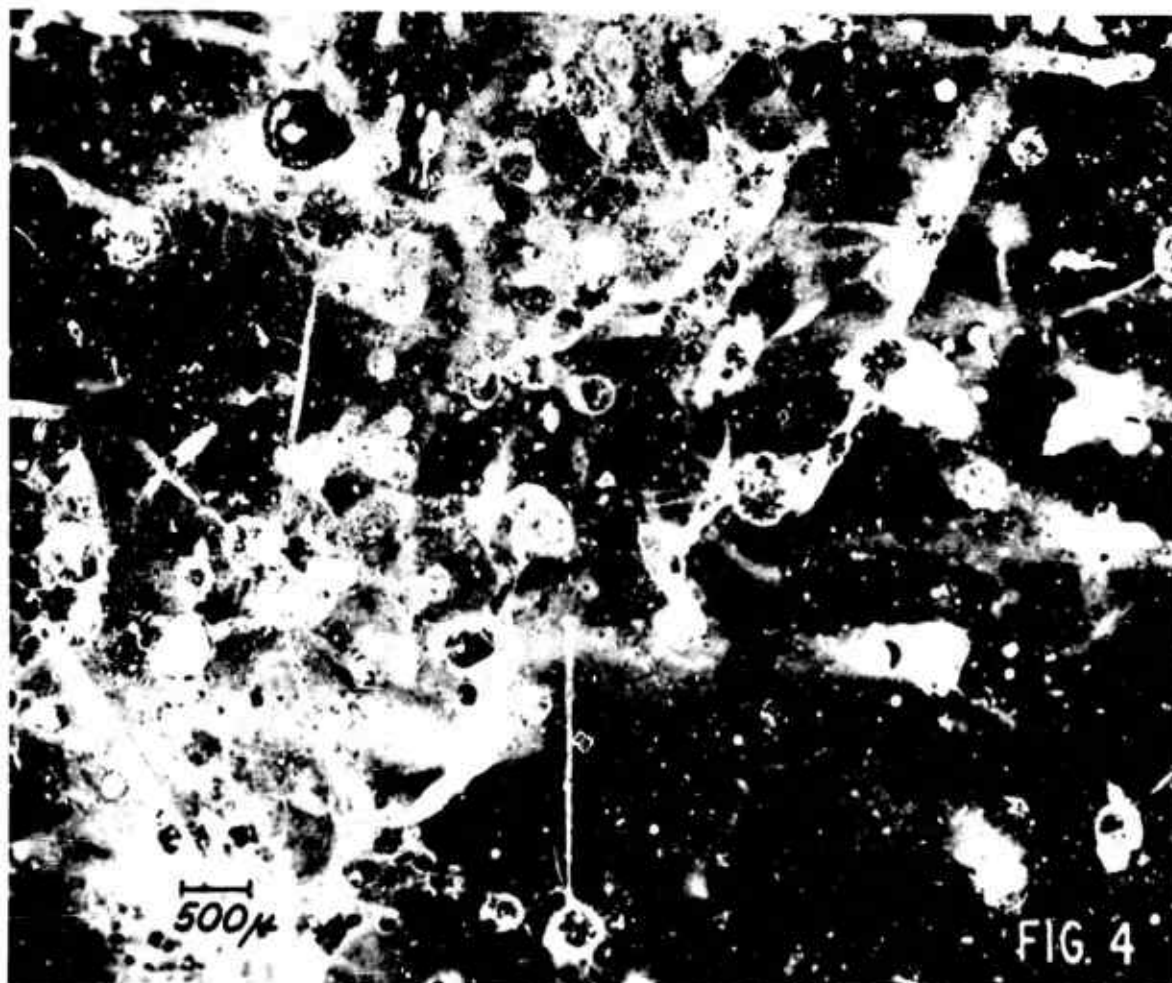


FIGURE 4. COMBUSTION PRODUCTS OF ZIRCONIUM FOIL ON M-5 ENVELOPE.

