

## Combustion of Metals

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### Introduction

**I**N contrast to the extensive literature on combustion of conventional fuels, a relatively small number of studies on combustion of metals have been performed. Until recently, interest in this field was related primarily to such practical problems as the prevention of metal-dust explosions, the attainment of high temperatures, and the production of intensive transient or continuous light emission. References to many earlier studies of metal combustion may be found in two previous surveys.<sup>1, 2</sup>

In recent years, research in this field has been intensified under the stimulus of new technological developments. The severity of the problem of metal-fire prevention has increased greatly with the use of metals in high temperature and in corrosive environments encountered in supersonic flight, rocket and jet propulsion, and nuclear reactor technology. Work related to these problems has concentrated primarily on the study of ignition. The use of metal fuels in propulsion, on the other hand, has stimulated research both on ignition and on burning processes, particularly of metal powders.

In spite of rapidly increasing interest, our present understanding of metal combustion lags far behind that of the combustion of conventional gaseous and liquid fuels. The reason for this comparative lack of understanding lies not only in the still relatively small research effort but also, to a large extent, in certain distinctive aspects of metal combustion. These distinctive features, which introduce additional com-

plications into the already involved field of combustion in general, will be discussed in the next section, before entering into a more detailed review of the field.

### Distinctive Aspects of Metal Combustion

The advantage of using certain metals as fuels for propulsion and in other applications rests on their very large heats of combustion. Grosse and Conway<sup>1</sup> stressed the relationship between position in the periodic table and heat of combustion and showed that the highest flame temperatures are to be expected with metals in groups II, III, and IV.

A penalty must be paid, however, for the potential high performance attainable with metal fuels. The large exothermic heat of formation of the combustion products implies that they must be highly stable condensed-phase substances. For this reason, not only the fuel but also the products of combustion are present in the combustion zone in the liquid or solid state. Most of the peculiarities of metal combustion arise from this participation of condensed-phase products.

An immediate consequence of the refractory nature of the metal oxides, as noted by many authors, is the upper limit on flame temperature imposed by the boiling point of the oxide. Since the majority of metal oxides decompose partially or completely at high temperatures, the oxide boiling point is defined in terms of the equilibrium of the condensed oxide with its vapor-phase decomposition products at the ambient pressure. One of the difficulties currently encountered in the

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Presented at the ARS 17th Annual Meeting and Space Flight Exposition, Los Angeles, Calif., November 13-18, 1962. This work was sponsored by Project Squid, which is supported by the Office of Naval Research, Department of the Navy. Reproduction in full or in part is permitted for any use of the U. S. Government. The author wishes to thank I. R. Hurle, A. L. Myerson, and G. Rudinger for valuable discussions, and J. K. Webster for assistance in the literature search. He is especially grateful to C. M. Drew and A. S. Gordon of the Naval Ordnance Test Station for the loan of several of their original slides.

field of metal combustion lies in the lack of reliable thermodynamic data required in the computation of these equilibria. For discussions of the uncertainties and problems associated with the determination of pertinent thermodynamic data, and for extensive thermodynamic tables, Refs. 3-15 should be consulted. A rather small number of thermodynamic computations of metal-flame temperatures<sup>22, 53</sup> and of the performance of metallized propellants<sup>16-19</sup> have appeared in the open literature.

A further important consequence of the presence of condensed-phase reactants and products is the predominance of heterogeneous reaction processes in metal combustion. Thus, unless the metal is vaporized artificially, ignition of metals always is preceded by reaction on the metal surface or on and within a protective oxide layer. Since an understanding of low-temperature oxidation of metals is required for the study of ignition phenomena, a brief discussion of this subject will be presented later on.

After ignition, the combustion process may continue to take place on the surface of the metal or on and within a usually molten layer of oxide covering the metal. Alternatively, the reaction may occur in the vapor phase. Characteristic for the latter mode of combustion is a high rate of burning, the presence of a luminous reaction zone that extends some distance from the metal surface, and the formation of oxide smoke consisting of particles in the submicron range. As discussed further in the section on reaction kinetics, even in the case of vapor-phase burning, heterogeneous reactions on the surface of the growing oxide particles may compete favorably with homogeneous gas-phase reactions.

A simple criterion for predicting whether surface or vapor-phase burning will take place was proposed by Glassman.<sup>2, 21</sup> Since the flame temperature cannot exceed the boiling point of the oxide, he suggested that surface burning will occur if the oxide is more volatile than the metal, and that vapor-phase burning will occur in the opposite case. In view of recent experimental results, Brzustowski and Glassman<sup>27</sup> have proposed a modified version of the criterion: excess of metal boiling point over that of the oxide is a sufficient but not necessary condition for surface burning; conversely, excess of oxide boiling point over that of the metal is a necessary but not sufficient condition for vapor-phase burning. The suppression of vapor-phase burning may be due to formation of a protective oxide layer, to reduction of the flame temperature below the metal boiling point by radiation losses, or to both causes combined.

Another distinctive characteristic of metal flames is the high emissivity, owing to the presence of condensed-phase products. Finally, it has been suggested<sup>2</sup> that in view of the high temperatures attained in metal flames the burned gases should be ionized to a considerable extent. However, no measurements of ionization in metal flames have been reported, and the chemical nature of the ions is not known.

### Low-Temperature Oxidation of Metals

In contrast to the combustion of metals, the slow oxidation processes that take place at low temperatures have been studied in great detail and are far better understood. This field will be discussed here only to the extent required in connection with the ignition problem. Comprehensive texts,<sup>25, 26</sup> literature surveys,<sup>27</sup> and reviews<sup>28</sup> on the subject have been published; for a shorter discussion, see also Ref. 29.

Experimentally determined rates of oxidation have been found to agree usually with expressions of the form

$$w^n = At \exp(-E/RT) \quad (1)$$

where  $w$  is the weight of oxygen per unit surface area which has reacted after time  $t$ ,  $A$  is a pre-exponential factor,  $E$  the activation energy,  $R$  the universal gas constant, and  $T$  the absolute temperature. The rate law is called linear, parabolic,

cubic, etc., depending on whether the exponent  $n$  has the values 1, 2, 3, . . . .

The value of  $n$  depends on the properties of the oxide layer that forms during oxidation. A nonprotective porous layer is formed if the volume of the oxide is smaller than that of the metal from which it originates. In this case, a linear rate law is observed. If the volume of the oxide exceeds that of the metal, a protective layer forms, and the oxidation rate is limited by diffusion of ions in the layer; this leads to a parabolic rate law. Cubic rate laws have been observed, e.g., with titanium and zirconium,<sup>30</sup> and it has been suggested that mutual solubility of metal and oxide in these two cases may be related to the cubic law.

The foregoing brief discussion is greatly oversimplified. In particular, the same metal may obey different rate laws in various temperature ranges.

### Ignition of Metals

A considerable amount of work has been carried out in recent years on experimental determinations of ignition temperatures of various metals and metal alloys under a wide variety of conditions. Only a few attempts have been made, however, to confront experimental results with theoretical analysis relating ignition temperature to other properties of the metal and its environment.

Grosse and Conway<sup>1</sup> reported ignition temperatures of various metals, measured partly by others and partly in their own work. These authors state that among the factors that may affect ignition temperature are the following: purity of the metal, gas composition including moisture content, pressure, velocity past the surface, state of subdivision, previous history of the metal, and apparatus and technique. In spite of this discouraging list, the authors expressed the hope that a definition of ignition temperature might be found which could be regarded as a characteristic property of the metal.

Reynolds<sup>29</sup> performed an analysis that links the ignition temperature with the low-temperature oxidation properties of the metal. The treatment is based on the generally accepted view that ignition will occur if the heat produced by the oxidation reaction exceeds the heat losses to such an extent that the temperature rise continues at an accelerating rate. The author considers both conductive and radiative heat losses. As he uses only one-dimensional expressions, the analysis applies only to the ignition of metal in bulk.

