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THE COMBUSTION OF TITANIUM AND ZIRCONIUM

P. L. HARRISON

The combustion of metals is becoming of increasing importance due to their high heats of oxidation. This can result in high temperatures being produced, and in certain cases the energy release may be very rapid. The rate at which combustion spreads depends upon a number of factors.

One of these is the balance between the rate of heat production and the rate at which it can be removed. This factor is largely dependent upon how finely the metal is divided. A greater division of the metal results in both a higher surface to volume ratio, and hence a higher rate of heat production per unit volume, and a lower cooling rate.

If the surface to volume ratio is very large, the conduction of heat from the combustion zone by the metal is very greatly reduced. Heat loss is then by the relatively slow process of radiation, convection and conduction in a gas, and this leads to neighbouring particles of metal reaching the ignition temperature with great rapidity. If the finely divided powder is loosely packed together, the heat loss by convection is largely eliminated and under such conditions of low heat loss, spontaneous ignition of the metal can occur[1,2].

When solid metal rods are used, conduction by the metal rapidly absorbs large quantities of heat from the burning zone, leaving little heat for raising the temperature of the adjacent metal to the ignition point.

Consequently, as with other combustible substances, when in bulk the metal can be made to burn at a controllable and potentially useful rate, whereas, when finely divided, it will burn with explosive violence.

A study of the combustion of metals is therefore relevant at the present time. On the one hand we have the potential usefulness of these substances when burnt under controlled conditions, as high energy, high temperature-producing, fuels for rocket propulsion. On the other hand, however, we have the hazard they present in the finely divided state—a hazard that is of great importance not only for the industries machining these materials but also for the mining industry, where the combustion of metal wear fragments can be important in the accidental ignition of the explosive gas mixture in the mine[3].

An investigation is being made in this laboratory on the more physical aspects of burning as well as on the rates of heat release.

Apart from the diffusion of oxygen to the surface of the metal an important consideration is the heat of combustion of the metal and whether the metal burns in the solid, liquid or vapour.

Table 1 gives the values for melting and boiling points of four metals and their oxides, together with heats of combustion of the metals.

TABLE 1

	Metals			*Oxides*	
	Melting point °C	*Boiling point* °C	*Heat of combustion* kcal/g	*Melting point* °C	*Boiling point* °C
Al	659	1,800	7·2	2,020	
Mg	651	1,110	6·0	2,800	
Ti	1,730	3,200	4·55	TiO_2 d. 1,640 Ti_2O_3 d. 2,130	—
Zr	1,900	3,000–3,600	2·86	2,600–3,000	4,000 ?

Other factors that must be considered are the strength and porosity of the oxide, and how tightly it binds on to the parent metal. The properties of the metals and their oxides that are likely to greatly influence the mode of combustion are the melting or boiling points and the stability of the oxide at high temperatures.

EXPERIMENTAL METHOD

The metals were studied in wire form, wire diameters of 1·0 mm and 0·5 mm being used. These wires were supported at the centre of a cylinder and were ignited at one end by passing a high current pulse through a small coil of 0·5 mm diameter titanium wire that was wrapped around the end of the wire. The pulse, obtained by discharging a bank of condensers through the coil, ignited the coil, and this melted and collapsed on to the wire to be studied, thus igniting it. The resulting combustion was followed either by a continuous recording camera or by a ciné camera.

The apparatus is shown in *Figure 1* and consists essentially of a brass cylinder 9 in. in diameter and 15 in. long, closed at both ends by a brass plate, and having a glass window along its length. One of the end plates has two terminals through it so that the igniting current pulse may be fed in.

This cylinder was sufficiently large to ensure that the percentage of oxygen changed by less than 1 per cent during combustion. Experiments were carried out with both vertical and horizontal wires. The wire was supported horizontally on mica knife-edges, as shown, and the field of view was restricted by the adjustable slit. *Figure 1* shows the horizontal set-up. When the vertical set-up was required, the mica supports and adjustable slit were removed. In the vertical set-up, the wire was supported by clamping at the top and was ignited at the bottom.