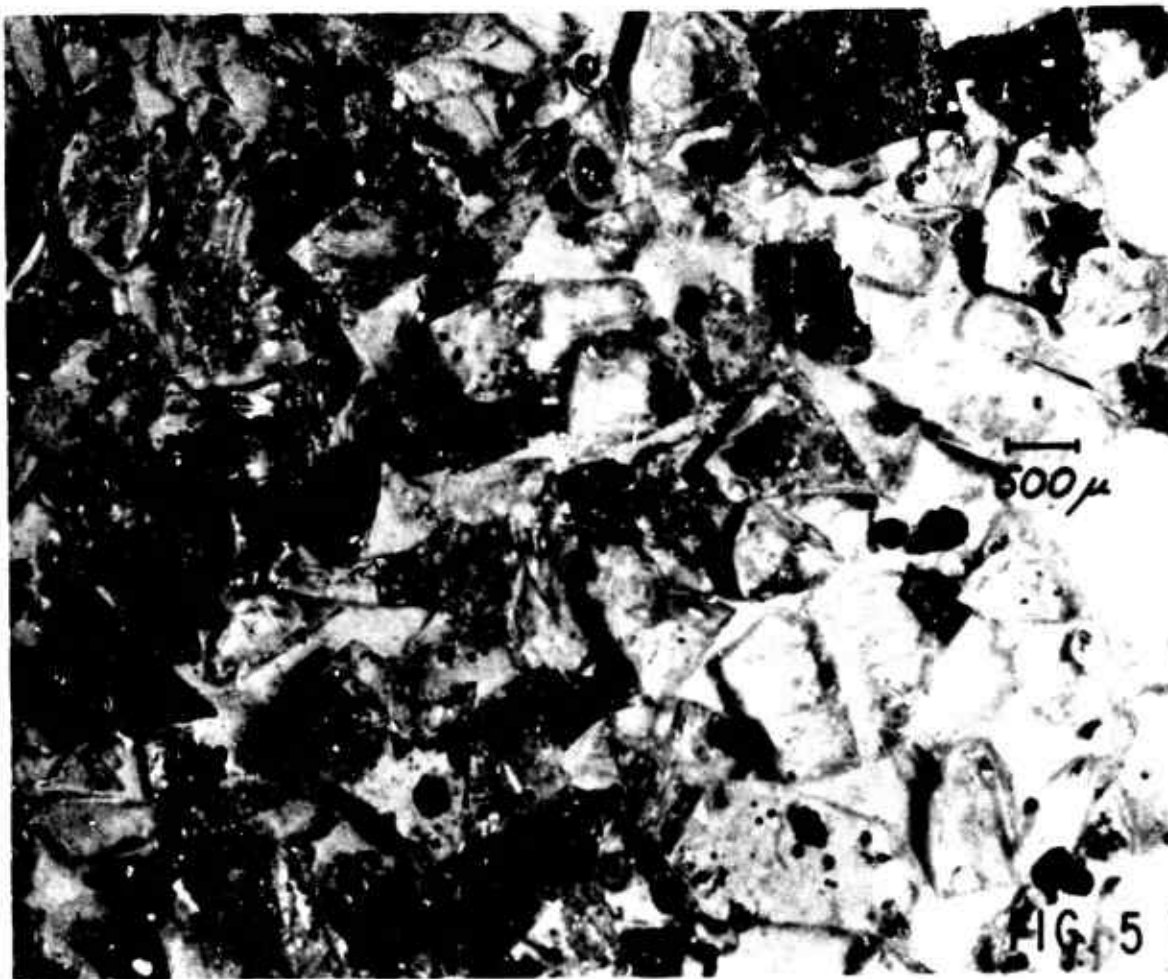


FIGURE 5. RESIDUE OBTAINED FROM A SPENT M-2 FLASHBULB.