Since the heat production depends on temperature by an Arrhenius law, whereas the losses increase with temperature only by power laws, the second derivative of the temperature-time curve changes from negative to positive values as temperature and time increase beyond a critical point. Reynolds regards this inflection point, characterized by the condition  $(d/dT)(dT/dt) = 0$ , as defining the ignition temperature. From this criterion, he derived the relation

$$\exp(-1/T^*) = \eta^{-1}T^{*5} + h^*T^{*2} \quad (2)$$

between the dimensionless quantities

$$T^* = T_{ig}(R/E) \quad (3)$$

$$\eta = (QA/4\sigma\epsilon n)(\gamma/\delta\rho_{ox})^{n-1}(R/E)^4 \quad (4)$$

and

$$h^* = (hn/AQ)(\delta\rho_{ox}/\gamma)^{n-1}(E/R) \quad (5)$$

In these expressions,  $T_{ig}$  is the ignition temperature,  $Q$  the heat of reaction per unit mass of oxygen,  $\sigma$  the Stefan-Boltzmann constant,  $\epsilon$  the emissivity, and  $h$  the heat transfer coefficient. The quantities  $A$ ,  $E$ , and  $n$  are defined by the oxidation rate law, Eq. (1),  $\delta$  is the thickness of the oxide layer,  $\rho_{ox}$  the density of the oxide, and  $\gamma$  the ratio of mass of oxide to the mass of oxygen that formed it. [In Ref. 29, the factor  $\gamma$  is erroneously placed in the denominator of Eq.

(4) and in the numerator of Eq. (5), respectively.] Only linear and parabolic rate laws are considered in this work. A plot of Eq. (2) is shown in Fig. 1.

Reynolds compared ignition temperatures measured in his own work, as well as by others, with relation (2) for vanishing heat transfer. In view of the uncertainties of the oxidation data, the agreement was regarded as reasonably good. However, some deviations exceed one order of magnitude in  $\eta$ . (Because of the apparent error by a factor  $\gamma^2$  in the expression for  $\eta$ , the values for those metals that obey a parabolic oxidation law may have to be revised. Moreover, the author does not state what value for the thickness  $\delta$  was used in the computation, nor on what basis it was selected.)

Reynolds also found that in his experiments the ignition temperatures essentially were independent of ambient pressure and not appreciably different in air and in oxygen. These results, obtained with metals that obey parabolic rate laws, are regarded as confirmation of an oxidation mechanism controlled by diffusion in the oxide layer.

Recent experimental studies<sup>30-35</sup> indicate that ignition temperatures seem well defined only for those metals that do not form a protective oxide layer, such as magnesium. Minor complications arise even in these cases.<sup>31-33</sup> Thus, ignition will occur after an induction period if the metal is kept at a constant ambient temperature slightly below the temperature of instantaneous ignition, owing to gradual rise of metal-surface temperature above the ambient temperature. Water vapor was found to have only a small effect on ignition of magnesium in air but lowered the ignition temperature in  $\text{CO}_2$  appreciably.<sup>32, 33</sup>

In contrast to the fairly reproducible results obtained with metals that obey linear oxidation laws, widely diverging data have been reported for many metals that form protective oxide layers. For this reason, attempts have been made to eliminate the effect of the oxide layer by suddenly exposing a clean metal surface to an oxidizing atmosphere. Even these techniques did not remove large discrepancies between results of different investigators. Thus, both Jackson and co-workers<sup>35</sup> and Littman's group<sup>34</sup> measured the ignition temperatures of titanium rods ruptured in oxygen at various pressures. The former workers find that ignition occurred at  $-123^\circ\text{C}$  with an oxygen pressure of 100 psig and at room temperature with a pressure of 75 psig. Littman and co-workers, using almost identical experimental methods, report ignition at room temperature only for pressures above 350 psig. At 75 psig, the temperature of the sample had to be raised to  $1100^\circ\text{C}$  to obtain ignition upon rupturing.

Undoubtedly, the wide discrepancies indicate that in these experiments ignition occurs not simply by exposure of a freshly formed oxide-free surface to oxygen, but that details of the rupture process may play an important role. This conclusion also is confirmed by similar studies of Littman's

group on zirconium. It was found that under otherwise identical conditions rupture under tension always caused ignition above 1000 psig, whereas rupture by torsion did not lead to ignition up to the highest pressure of 2000 psig which was used.

Littman's results with zirconium also showed that, at least with this metal, ignition was not related to oxidation rate controlled by diffusion in the oxide layer, in contrast to Reynolds' conclusions. The ignition of zirconium sheets with oxide-free surfaces prepared by heating in vacuum was compared with that of sheets covered with oxide layers. It was found that the oxygen pressure required for ignition at room temperature rose only from 300 psig for clean surfaces to 400 psig for oxide-covered ones. Moreover, ignition was found to depend strongly on total gas pressure as well as on oxygen partial pressure in  $\text{O}_2$ -He mixtures, contrary to Reynolds' results obtained with other metals. The ignition behavior of zirconium and titanium might possibly be anomalous, owing to the solubility of oxygen in these metals.

The work discussed thus far has dealt only with ignition of metals in bulk. The effects of subdivision have been studied by many investigators.<sup>30, 36-42</sup> Attempts have been made to take the influence of subdivision into account by correlating ignition temperature with specific surface area. Thus, Schnitzlein<sup>30</sup> reports the empirical relationships

$$T_{ig} = 1343 - 208 \log a \quad (6)$$

for zirconium, and

$$T_{ig} = 4190 / (\log a - 5.23) \quad (7)$$

for uranium, where  $a$  is the specific surface area in square centimeters per gram. The early work by Hartmann<sup>36-38</sup> and later studies<sup>39, 40</sup> show, however, that specific surface area is not the only factor that determines the ignition temperature of finely divided metal. Thus, Andersen and Belz<sup>39</sup> observed a decrease of ignition temperature of close-packed zirconium powder with increasing total mass of the sample and presented an analysis of this effect.

The influence of particle concentration in dust clouds on ignition temperature was studied by Cassel and Liebman.<sup>40</sup> These authors measured ignition temperatures of single magnesium particles and of particle clouds carried in a stream of air into a furnace. The results of this work are shown in Fig. 2. In agreement with analytical results, the ignition temperature of single particles was found to increase

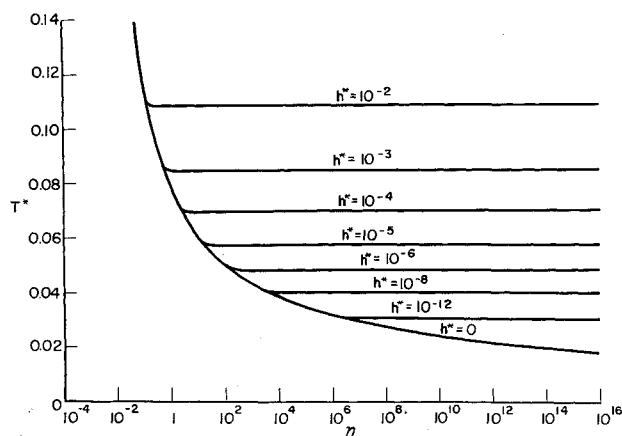


Fig. 1 Prediction of ignition temperatures from oxidation data<sup>29</sup>

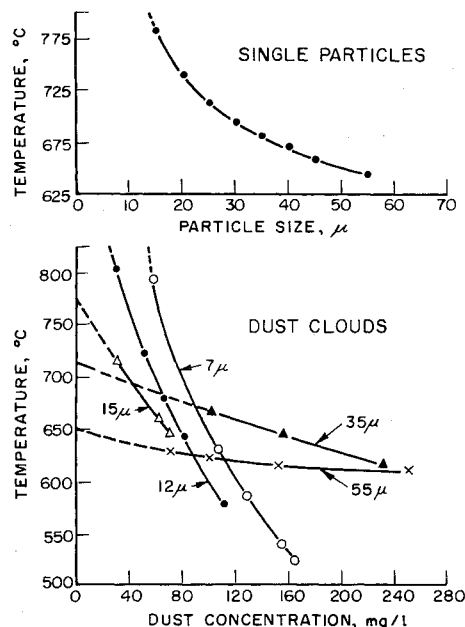


Fig. 2 Ignition temperatures of magnesium particles<sup>40</sup>

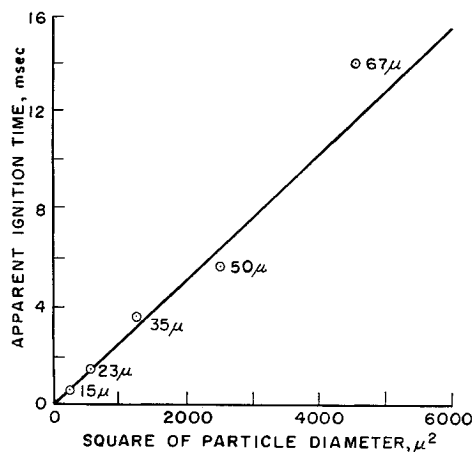


Fig. 3 Apparent ignition time of aluminum particles vs particle diameter<sup>41</sup>

with decreasing particle size. As the particle concentration was increased, however, the dependence on particle size reversed, as indicated by the intersections of the curves in the lower part of the figure. The influence of particle concentration is attributed to the cooperative effect of heat transfer from neighboring particles which shields the interior of the cloud against heat loss. The authors do not treat this cooperative effect analytically.