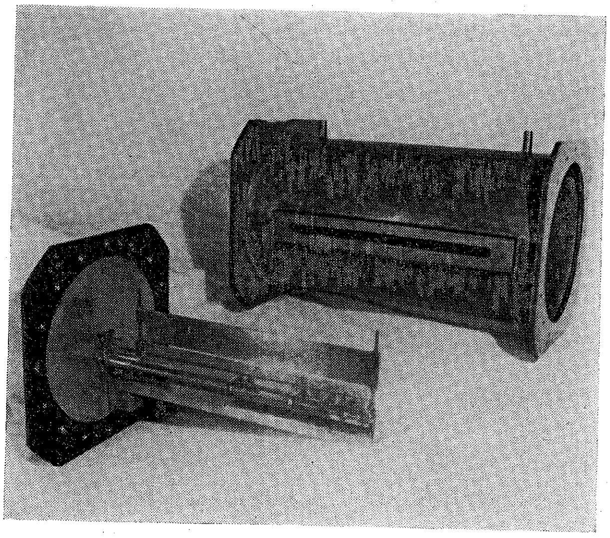

Figure 1

In order to fill the chamber with gas of the desired composition it was evacuated and filled with the correct proportions of air and oxygen. All the experiments were done at atmospheric pressure. The velocity of the burning zone along the wire was obtained from the traces produced with the continuous recording camera.

EXPERIMENTAL RESULTS

In the description of the experimental results, the two metals will be dealt with separately.

Burning of titanium wire

Vertical wire—The variation of burning velocity with oxygen percentage for vertical titanium wires is shown in *Figure 2*. It is seen that this velocity increases rapidly with increasing oxygen percentage. With 1 mm diameter wire there is a critical oxygen percentage (51 per cent) below which no burning takes place. Above this percentage, the velocity rises more and more sharply with increasing oxygen percentage up to the upper limit of 100 per cent.

With 0·5 mm diameter titanium wire however this is not the case. First there is no definite cut-off at low percentages. At 40 per cent the combustion often dies out part way along the wire, thus making measurement of velocities difficult. This also occurs above 85 per cent, a fact which will be discussed later. Secondly, the rate of rise of velocity with oxygen percentage shows a marked drop at about 85 per cent.

Figure 2 also shows how the ratio of the velocities for the two wire diameters varies with oxygen percentage. This shows up the marked change of velocity for the thinner wire at 85 per cent.

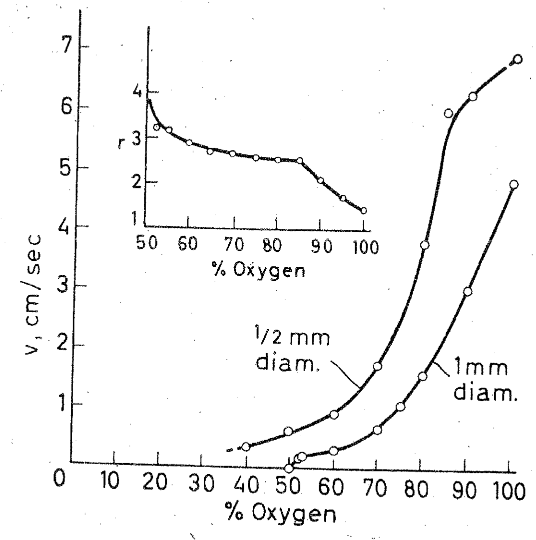

Figure 2

A typical photographic record is shown in *Figure 3*. It is seen that the burning appears to progress discontinuously along the wire, and that hot material falls from the burning zone at regular intervals along the wire. This was more clearly seen by studying the combustion with a ciné camera.