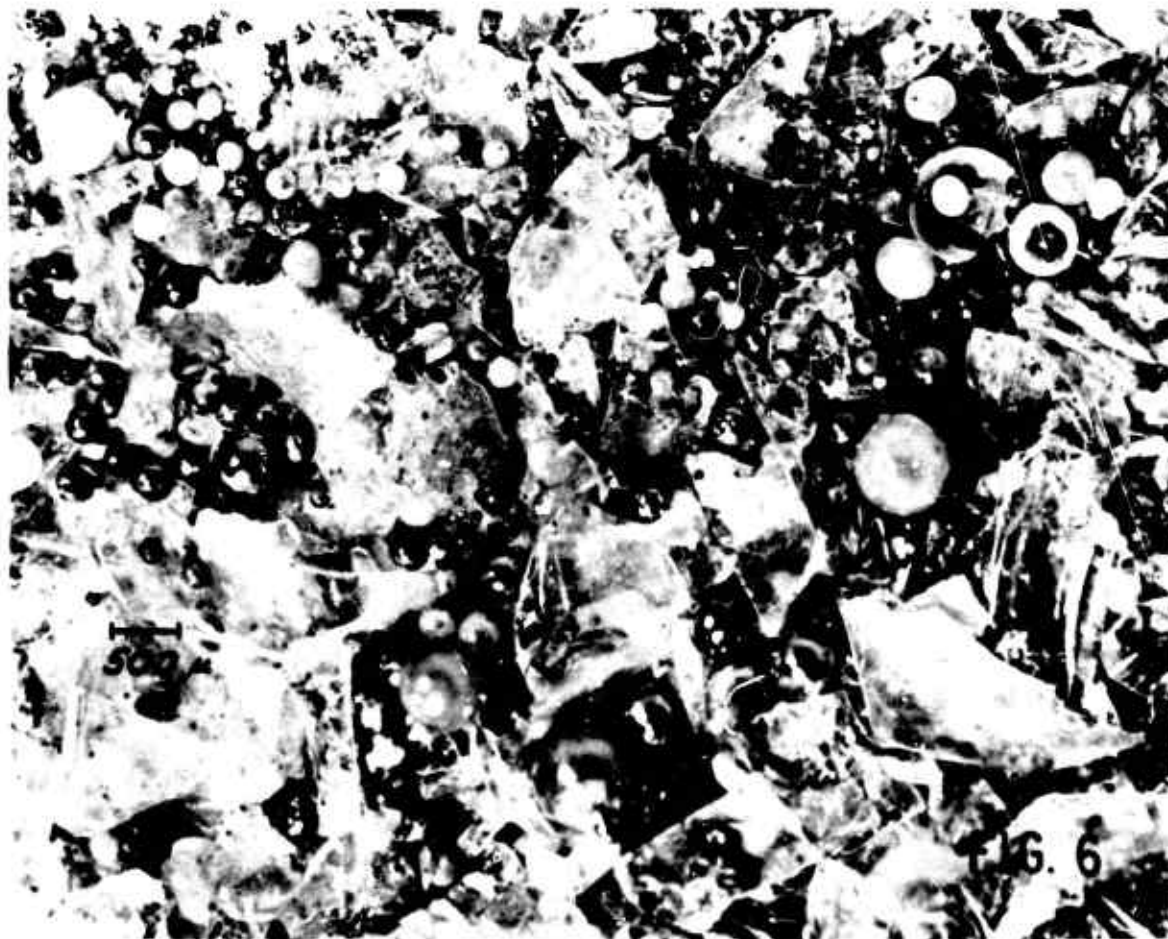


FIGURE 6. COMBUSTION PRODUCTS OF ZIRCONIUM FOIL AND RESIDUE OBTAINED FROM THE M-5.