The ignition and burning of single aluminum particles injected into a hot gas stream of known uniform temperature, composition, and flow velocity were investigated by Friedman and Macek.<sup>41</sup> The gas stream was produced by burning propane-oxygen-nitrogen mixtures on a porous-plug flat-flame burner. Ignition and burning of the axially injected particles were studied photographically.

The apparent ignition delay, based on distance from burner top to ignition point and on gas velocity, was found to be proportional to the square of particle diameter, as shown in Fig. 3. Ignition occurred only if the gas temperature exceeded a critical temperature that depended on oxygen concentration. This ignition limit for one particle size is shown in Fig. 4. The effect of particle size on ignition temperature was found to be small.

The authors show that the true ignition time delay, corrected for acceleration of the particle from small initial velocity to full gas-flow velocity, must also be proportional to the square of particle diameter. For this true delay time, they derive the relation

$$t_i = \frac{\rho d^2}{12\lambda} \left[ c \ln \left( \frac{T_a - T_0}{T_a - T_i} \right) + \frac{L}{T_a - T_m} \right] \quad (8)$$

where  $d$  is the particle diameter,  $\rho$  is the density,  $c$  the heat capacity,  $L$  the heat of fusion, and  $T_m$  the melting point of the metal,  $\lambda$  is the thermal conductivity, and  $T_a$  the temperature of the ambient gaseous medium,  $T_0$  is the initial particle temperature, and  $T_i$  the ignition temperature. The analysis thus confirmed the proportionality between ignition delay and  $d^2$  and gave satisfactory numerical agreement between calculated and experimental delays.

Turning to the problem of ignition limit, the authors note that Frank-Kamenetskii's thermal theory cannot apply to the ignition of aluminum particles, since it predicts a strong dependence on oxygen concentration and particle size. (The results of Ref. 40 for single Mg particles agree qualitatively with the Frank-Kamenetskii theory, which should be applicable to metals that do not form a protective oxide layer.) Since the observed ignition limit (Fig. 4) fell near the melting point of aluminum oxide ( $2303 \pm 20^\circ\text{C}$ ), Friedman and Maček assume that the surface reaction rate increases discontinuously upon melting of the protective oxide layer

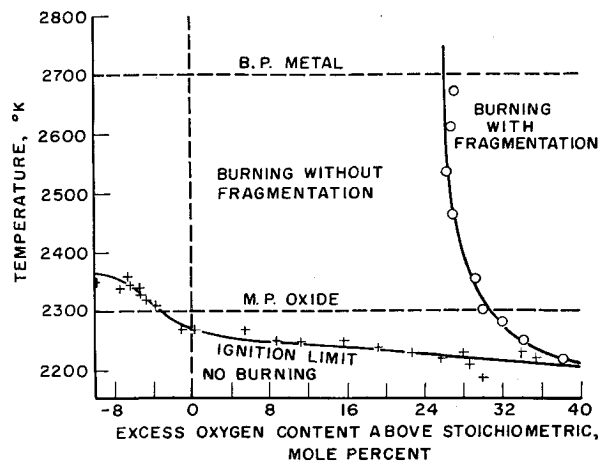


Fig. 4 Ignition and fragmentation limits of 35-μ-diam aluminum particles<sup>41</sup>

that forms during pre-ignition reaction. The thermal theory, modified by this assumption, showed that ignition should occur when the surface temperature of the particle reaches the melting point  $T_{mo}$  of the oxide. The corresponding temperature  $T_{ai}$  of the ambient gas is given by

$$T_{ai} = T_{mo} - \frac{qC_a}{\lambda[(1/D) + (2/dk)]} \quad (9)$$

where  $q$  is the heat of reaction per mole of oxygen,  $C_a$  is the ambient oxygen concentration,  $D$  the diffusion coefficient of oxygen in the ambient gas, and  $k$  the rate constant of the surface reaction in the presence of solid oxide at its melting point. The second term of Eq. (9) was found to be small compared with  $T_{mo}$ , so that the analysis confirmed the experimental ignition limit and its slight dependence on oxygen concentration and particle diameter.

In a subsequent study,<sup>42</sup> Friedman and Maček replaced the propane fuel with carbon monoxide in order to assess the influence of water vapor content on the ignition and burning process. The ignition results of this investigation were identical with those of the earlier work and thus showed no influence of water vapor on the ignition process. Appreciable differences were observed, however, between the burning behavior in the two investigations; these will be discussed in the next section.

## Burning of Metals

Like the ignition process, the burning of metals depends greatly on the degree of subdivision of the fuel. Only a few cases of burning in bulk have been reported. Grosse and Conway<sup>1,52</sup> describe the combustion of aluminum with oxygen in a molten pool floating on molten aluminum oxide, and in centrifugal reactors. A study of the burning of sodium in bulk was performed by Gracie and Droher.<sup>54</sup>

Several investigators studied the burning of metals in form of wires, rods, and ribbons. One of the earlier investigations is that of burning magnesium ribbons by Coffin.<sup>43</sup> Burning times in various atmospheres were measured by a motion-picture technique. Figure 5 shows the influence of diluting the oxygen atmosphere with argon, nitrogen, and helium. Addition of small amounts of water vapor had a surprisingly large effect, as shown in Fig. 6.

From the appearance of the flame and the formation of oxide smoke, Coffin concluded that magnesium burned in a vapor-phase diffusion flame. An attempt was made to compute burning times under the assumption that the transport processes were much slower than the chemical reactions and therefore controlled the rate of the burning process. The computed burning times were too low by a factor of about 2,

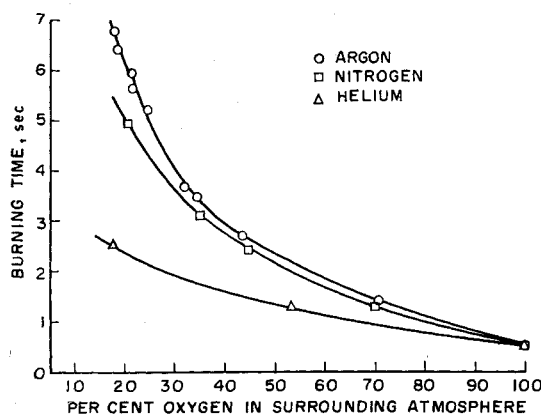


Fig. 5 Burning time of magnesium ribbons vs oxygen concentration for several diluents<sup>43</sup>

in comparison with the results in argon-oxygen and nitrogen-oxygen mixtures, but predicted the dependence on oxygen concentration fairly well. Larger discrepancies were found for helium dilution. Coffin admits that the effect of water vapor is probably chemical and cannot be explained satisfactorily by the assumed model.

The burning of titanium and zirconium wires was studied by Harrison.<sup>44</sup> The work was later continued, and extended to other metals, by Harrison and Yoffe.<sup>45</sup> Most of the experiments were performed with vertically suspended wires ignited at their lower end. Magnesium and aluminum wires were found to burn with a diffuse combustion zone and to produce large quantities of oxide smoke, indicating a vapor-phase burning process. Burning rates of these metals were not measured because the luminous smoke obscured the wire.

Titanium and iron wires were observed to form a molten droplet, consisting of a mixture of metal and oxide, that hung at the end of the wire during combustion. The droplet periodically grew in size and then dropped off, so that the propagation of the combustion zone along the wire had an intermittent character. Very little oxide smoke was formed by these metals, and it was concluded that the reaction took place on the surface of the molten material.

Zirconium wires burned in a similar manner above a critical oxygen concentration that depended on wire diameter. Below this concentration, a solid oxide layer formed on the wire. Fragmentation phenomena caused by splitting of the oxide layer and formation of oxide in the form of hollow shells were observed with this metal. Similar effects were produced with titanium when the burning was quenched artificially. Molybdenum was found to burn on the surface but to produce large amounts of oxide smoke, owing to sublimation of the oxide.