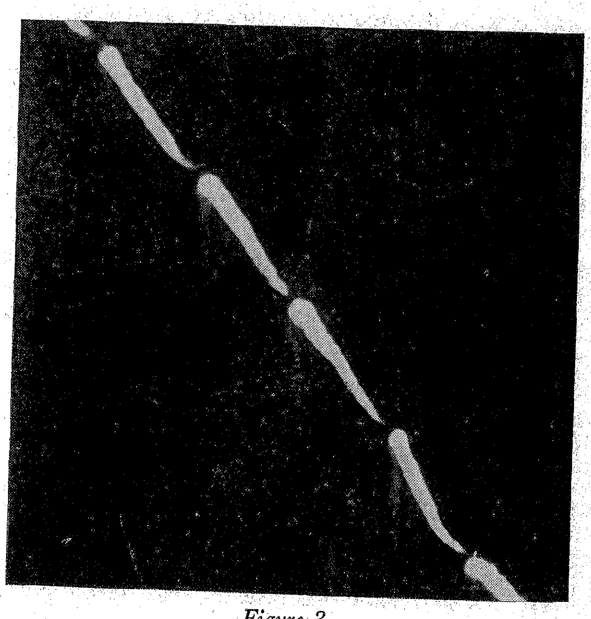

Figure 3

Figure 4 is a sequence from such a study. It is seen that the burning is associated with a molten globule hanging from the end of the wire. It is this globule that is drawn up in a discontinuous fashion thus producing the jumps in the combustion record. The globule remains stationary in space while the burning front moves along the wire. After this has moved a certain distance, the globule suddenly springs up into a new stationary position and the cycle is repeated. Since the globule is constantly increasing in weight there comes a time when it falls off because it has become too heavy to be kept on the wire by surface tension. Since the wire is uniform in diameter and density, and the combustion is in a steady state we would expect such occurrences to be regularly spaced along the wire. *Figure 3* shows that these globules do drop off very regularly.

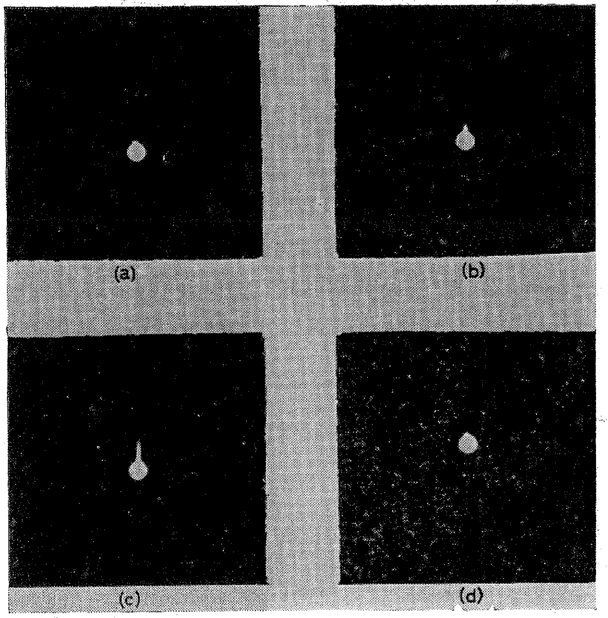

Figure 4

If this falling of the globule is determined almost entirely by surface tension effects it could be expected that the maximum weight of the droplet would be directly proportional to the diameter of the wire used, and therefore that the distance along the wire between two falls would be inversely proportional to the diameter. The experimental value for the ratio of this distance for the thinner wire to that for the thicker wire equals 2 to within a few per cent, and suggests that surface tension is playing an important part in the combustion.

In the records obtained when the thinner wire is burnt in oxygen percentages in excess of 85, all regularity has gone both in the movement of the globule along the wire and in the rate at which successive globules fall away. In these cases the average rate of falling is very much greater than that for wire of the same diameter at lower percentages.

Horizontal wire—Experiments with horizontal titanium wires of 1·0 mm diameter gave variations of velocity of propagation with percentages that were very similar to those obtained with vertical wires of the same diameter.

The records obtained have precisely the same discontinuous nature, and the studies using the ciné camera with horizontal wires have shown exactly the same globule formation and movement. The mica supports had no effect upon the velocity of burning below 80 per cent oxygen. Above this, each support gave rise to a slight reduction of the velocity. The points for the high percentages were therefore obtained from the records produced by the half of the wire that projected beyond the first support (see *Figure 1*).