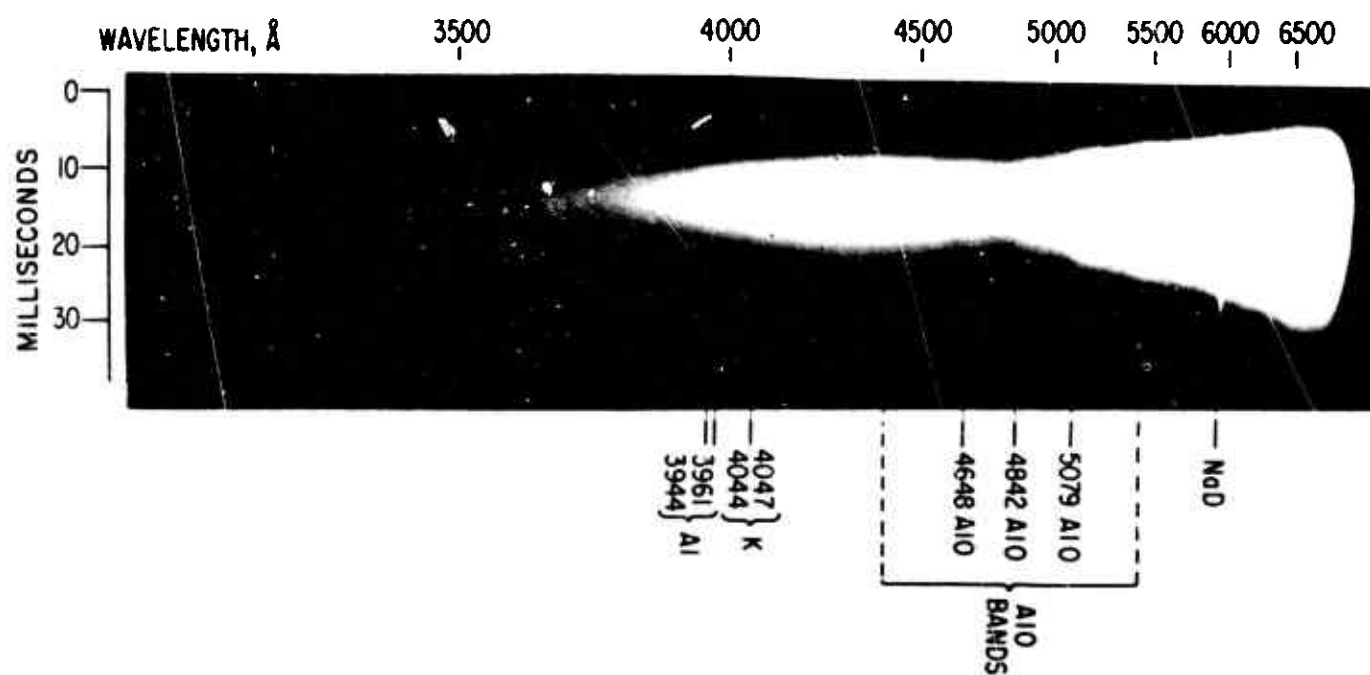


FIG. 7
M 2: TIME-RESOLVED
SPECTRUM

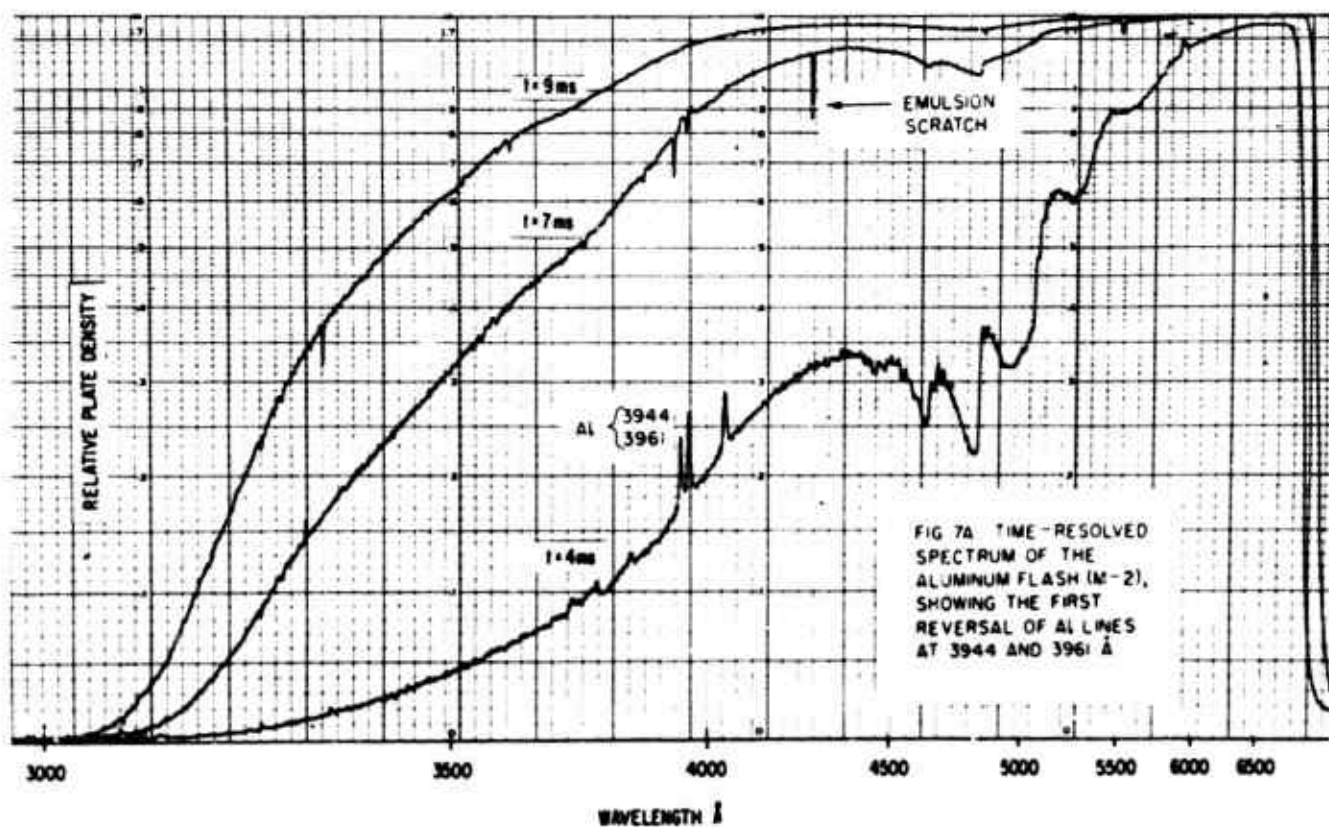


FIGURE 7A. TIME-RESOLVED SPECTRUM OF THE ALUMINUM FLASH (M-2), SHOWING THE FIRST REVERSAL OF AL LINES AT 3944 AND 3961 Å.