The rates of propagation measured by Harrison and Yoffe are shown in Fig. 7. Except for zirconium at low rates, where the oxide is formed as a solid layer, the propagation rates depended strongly on oxygen percentage. Figure 8

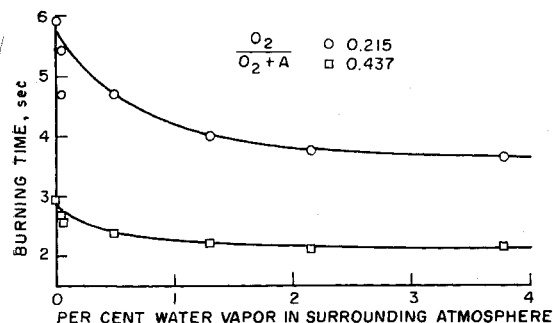


Fig. 6 Burning time of magnesium ribbons vs water concentration<sup>43</sup>

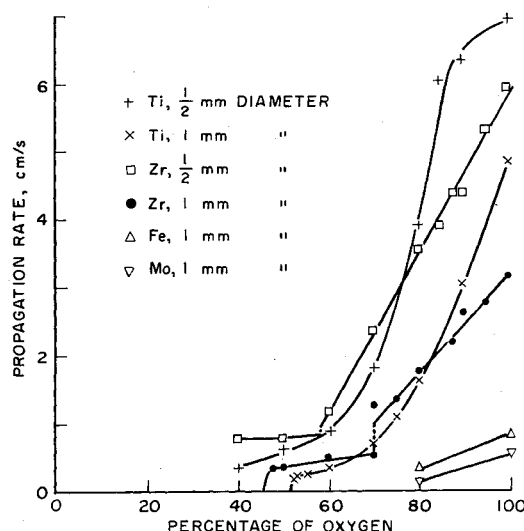


Fig. 7 Propagation rate of combustion zone along metal wires in oxygen-nitrogen mixtures at 1-atm pressure<sup>45</sup>

shows the dependence of propagation rate with zirconium, burning in pure oxygen, on oxygen pressure. Photoelectrically measured color temperatures of the combustion zone are presented in Fig. 9. The authors also determined oxidation rates of thin zirconium wires at low oxygen concentrations, in the range of formation of solid oxide, by measuring the rate of change of electrical resistance. Contrary to results of others,<sup>30</sup> their data indicate a linear rate law.

In view of the large dependence of burning rate on oxygen percentage, the authors conclude that the rate of burning on the surface of molten oxide-metal mixture is controlled primarily by diffusion of oxygen through the surrounding atmosphere. Temperatures of the burning zone were computed on the basis of balance of heat production and loss, with the heat production limited by diffusion of oxygen. (An Arrhenius factor was, however, included in the rate expression.) The computed temperatures, shown in Fig. 9, were in reasonable agreement with the trends of the experimental results. For various other details of this work, such as metallographic studies of zirconium quenched during combustion, reference to the original papers<sup>44, 45</sup> should be made.

Results in close agreement with Harrison and Yoffe's are reported in Kirschfeld's study of burning iron wires.<sup>46</sup> Burning rates were found to be approximately proportional to the square root of pressure, similar to the results for zirconium shown in Fig. 8. A surface reaction mechanism is proposed. The author discusses several alternative rate-limiting processes, which could not be distinguished since they were all compatible with the results. In a subsequent investigation<sup>46a</sup> performed at pressures up to 100 atm, a transition to vapor-phase burning at high pressures is suggested. Continuation of the work with copper wires<sup>46b</sup> gave

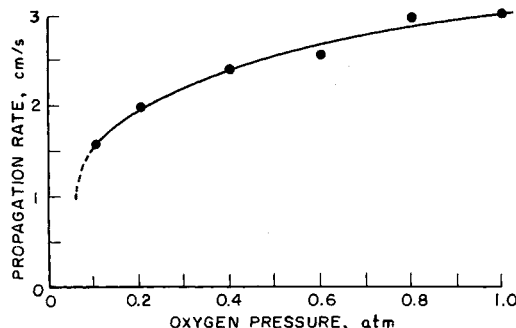


Fig. 8 Propagation rate of combustion zone along 1.2-mm-diam zirconium wire vs oxygen pressure<sup>45</sup>

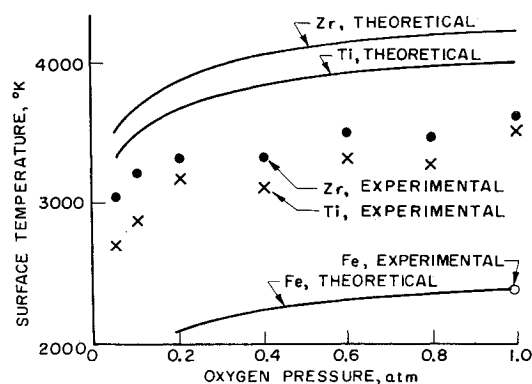


Fig. 9 Surface temperature of combustion zone of burning wires vs oxygen pressure<sup>45</sup>

similar results; from the ratio of burning rates of iron and copper, the author deduces that diffusion in the molten oxide was rate-limiting. Work with zinc and brass wires indicated a vapor-phase mechanism.

The same author's investigations of burning aluminum and magnesium wires<sup>47</sup> indicated a vapor-phase burning process. At high burning rates, aluminum wires extinguished with violent fragmentation before burning to completion. Propagation rates of aluminum were proportional to the square root of pressure between 0.5 and 16 atm and decreased between 16 and 32 atm; above this pressure, they were again proportional to  $p^{1/2}$ , with a lower proportionality constant than in the low-pressure range. An increase of burning rate with decreasing pressure below 0.5 atm also was observed. The burning rate of magnesium wires exhibited a minimum at about 2 atm. The author suggests reaction mechanisms and rate-limiting steps intended to explain the observed behavior which seem, however, speculative and unconvincing.

The combustion of boron has been studied by Talley.<sup>24</sup> Boron rods of about 1 mm in diam were prepared by vapor-phase chemical deposition on heated tungsten wires. Rates of burning were determined either by measuring the uptake of oxygen or by determining the change of diameter of the rods, which were maintained at various temperatures by electrical heating. Alternatively, the rate of propagation of the burning zone along rods ignited at one end in a stream of oxygen was measured.

In order to interpret his results, the author distinguishes a number of regions, referred to temperature-pressure coordinates, in which different processes become rate-determining. This plot is shown in Fig. 10. Throughout regions I-III, diffusion across the oxide film is regarded as the primary rate-determining process, but secondary factors determine the actual rate. Thus, region I, in which the oxide remains solid, corresponds to slow oxidation. No measurements are reported by Talley, but in view of the growth of the protective layer a parabolic rate law is anticipated. Region II is entered upon melting of the oxide at 723°K. In this region the oxide film approaches after initial growth a constant thickness, determined by balance between rate of oxidation and removal by gravity flow. The latter depends in turn on various factors such as viscosity and surface tension of the liquid oxide and the geometry of the burning solid. Region II was not investigated extensively, but the experiments confirmed the postulated mechanism and showed that a linear rate law was obtained when the oxide layer reached constant thickness.

As region III is approached, evaporation of the oxide begins to compete with removal by flow. Since both processes can occur simultaneously, the transition between regions II and III cannot be defined very sharply. The author states that the boundary plotted in Fig. 10 corresponds to an electrically heated 1-mm-diam rod burning in oxygen in a small cold-walled Pyrex tube. In region III, the oxide is removed

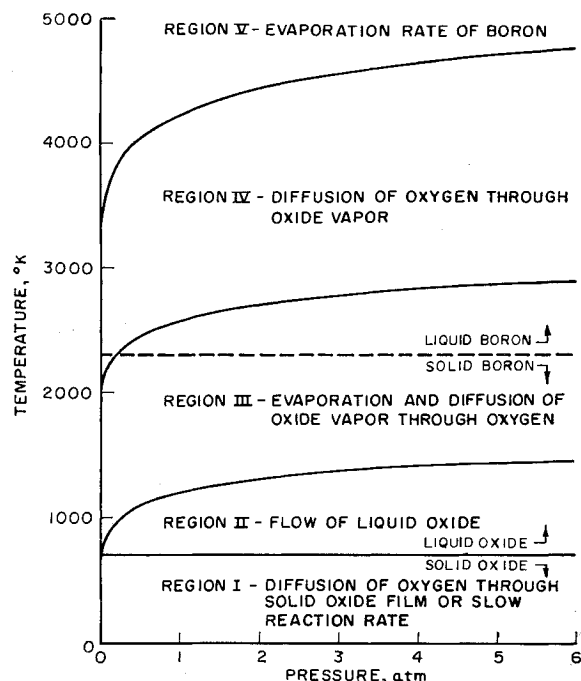


Fig. 10 Semiquantitative map showing various rate-limiting processes in the oxidation of boron in oxygen<sup>24</sup>

exclusively by evaporation, and the thickness of the oxide film is thought to depend on diffusion of oxide vapor into the surrounding atmosphere. Talley's experimental studies were performed primarily in this region. Combustion rates were found to be inversely proportional to pressure and to depend on temperature by an Arrhenius law with an activation energy of 77 kcal/mole. The upper portion of curve 1 in Fig. 11 corresponds to these results for a pressure of 1 atm, whereas the lower portion corresponds to burning rates in region II.