Combustion of zirconium

High oxygen percentages—*Figure 5* shows the variation of burning velocity with oxygen percentage for vertical wires of zirconium of 0·5 mm diameter. It is seen that the general trend of this variation is the same as for titanium. A mixture containing 35 per cent oxygen does not represent the lowest limit of combustion. Failure of the ignition wire to burn has not allowed the effect of still lower percentages to be studied.

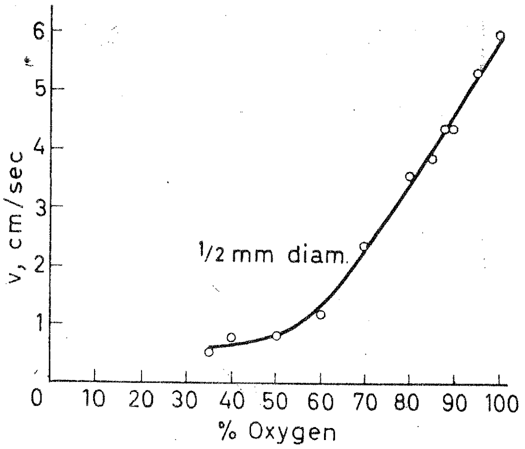

Figure 5

The mode of burning for the higher percentages is the same as for titanium, namely, the combustion is associated with a molten globule that hangs from the end of the wire. The movement of this globule along the wire is similar to the movement of the globule along the titanium wire.

Low oxygen percentages—At oxygen percentages of 50 or lower the mode of burning is different. The temperature reached is not high enough to melt the bulk of the oxide formed and this therefore forms a solid sheath over the metal, preventing the formation of a globule. It also hinders the oxygen reaching the surface of the metal, and consequently the combustion of any section of the wire is extinguished before combustion has reached completion. *Figure 6* shows the cross-section of the wire after combustion. The resultant wire is extremely brittle and breaks at the slightest jolt. The oxide layer is comparatively thin; of the order of 0·1 mm for 50 per cent and less for the lower percentages. The cavity at the centre is due to shrinkage of the metal on cooling. The metal is obviously very highly stressed during the cooling and solidification and this undoubtedly explains the resulting brittleness.

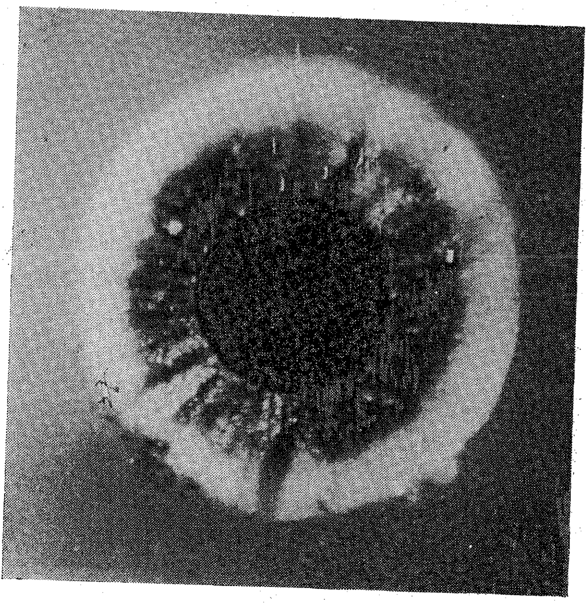

Figure 6

A further characteristic of this mode of burning is the splitting open of the oxide layer near the end of combustion. This is due to the solidification of the metal.

Experiments with aluminium wires show the cause of the effect. Currents sufficient to melt the aluminium were passed through these wires, the thin tough oxide formed containing the molten metal in the wire form. When the current was switched off, the wire rapidly cooled, and bulges suddenly appeared in the wire, some of them being of sufficient size to split the oxide film open. It was discovered that between these bulges the oxide skin had buckled and collapsed, there being little metal at these points. This was the result of the high surface tension of the molten metal, at temperatures only a little above the melting point, causing the metal to form droplets beneath the oxide skin. The metal bunched itself together at various points along the wire immediately prior to solidifying, and where this was of sufficient magnitude the oxide skin was stretched to breaking point.