FIGURE 9
COMBUSTION OF VOLATILE METAL PARTICLE
IN A HOT OXIDIZING ATMOSPHERE

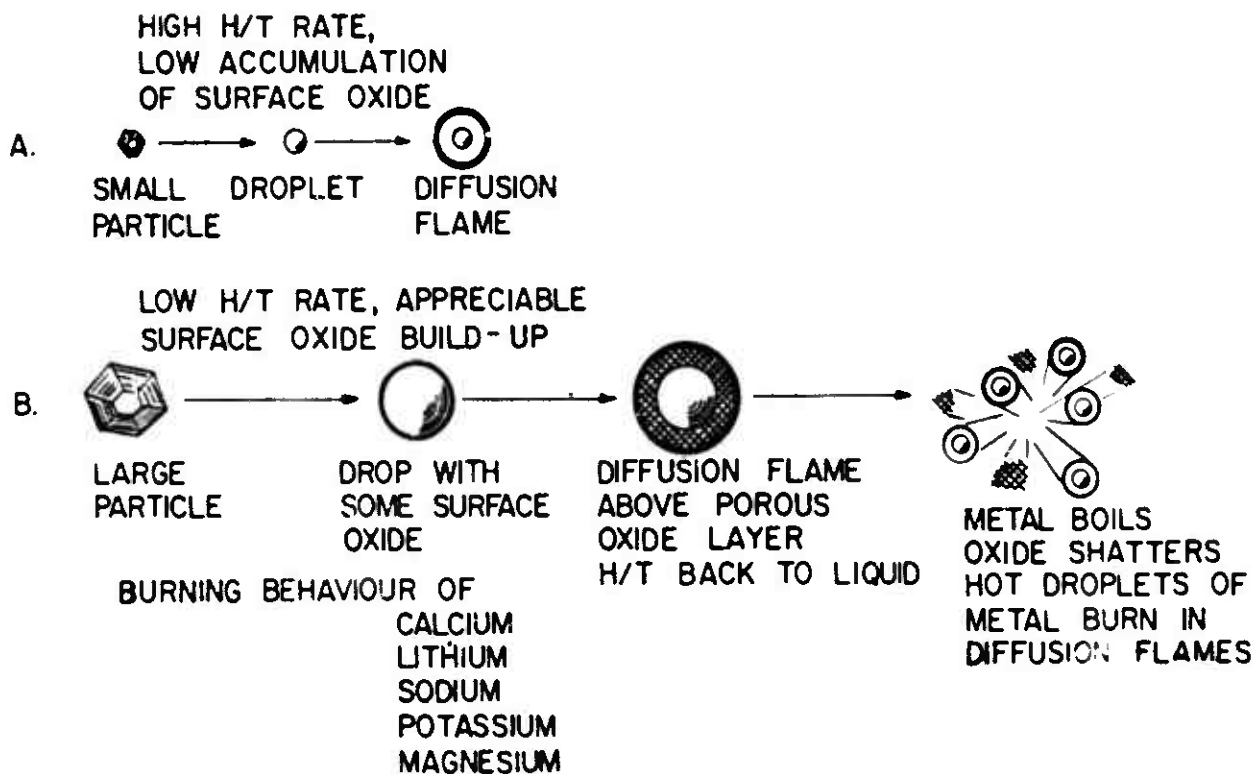


FIGURE 10
COMBUSTION OF NON-VOLATILE METAL