The observed activation energy equals the heat of vaporization of  $B_2O_3$ , as demonstrated also by curve 3 of Fig. 11. The observed pressure and temperature dependence is regarded as confirmation of the proposed rate-controlling process in this region. It seems somewhat surprising, however, that the activation energy was not larger than the

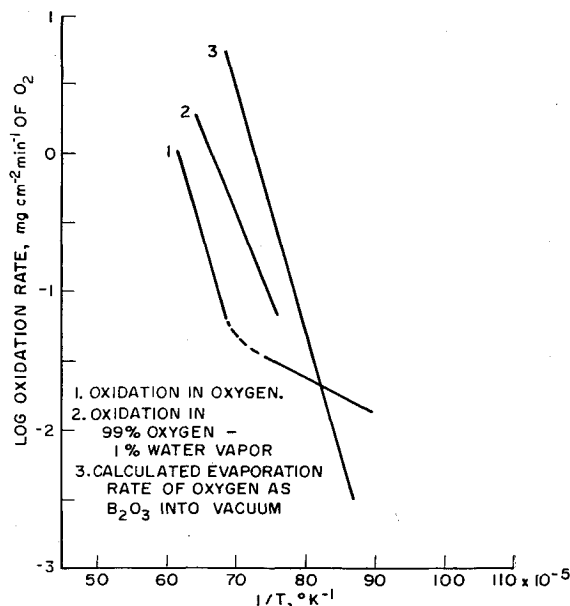


Fig. 11 Oxidation rate of boron vs reciprocal temperature<sup>24</sup>

heat of vaporization, since one would expect a contribution to the Arrhenius factor from the rate-limiting diffusion across the liquid oxide layer.

A large effect of addition of water vapor was observed in the temperature range of region III, as shown by curve 2 of Fig. 11. The rates increased substantially, but the activation energy decreased to 56 kcal/mole. The inverse-pressure dependence persisted, indicating that the process was still controlled by diffusion of an evaporating species. The author states that thermodynamic arguments suggest  $\text{HBO}_2$  as the evaporating species.

As the temperature is raised in region III, the thickness of the oxide film decreases, until, at the boiling point of  $\text{B}_2\text{O}_3$ , the film disappears. The boundary between regions III and IV therefore was drawn as the boiling point of the oxide. In region IV, diffusion of oxygen towards the burning metal surface is regarded as the rate-limiting step.

The spontaneous combustion of boron rods ignited at one end in oxygen at a pressure of 1 atm was found to occur at a temperature of about 2500°K, corresponding to the boiling point of the oxide. At lower pressures the temperature was found to exceed the corresponding boiling point, so that the burning process fell into region IV. (Because of the volatility of  $\text{B}_2\text{O}_3$ , the temperature of the boron flame is not limited by the oxide boiling point; see computation in Ref. 22.) The burning rate under these conditions was found to be almost independent of pressure, in agreement with a reaction controlled by diffusion of oxygen.

Finally, the boiling point of boron is plotted as the boundary between regions IV and V. In the latter region, Talley regards evaporation of the metal as the rate-limiting step. No attempt was made to reach this region experimentally, since this would have required raising the temperature above that of spontaneous combustion.

The majority of metal-combustion studies were performed with metal powders. In earlier investigations,<sup>48-51</sup> the main reason for using powdered metal may have been the comparative ease of experimental technique. Later work<sup>1, 52, 53</sup> had the practical aim of obtaining torch flames producing very high temperatures and heat transfer rates. More recently, studies of metal-powder burning were stimulated largely by the use of metal additives in propellants.

Gordon<sup>23</sup> studied the burning of various metals and metal compounds injected into the central gas stream of a simple torch burner. In the majority of his studies, oxygen was the particle carrier; an annular natural-gas-air flame was adjusted to the minimum size required for ignition. Still and motion-picture photographs of the burning particles were taken. Appearance of nebulous streaks, combined with high burning rate, was considered as evidence for a vapor-phase diffusion flame, whereas sharply defined streaks and slow burning rate were regarded as an indication of surface reaction. With many substances, fragmentation of the particles was observed.

To account for his observations, Gordon proposed a subdivision of the substances used in his work into five classes, as follows:

A) *Volatile substances* ( $\text{Mg}$ ,  $\text{MgH}_2$ ,  $\text{LiH}$ ,  $\text{CaH}_2$ ) were found to burn in the vapor phase. Larger particles had spiral and erratic trajectories and were subject to fragmentation. These substances are characterized by easy ignitability and high burning rate.

B) *Nonvolatile substances with soluble oxide* ( $\text{Ti}$ ,  $\text{Zr}$ ,  $\text{TiH}_4$ ,  $\text{ZrH}_4$ ,  $\text{TiC}$ ,  $\text{ZrN}$ ) were characterized by easy ignitability, even for large particle size, but by slow burning rates. Fragmentation occurred even with very small particles ( $<44\mu$ ). Long burning times and sharp streaks indicated surface reaction. Comparatively large diffusion transport through the oxide layer, owing to solubility, is regarded as cause of easy ignitability.

C) *Nonvolatile substances with insoluble nonvolatile oxides* were difficult ( $\text{Al}$ ) or impossible ( $\text{Be}$ ) to ignite under Gordon's

experimental conditions. Only the smallest  $\text{Al}$  particles ignited in a large natural-gas-air flame of temperature  $<1500^\circ\text{C}$ . (This ignition temperature is far below the values of Ref. 41, shown in Fig. 4.) In this case the particles burned slowly without fragmentation and irregularities of the streaks. In a long oxidizing hydrogen-oxygen flame,  $T > 2000^\circ\text{C}$ , burning was faster and fragmentation occurred. The sharp traces indicated a surface reaction. At high particle concentration, however, small aluminum particles were found to ignite easily and to burn in a Bunsen-type vapor-phase flame. The protective oxide of narrow composition range is regarded as retarding diffusion, thereby reducing ignitability and burning rate.

D) *Nonvolatile substance with volatile oxide*. Small boron particles were found to burn slowly without fragmentation. Combustion was incomplete with single particles, but complete combustion could be achieved at high particle concentrations. Incompletely burned particles were covered with a glassy oxide layer.

E) *Compounds or alloys with components that differed considerably in volatility* were found to burn in successive stages. Thus, the appearance of the streaks of burning  $\text{LiAlH}_4$  indicated successive burning of hydrogen, lithium, and aluminum. A similar observation was made with an  $\text{Al-28\% Mg}$  alloy. The particles burned rapidly in a diffusion flame that caused fragmentation. Sharp streaks emerging from this flame were regarded as evidence that  $\text{Mg}$  burned in the diffusion flame, whereas the streaks were due to  $\text{Al}$  fragments.

The classification into classes A-D also was adopted by Brzustowski and Glassman,<sup>57</sup> who discuss the respective mechanisms in great detail. They distinguish between burning of small and large particles and consider the influence of particle surface temperature, controlled by heat exchange with the surroundings.

A torch-burner technique very similar to that of Gordon was employed by Fassell's group<sup>22</sup> to study the burning characteristics of various metals and alloys. Burning times were determined by high-speed motion-picture methods. The highest combustion rates occurred with  $\text{Mg-Al}$  alloys, and in this group, fastest burning was obtained with the  $\text{MgAl}_2$  composition. Addition of 2% of various other metals to the  $\text{MgAl}_2$  alloy decreased the burning rate by a factor of about 6.

Combustion products were trapped on slides inserted into the flame at various heights and were examined metallographically and by x-ray diffraction. Metallic particles collected just above the ignition flame were found to be spherical regardless of initial shape. This observation indicated melting within 1 to 3 msec and burning involving liquid metal droplets. The oxide products were also spherical, and the larger spheres were hollow shells that often contained a single spherical droplet of the metal. The sizes of these metal droplets decreased as the collection position was moved away from the ignition flame. As its most remarkable result, x-ray diffraction analysis of the products of  $\text{Mg-Al}$  alloy combustion showed the presence of the spinel  $\text{MgAl}_2\text{O}_4$  as product over the whole alloy range and as a major product between 12 and 65%  $\text{Mg}$ .