With the zirconium wires, the nature of the oxide is such that it stretches very little before it splits, so that there is very little variation of overall diameter of the resulting wire, but the oxide is split open at places along its length. At oxygen percentages only a little below 50 this bursting open is fairly violent and produces a shower of white-hot sparks. At the low percentages however very few sparks are formed and the metal that bursts through forms a collection of small globules in the split. One or two of these globules were found to consist entirely of a very thin hollow shell of oxide.

It should be noted that the division between the mode of burning at the low oxygen percentages and the globule mode in the high percentages is not a sharp one. There is an intermediate zone of percentages where the point of the burning zone travels some distance ahead of the globule. The part of the burning wire that is ahead of the globule commences to form a second globule before the first falls away.

Combustion of metals in bulk

A small furnace was constructed by tying two fire-clay boats together with thick copper wire. This was held horizontal and packed with short lengths of metal wire. A length of 0·5 mm zirconium wire along the centre acted as an ignition wire. A stream of oxygen was passed through the furnace and a high current pulse was switched through the zirconium ignition wire.

With titanium the metal burnt completely. The product of the combustion was a brittle porous bluish-black mass which had a yellow-white coating on the surface. Occasionally intense colours, deep mauves, blues and golden yellows, were formed within this mass. It is not certain whether these were due to lesser oxides of titanium or contamination from the fire-clay troughs. Large quantities of the yellow-white oxide were found deposited at the exhaust end of the furnace which was cooler than the rest.

With zirconium, the oxide formed in the first stages of combustion coated the unburnt metal and extinguished the combustion before much metal had burnt.

Estimate of the temperature

A preliminary investigation of the temperatures reached in metal combustion processes was made in the case of titanium, using this furnace method. A small coil of gold wire was placed in the bottom of the furnace near the oxygen inlet end, and the titanium wire packed in on top of it. The metal was ignited, and when the combustion was complete the furnace was broken open. None of the gold was found in the original position, but most of it was found deposited at the exhaust end of the furnace, and on the asbestos shield placed nearby, as the grey-violet coloured aurous oxide. The inference is that the gold all boiled away and that the vapour was swept to the exhaust end of the furnace. The boiling point of gold is 2,950°C, and the temperature produced during the combustion must therefore be greater than this.

When a small coil of platinum was placed in a similar place in another furnace, the platinum was found as a spherical lump in the original place. The metal had obviously melted (m.p. 1,769°C)[4] but the temperature had not been above the boiling point of platinum. The boiling point temperature of platinum is in doubt, but it is probable that it is as low as 3,500°C, and so this may be taken as the upper limit of the temperature that can be assigned to the combustion of titanium. These are obviously crude methods of estimating temperatures, and spectroscopic and other methods are being considered.

DISCUSSION

The results of this study show that the combustion of titanium and zirconium takes place at the surface of the molten metal. There is no evidence of substantial vaporization of the metal. The combustion appears confined entirely to the surface of the burning mass and there is no appreciable formation of smoke as there is during the burning of magnesium, which vaporizes prior to burning[5].

Other factors which are shown to be important are the fusibility of the metal oxide and the balance between rate of heat production by oxidation, and rate of heat loss. In metals such as zirconium, where the melting point of the oxide is high, these two factors may interact, so that a slight increase in heat loss over heat production can completely change the mode of combustion. This was found to occur with zirconium wire 0·5 mm in diameter at about 50 per cent oxygen.