PARTICLES IN A HOT OXIDIZING ATMOSPHERE
 NON-SOLUBLE OXIDE

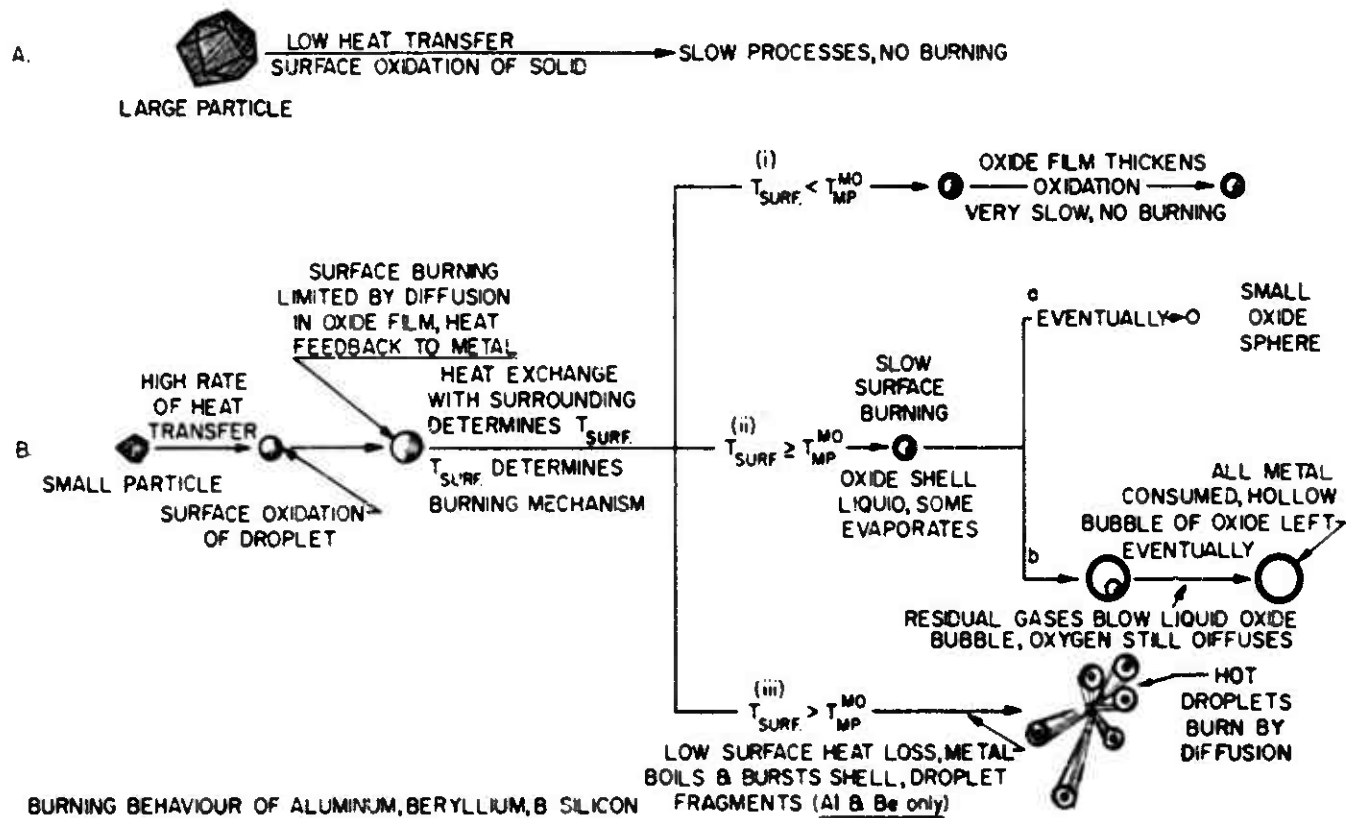


FIGURE 11
COMBUSTION OF NON-VOLATILE METAL PARTICLES IN A HOT OXIDIZING ATMOSPHERE