The authors conclude that the appearance of hollow oxide spheres and the formation of  $\text{MgAl}_2\text{O}_4$ , among other observations, are incompatible with a vapor-phase diffusion-flame mechanism. They propose, therefore, that all metals burn by a surface mechanism consisting of the following three stages: 1) preheating from room temperature to ignition temperature, yielding a spherical droplet of molten metal covered by a thin oxide coating; 2) increase of temperature to that present in sustained combustion process; the authors admit that a diffusion flame may form momentarily in this stage but state that the droplet will be covered subsequently by a continuous oxide layer; and 3) the oxide layer is blown up by the evaporating metal like a soap bubble; reaction



takes place on the surface of the oxide, with metal diffusing outward or oxygen inward through the oxide. Fragmentation may take place in the third stage, if the droplet exceeds a critical diameter beyond which the force of surface tension can no longer balance that of metal-vapor pressure.

The results of Fassell's group are clearly incompatible with Gordon's observations on materials of class A and E. The conflict might be eliminated by admitting that the experimental details may affect the burning mode to a large extent. Friedman and Maček's<sup>41, 42</sup> work provides evidence in support of this assumption. By burning premixed gases on a flat-flame burner, these authors achieved close control and uniformity of the hot-gas atmosphere into which aluminum particles were injected.

When this atmosphere was produced by a propane-oxygen-nitrogen flame,<sup>41</sup> the burning mode agreed essentially with that observed both by Gordon and by Fassell's group for aluminum: the streaks on the photographs were sharp, indicating a surface mechanism, and the combustion products were hollow spheres. A slight difference from Fassell's results was noted: incompletely burned particles consisted of oxide shells asymmetrically attached to the metal particles. In the absence of fragmentation, the burning time was found to be roughly proportional to the 1.5 power of the particle diameter. Periodic variation of light emission, owing to rotation of the particles, was observed frequently.

Fragmentation occurred above a critical oxygen content that decreased somewhat with increasing temperature (Fig. 4). At relatively low temperatures this limit was sharply defined, but as the boiling point of aluminum was approached, fragmentation was preceded by diffuse luminosity adjacent to the sharp streak of the particle. The authors interpret their results by a mechanism essentially identical with that proposed by Fassell. Changes of direction of motion, rotation, diffuse luminosity, and fragmentation are regarded as due to increasing degree of violence of bursting of the oxide films under the influence of excess of metal-vapor pressure over surface tension.

The water vapor content of the gases produced by the  $C_3H_8-O_2-N_2$  flame was about 14 to 18%. In order to assess the influence of this variable, the authors continued their work using  $CO-O_2-N_2$  flames.<sup>42</sup> To obtain stable flames, a small amount of hydrogen had to be added, so that the water vapor content of the flame gases was about 0.5%. Although the ignition was not affected by the reduction of water vapor concentration, the burning mode changed notably: the particle tracks showed diffuse luminosity, the burning times under comparable conditions was reduced markedly, and the combustion products consisted no longer of alumina bubbles, but of irregularly shaped particles that were smaller than the original metal particles and varied in size over a wide range. These observations were interpreted as evidence for vapor-phase diffusion burning in the absence of water vapor.

Glassman and Brzustowski<sup>56</sup> criticize the conclusion that the formation of hollow-sphere products should be caused by water vapor. They state that, in an as yet unpublished work, the formation of hollow spheres depended on several other variables and occurred in the absence as well as in the presence of water vapor. Hollow oxide spheres were produced with burning wires of Al, Mg, Zr, and Ti.

Drew and co-workers<sup>55</sup> used, among other methods, an ingenious technique that gave direct evidence of transition from surface to vapor-phase burning during the combustion of aluminum particles. The particles were injected into a downward-directed oxygen-hydrogen torch flame, and their burning was quenched by impingement on polished black glass inserted into various regions of the flame. Photomicrographs of the deposited material gave images of the oxide distribution in the flight path of the particle immediately preceding impingement.

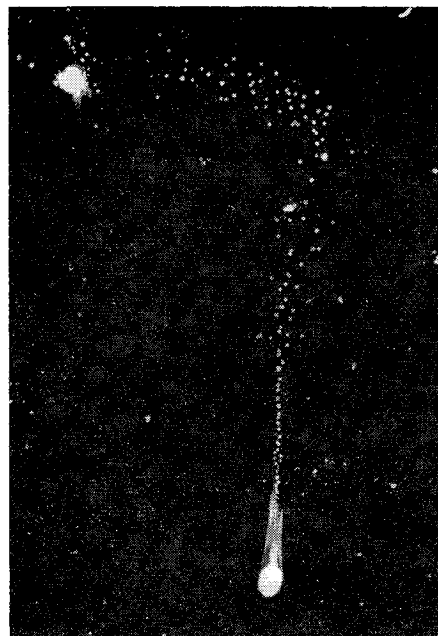


Fig. 12 Photomicrograph of deposit formed on polished black glass by impingement of burning aluminum particle. Early stage after ignition of 72- $\mu$  particle, showing formation of 5- $\mu$  oxide spheres<sup>55</sup>

Three of these photographs are shown in Figs. 12-14. (The originals were taken in color and allow estimates of the size of small deposited particles from the colors caused by light scattering.) Figure 12 shows an early stage in the burning of an aluminum particle of 72  $\mu$  in diameter. A stream of 5- $\mu$ -diam oxide spheres is seen to originate at a single point of the particle. The short diffuse tail seems to indicate incipient vapor-phase burning. A later stage, in which the particle leaves a helical trail of very small oxide spheres, indicating vapor-phase burning, is shown in Fig. 13. Finally, well-developed vapor-phase burning of a 100- $\mu$ -diam sphere is shown in Fig. 14. The shape of the impression of the particle indicates that the portion opposite the tail was covered with a cap of oxide.

Since these authors recovered hollow oxide spheres from their flames, their results show conclusively that formation of hollow spheres does not imply absence of vapor-phase burning and, further, that the latter can occur in the presence of water vapor. Their results thus support Glassman and Brzustowski's remarks.<sup>56</sup>

Only one analytical treatment of the burning time of metal particles has been published.<sup>58</sup> This analysis is a generalization of Coffin's earlier approximate treatment.<sup>43</sup> As in the earlier work, the burning process is treated under the assumption that the transport processes in the vapor phase are rate-controlling, whereas the reaction rates are so fast that local chemical equilibrium may be assumed throughout the reaction zone. The results for magnesium are not appreciably different from those of the earlier analysis. Good agreement between the results of Ref. 58 for boron and the experimental burning rate and surface temperature during spontaneous combustion of boron was noted.<sup>24</sup> Glassman<sup>2</sup> suggested inclusion of radiant-energy-transfer terms in the treatment of Ref. 58 but did not carry out any numerical evaluations.

### Combustion of Metals in Propellants and Propulsion Devices

The use of metal additives in solid propellants is now common practice. The first extensive studies concerned with the use of metals in propulsion, however, were those on liquid-





Fig. 13 Photomicrograph obtained as in Fig. 12. Helical trace of small oxide particles formed after development of vapor-phase burning<sup>55</sup>

fuel/metal-powder slurries at the NACA. This work has been summarized in Ref. 59. The slurries consisted of 50% or more magnesium or boron in jet propulsion fuels. Tests in various pipe-connected combustors showed that slurried magnesium burned readily even under conditions where jet hydrocarbon fuel itself did not burn, and the expected improvement in thrust was obtained. Small ramjet vehicles fueled with magnesium slurry were flown successfully. In contrast to the results with magnesium slurries, the boron slurries were found to be more difficult to burn than jet fuel and to form objectionable deposits in the combustor. The slurry-fuel program was terminated when work on liquid nonhydrocarbon fuels that had superior properties in comparison with magnesium slurry was started.

Although metalized solid propellants are now in general use, the open literature contains very little information on burning studies. Wood<sup>60</sup> gave a brief account of an investigation of the burning of composite propellants that contained metal powders. High-speed motion-picture techniques were employed. Ignition was found to depend on particle size: 5- $\mu$  aluminum particles ignited at the propellant burning surface, whereas most 40- $\mu$ -diam particles ignited only after leaving the surface; 80- $\mu$  particles and larger ones did not ignite within the field of view ( $\sim 1$  cm). Magnesium showed a similar dependence on particle size, but both ignition distance and burning times were shorter than those of aluminum. Addition of moderate amounts of small particles to coarse material strikingly shortened the ignition lag. Particles of magnesium and aluminum showed flashes and streamers that indicated a vapor-phase burning mechanism, whereas these effects were absent with zirconium and silicon particles.

Friedman and Maček<sup>42</sup> report preliminary results on ignition and burning of aluminum particles in ammonium perchlorate-organic fuel flames. The results confirm their earlier conclusions obtained with premixed gaseous-fuel flames.<sup>41, 42</sup>

Although it is well known that addition of aluminum to solid propellants suppresses high-frequency combustion instability, this effect thus far has not been explained satisfactorily. A theoretical treatment by Cheng<sup>61</sup> showed

that the oscillatory heat source from the oxidation of the metal powders may be out of phase with that of the combustion of the basic propellant and thus may suppress oscillations. However, the analysis gave no assurance that addition of metal powders always would improve the stability.

The writer feels that increase of radiative energy transfer upon adding metal fuels might play a major role in smoothing the burning process, thereby suppressing instability. This possibility has not yet been considered in analyses.

An experimental study of possible contributions of aluminum additives to unstable combustion was carried out recently by Watermeier and co-workers.<sup>62</sup> The authors state that, although for some years powdered aluminum had been regarded as the best cure for unstable combustion, it is now feared that aluminum may in some cases contribute to low-frequency combustion instability. To study this possibility, propellant slabs that contained aluminum of various particle sizes and concentrations were burned in a transparent-walled chamber under ambient pressures of 200 to 800 psi of nitrogen. Runs were made under steady-flow conditions and under oscillating-flow conditions imposed by a siren rotating over the exhaust port.

High-speed motion pictures showed that the aluminum always melted at the burning propellant surface. Particles were observed to agglomerate by rolling around and coalescing with other particles before rising into the flame zone. At high pressures and aluminum concentrations, the propellant burning surface appeared almost covered with a blanket of molten aluminum. The authors suggest that agglomeration in these cases might alter the acoustic admittance of the burning propellant.

As the droplets left the propellant surface, they assumed a roughly spherical shape with a vapor trail preceding them. The apparent droplet diameter grew at first, up to a certain distance above the surface, and then decreased. This distance had a pronounced minimum at a chamber pressure that depended on particle size; it was not affected by siren pulsation, but the latter increased the rate at which particle diameter decreased after attaining its maximum value. The authors rule out the possibility that the apparent diameter growth may be due to blowing up of hollow oxide spheres; they suggest further coalescence of large particles with small ones that are not visible on the photographs, or diameter growth of a diffusion-flame envelope, as possible mechanisms.

Oscillations of the major and minor dimensions of the ellipsoidal droplets were observed. Frequencies between 500 and 1100 cps were measured for mean particle diameters between 700 and 200  $\mu$ . Smaller particles vibrated with higher frequencies that could not be measured by the motion-picture technique. These vibrations occurred in the absence of siren pulsation. When siren pulsations were introduced, the larger droplets vibrated with a frequency close to that of the siren. Computation of vibration frequency showed that the measured frequencies corresponded to those of liquid aluminum drops and not to those of hollow spheres. The authors do not regard these vibrations as a major contributor to low-frequency pressure oscillations. They observed, however, that the mass flux of aluminum varied periodically with time at a low frequency, and they regard this effect as a possible source of instability.

The use of metalized propellants has introduced new problems into rocket technology, owing to the growth and presence of condensed-phase combustion products in the nozzle flow. The subjects of condensation<sup>63, 64</sup> and two-phase flow in nozzles<sup>65, 66</sup> have been reviewed recently. Measurements on oxide particles in rocket exhausts<sup>67</sup> showed surprisingly constant mass-average particle sizes of about 2 to 3  $\mu$  over a wide range of conditions.

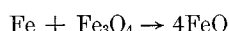
The unusual bipropellant system liquid Li-H<sub>2</sub>O<sub>2</sub> was tested in experimental rocket motors by Hardin and co-workers.<sup>68</sup> Abnormally high performance was obtained and was inter-

puted as an indication of erroneous thermodynamic data. Corrosion of the lithium injection system and of the rocket nozzle presented serious problems.

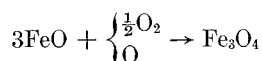
### Reaction Kinetics and Mechanisms of Metal Combustion

There exists at present almost no information on reaction kinetics and mechanisms of metal combustion. In the case of surface burning, the reaction must include adsorption of oxygen on the surface of the molten oxide and transport of oxygen or metal through the oxide layer. Reactions may occur at the oxide-gas and at the oxide-metal interface as well as within the oxide layer. Further complications may arise if the metal and the oxide are mutually soluble, as with Ti and Zr, or if several condensed oxide species participate.

The only cases of surface burning for which reaction mechanisms have been proposed are those of iron and copper. Kirschfeld<sup>46</sup> suggested that the reaction



takes place at the metal-oxide interface. This reaction is followed by diffusion of FeO through the oxide layer and reaction on the surface according to



Analogous reactions involving CuO and Cu<sub>2</sub>O are proposed for copper.<sup>46b</sup>

The hollow-sphere mechanism proposed by several authors, in which molten oxide is blown up by metal vapor like a soap bubble, is very similar in principle to surface burning, with the difference that the liquid-metal/liquid-oxide interface is replaced by a metal-vapor/liquid-oxide interface. One may speculate that this mechanism should be indistinguishable from surface burning, as long as the oxidation reaction takes place within the oxide layer or on one of the interfaces. However, if oxygen can penetrate into the vapor-phase interior of the bubble, a drastic change of mechanism should occur. The sharp fragmentation limit observed by Friedman and Maček,<sup>41</sup> shown in Fig. 4, might indicate the onset of this penetration effect.

In general, our ignorance about reactions during vapor-phase burning of metals is as great as that in the case of surface burning. There is, however, one exception: mechanisms and rates of various reactions between alkali metals and halogens or halogen compounds were determined by the "dilute-diffusion-flame" method developed more than 30 years ago by Polanyi and co-workers.<sup>69, 70</sup>

A first attempt to apply this method to a metal-oxygen system was made recently by Markstein.<sup>71</sup> Diffusion flames of magnesium were obtained at pressures of a few mm Hg by carrying the metal vapor in an argon stream into an atmosphere of oxygen-argon. Photographic photometry was used to measure reaction rates. The data favored a unimolecular rate law, independent of oxygen concentration. Based on an estimated flame temperature of 1000°K, a unimolecular rate constant of  $2.5 \pm 1.2 \times 10^3 \text{ sec}^{-1}$  was determined. The emission spectrum of the flame consisted of continuum radiation with a broad maximum in the blue and narrower maxima in the near ultraviolet and the red. The spectrum of surface luminescence of MgO deposits growing in the flame zone consisted of a continuum in the blue resembling the broad maximum of the flame spectrum.

On the basis of the rate data and the spectroscopic evidence, as well as of thermodynamic arguments, it was concluded that, at the low pressures and temperatures prevailing in these flames, most of the oxidation took place as a heterogeneous reaction on the surface of growing oxide particles. It further was suggested that the reaction, under conditions of excess of oxygen over magnesium vapor, occurred as follows: be-

cause of the oxygen excess, many more oxygen molecules than magnesium atoms collide with the particle surface in unit time. The surface is therefore normally covered by a monatomic layer of oxygen atoms, which react with arriving Mg atoms with high collision efficiency. On the sites where Mg atoms have reacted, a clean oxide surface temporarily is formed which is able to dissociate arriving O<sub>2</sub> molecules, so that the monatomic oxygen layer is continuously re-established. The rate of oxide formation thus will depend only on the collision frequency of Mg atoms with the particle surface, in agreement with the observed unimolecular rate law.

The question naturally arises as to whether the proposed heterogeneous reaction mechanism is of importance only under the special conditions of the low-pressure dilute diffusion flame or whether it may participate also in vapor-phase burning at higher pressures and temperatures. At least from a thermodynamic viewpoint, the heterogeneous reaction path would seem to be favored always over homogeneous formation of oxide vapor, as long as the temperature of the vapor phase stays below the theoretical upper limit given by the boiling point of the oxide. The relative importance of heterogeneous and homogeneous reactions will depend, however, on currently unknown factors, such as the activation energies of the various elementary reaction steps and the total surface area of the oxide particles contained in unit volume.

A simple argument in favor of heterogeneous reaction can be advanced in those cases in which the condensed-phase oxide species does not exist in the vapor phase. This is the case, for instance, with Al<sub>2</sub>O<sub>3</sub>; since Al<sub>2</sub>O<sub>3</sub>(*g*) has not been observed, the formation of condensed oxide must proceed by heterogeneous reaction between vapor-phase species such as Al, AlO, Al<sub>2</sub>O, and O<sub>2</sub> on the oxide surface.

The growth of oxide particles by heterogeneous reaction might remove the difficulty of reconciling the formation of MgAl<sub>2</sub>O<sub>4</sub> in Fassell's work<sup>22</sup> with a vapor-phase mechanism. Application of Coffin and Brokaw's analysis<sup>58</sup> should not be affected by heterogeneous reaction, as long as the rate remains large compared with the transport rates.