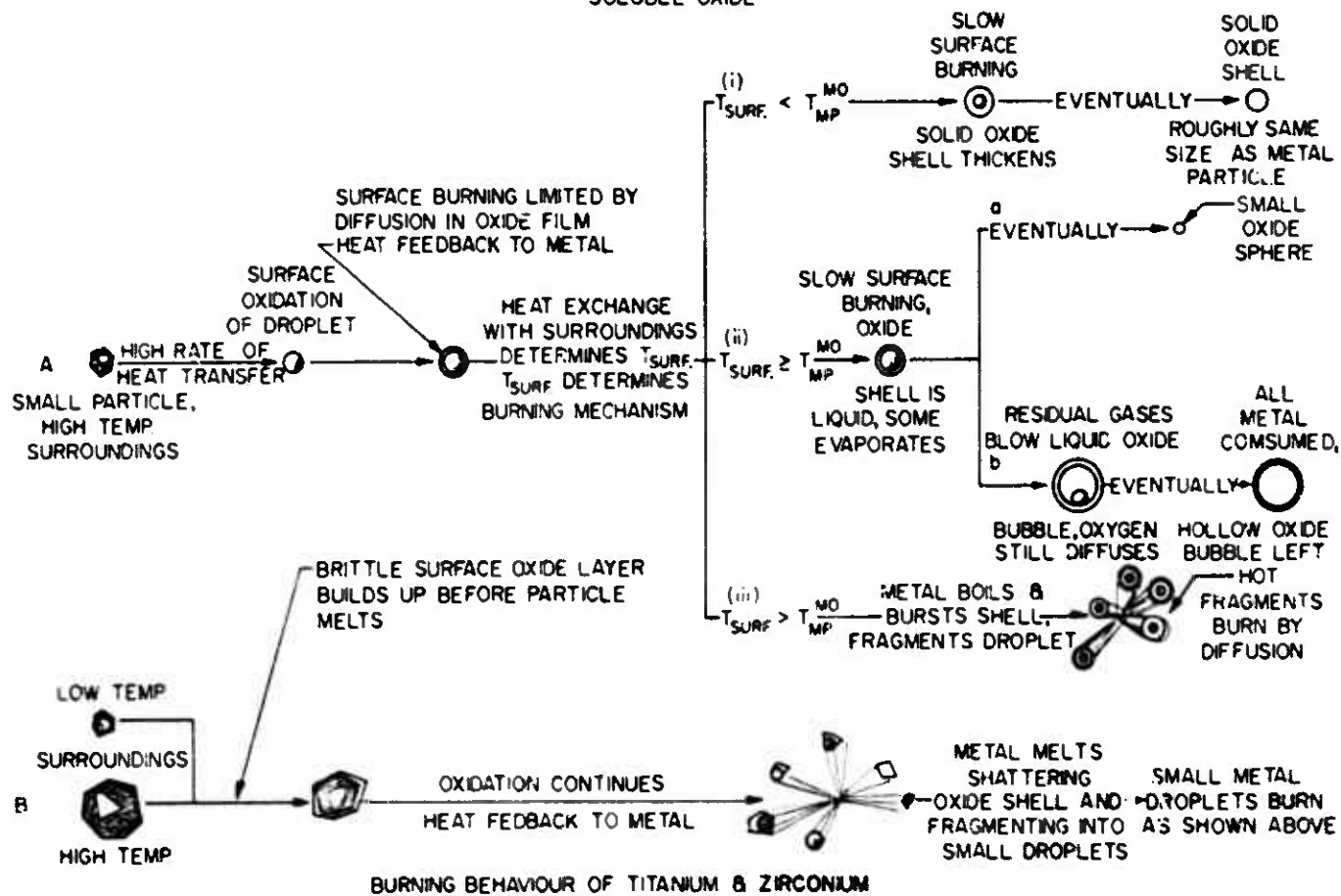


FIGURE 12

COMBUSTION OF HIGH-MELTING METAL PARTICLE IN A HOT DRY OXIDIZING ATMOSPHERE FORMING A VOLATILE OXIDE