### Radiation and Spectra of Metal Flames

Radiation studies have been performed primarily on aluminum and magnesium flames. Wolfhard and Parker<sup>48</sup> compared temperatures measured by line-reversal and ab-



Fig. 14 Photomicrograph obtained as in Fig. 12. Well-developed vapor-phase burning of 100-μ particle<sup>55</sup>

solute-intensity methods with color temperatures. The former methods gave temperatures of about 3000°C for both metals, whereas the color temperatures were 3600°C and above 3900°C, respectively, for aluminum and magnesium. The discrepancies were explained by anomalous absorptivity of the small oxide particles which was found to increase from small values in the visible to unity at about 3000 Å.

Based on values of the oxide boiling points available at the time of their work, the authors concluded that the true flame temperatures were those determined by the line-reversal and the absolute-intensity methods, whereas the color temperature had no physical significance. Comparison with currently accepted values of the oxide boiling points shows, however, that the line-reversal value agrees with the boiling point only in the case of MgO, whereas the boiling point of  $\text{Al}_2\text{O}_3$  is closer to the measured color temperature. A plausible explanation might be that the temperature of the aluminum flame was reduced appreciably below the theoretical maximum by radiation losses.

Further radiation studies on aluminum and magnesium flames are reported in Refs. 49–51. Maximum brightness temperatures of 3260°C for aluminum<sup>49</sup> and of 2620°C for magnesium<sup>50</sup> were measured. These results are more consistent than Wolfhard and Parker's data, since they both lie somewhat below the presently accepted values of the respective oxide boiling points. The color temperature of the Mg flame was 4000°C, in agreement with Wolfhard and Parker's findings.

The flame spectra described in Refs. 49–51 consisted of continuum background due to thermal radiation from condensed oxide particles, and various atomic lines and molecular bands. In the aluminum flame spectrum,<sup>49, 51</sup> all lines as well as the bands of AlO appeared in emission. In the magnesium flame spectrum,<sup>50</sup> the Mg resonance line at 2852 Å was self-reversed; all other atomic lines as well as the molecular bands appeared in emission. These bands have been investigated extensively;<sup>72</sup> the green band is assigned to MgO, whereas the ultraviolet system now is ascribed partly to MgO and partly to MgOH.

The preceding studies were performed with metal-powder flames. A different technique was employed by Rautenberg and Johnson.<sup>73</sup> In order to eliminate the background continuum due to condensed reactants and products, they vaporized aluminum foil in oxygen by means of an electric current pulse and examined the emitted radiation by time-resolved spectroscopy. The observed spectra consisted only of Al and Na lines and AlO bands. Line-reversal measurements, performed with a xenon flash source for background illumination, were interpreted as showing that Al, Na, and AlO were all at the same temperature of about 2000°K.

The authors conclude further that the excitation of AlO was thermal, under the assumption that Al and Na are thermally excited. It is well known, however, that line-reversal temperatures measured in the reaction zones of flames may be abnormally high, owing to chemiluminescence.<sup>74</sup> The interpretation of line-reversal values as true temperatures in Ref. 73 as well as in other studies of metal-flame spectra therefore should be accepted with some reserve.

Rautenberg and Johnson also obtained time-resolved spectra of the radiation of flashbulbs that contained aluminum. The AlO spectrum appeared initially, but at the peak of intensity it disappeared in the continuum background. The latter is interpreted as blackbody radiation by the authors. In contrast to Wolfhard and Parker, they ascribe the difference between brightness and color temperature to nonuniform distribution of emitters, and they identify the color temperature with the true flame temperature. It seems difficult to reconcile these views with the measurements of Wolfhard and Parker which gave direct evidence of the variation of emissivity with wavelength.

Partly in continuation of the work of Rautenberg and

Johnson, a spectroscopic study of metal combustion was carried out by Brzustowski and Glassman.<sup>57</sup> Time-resolved spectra of aluminum and zirconium combustion were obtained by using commercial flashbulbs. The spectrum of magnesium flames was obtained by burning Mg ribbons in a bell jar at various pressures and compositions of the oxidizing atmosphere.

The magnesium flame had the appearance of a vapor-phase diffusion flame. The total radiation intensity, and that of continuum background relative to that of line and band spectra, decreased with decreasing pressure. Molecular bands and atomic lines of the magnesium flame spectrum agreed with the features described in Ref. 50. The most prominent feature of the time-resolved spectrum of aluminum burning in a flashbulb was the continuum. Against this background, the Al resonance doublet appeared initially in emission, reversed at about 5 msec, and changed back to emission at about 16 msec. The AlO bands remained in emission throughout the flash duration but almost disappeared in the continuum background at the emission peak. In the time-resolved spectrum of zirconium flashbulb combustion, atomic lines of Zr and ZrO bands remained in emission against the continuum throughout the flash duration.

The authors conclude from the spectroscopic results and from the nature of combustion products found in the flashbulbs that Mg and Al burned in the vapor phase, whereas Zr burned on the surface. Although this conclusion can be accepted without reserve, the authors' interpretation of the spectra, based on the assumption of thermal excitation of line and band spectra and of blackbody continuum radiation, should be regarded with caution. Thus, from the appearance of lines or bands in emission, it is concluded that the corresponding species are products of evaporation or decomposition of the condensed oxide and are at the highest temperature that exists in the flame zone. It would seem, however, that the temperature of evaporating species never could exceed that of the condensed phase. Appearance in emission of lines and bands in the visible or near-ultraviolet may be explained on the basis of Wolfhard and Parker's results, which indicated particle emissivities appreciably below unity for wavelengths above about 3000 Å.

As a further cause of emission above the continuum background, chemiluminescent excitation should be considered. This possibility was recently investigated by Nazimova and Sokolov,<sup>75</sup> who found, however, that the vibrational structure of the green MgO band spectrum emitted by a magnesium flame corresponded to thermal equilibrium.

As discussed in the section on reaction kinetics, the spectrum of a magnesium-oxygen diffusion flame, strongly diluted with argon and burning at pressures of a few mm Hg, was entirely different from that of magnesium flames at higher pressures.<sup>71</sup>

## Summary and Conclusion

Compared with the present knowledge of combustion of conventional fuels, as yet the burning of metals is understood poorly. Primarily responsible for the current lack of understanding is the formation of condensed-phase products. One consequence of this characteristic of metal flames is the upper limit on flame temperature imposed by the equilibrium between condensed-phase oxide and its vaporization and decomposition products. Lack of reliable thermodynamic data required for equilibrium computations is one cause of difficulties encountered in the field.

The presence of condensed-phase products also implies the predominant participation of heterogeneous reactions. Ignition of metals is thought to be preceded always by slow oxidation that takes place on the metal surface. The ignition temperatures of metals have been linked with their low-temperature oxidation properties. This approach has been

reasonably successful with metals that do not form a protective oxide layer. However, difficulties have been encountered with metals that form protective layers, particularly if metal and oxide are mutually soluble. Further complications arise when the metal is finely subdivided. Ignition properties of metal powders depend strongly on particle concentration, owing to cooperative effects that have not yet been treated analytically.

After ignition, either the burning process may continue to take place on the surface of a usually molten oxide layer covering the metal or the reaction may occur in the surrounding vapor phase. Even in the latter case, heterogeneous reactions on the surface of growing oxide-smoke particles may play a predominant role. Surface burning has been observed to take place, without exception, if the oxide is more volatile than the metal. Vapor-phase burning may occur only if the metal is more volatile than the oxide but may be suppressed by formation of a protective oxide layer or by reduction of flame temperature below the metal boiling point, owing to heat losses. Suppression of vapor-phase burning has been observed primarily with aluminum under certain conditions.

Most of the studies of metal combustion thus far have been of an exploratory and often primarily qualitative nature. Various transport processes have been suggested as rate-limiting steps in metal burning, but the experimental evidence is often inconclusive. Chemical reaction rates usually are regarded as fast compared with transport processes, although there are indications, such as the influence of small amounts of water vapor, that chemical effects may become rate-determining. Knowledge of reaction kinetics and mechanisms is as yet almost totally lacking.

A trend toward careful control of experimental conditions and toward measurement by a greater variety of techniques is discernible in recent works. Among these, spectroscopy undoubtedly will continue to yield very valuable information. The method of flash vaporization combined with absorption spectroscopy<sup>76</sup> should be especially useful for metal-combustion studies. A study using mass spectrometry has been started recently.<sup>77</sup> Work in related fields, such as high-temperature chemistry, evaporation and condensation, surface processes, and transport phenomena, is of utmost importance for improving our understanding of metal combustion.

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