Wolfhard and Parker[6] have made measurements of the temperature of oxy-magnesium-powder flames and obtained a value of about 3,000°C. The experiments in this study carried out with the use of gold and platinum wire show that the temperature obtained with burning titanium was of this order. The absence of any appreciable vaporization of the titanium metal shows that the temperature reached in these experiments, during combustion, was below the boiling point of the metal. The majority of references give this as about 3,200°C and this may therefore be taken as the upper limit to the temperature reached. The experiments with zirconium suggest that for conditions that produce a low rate of burning, the temperature is a little lower than the melting point of the oxide which is between 2,600 and 3,000°C. Hence, again, the temperature is of the same order as that found for magnesium by Wolfhard and Parker.

A detailed analytical study of the combustion process is not yet possible, but the following simplified study gives some idea of the results that can be obtained.

We assume that the combustion travels through the wire as a definite flame front with velocity v, and that there is no production of heat ahead of this flame front. A second assumption is that no heat is lost from the surface of the wire ahead of the flame front.

With the x axis along the wire, the heat equation for the wire ahead of the flame front is:

$$k\frac{\partial^2\theta}{\partial x^2} + \rho s v\frac{\partial\theta}{\partial x} = 0$$

where θ is the temperature, k is the thermal conductivity, ρ is the density and s is the specific heat.

The solution of this is

$$(\theta - \theta_a) = (\theta_f - \theta_a)e^{(\rho s v/k)(vt-x)} \qquad (x \geqslant vt)$$

where θ_f is the temperature of the flame front and θ_a is the ambient temperature.

This gives the temperature gradient at the flame front ($x = vt$) as

$$\frac{\partial\theta}{\partial x} = -(\theta_f - \theta_a)\frac{\rho s v}{k}$$

If H is the total heat flowing across the flame front

$$H = -kA\left(\frac{\partial\theta}{\partial x}\right)_{x=vt}$$

which gives an expression for v

$$v = H/A\rho s(\theta_f - \theta_a)$$

where A is the cross-sectional area of the wire.

This analysis is, of course, a very simplified one. In practice there is no definite 'flame' front. Also the burning takes place on the surface only and hence there is conduction into the centre of the wire as well as along it. However, for the globule mode of combustion these differences may not be serious, and this study does give at least qualitative agreement with experimental results.

The temperature gradient at the flame point is given by $\partial\theta/\partial x = -(\theta_f - \theta_a)\rho s v/k$ and is therefore steeper for the higher velocities of propagation. A study of the wire, after combustion had ceased, suggested that this was definitely so. If the combustion is extinguished, conditions are frozen, and the solidified globule is left attached to the unburnt wire. This unburnt wire has an oxide layer of decreasing thickness along the short section of its length immediately adjacent to the globule. The extent, and variation of thickness with distance from the globule, of this oxide film gives some indication of the temperature gradient occurring at the moment combustion ceased.

At the lower oxygen percentages, corresponding to low velocities, the oxide extends along the wire for a few millimetres. At the high percentages, especially above 85 per cent with 0·5 mm diameter titanium wire, when the highest recorded velocities are obtained, the extent of the oxide is less than 1 mm.

This may provide an explanation of the difficulty experienced in the combustion of 0·5 mm diameter titanium wire at percentages of oxygen greater than 85 per cent. When a globule falls from the end of the wire, the thermal gradient is so steep that only a very little of the metal left is above the ignition temperature. If this portion of the wire is small enough, heat will be conducted away quicker than it is produced and the combustion will die out.

The expression for v makes possible a calculation of the ratio of velocity for two wires of the same material but differing diameter, assuming that $\rho . s$ and $(\theta_f - \theta_a)$ are the same in both cases. With the titanium wire it has been shown that the weight and hence the volume of the globule is proportional to the diameter of the wire. If we assume that the rate of heat production is proportional to the surface area of the globule we have $H \propto a^{2/3}$ and hence $H/A \propto a^{-4/3}$ where a is the radius of the wire. For the two titanium wires used we have $a_1/a_2 = 2$ and this leads to a value for v_2/v_1 of 2·52. Considering the simplified form of the calculations this is in good agreement with the experimentally observed values shown in *Figure 2* in the range 85 to 65 per cent oxygen.

The sudden fall in the ratio of velocities for the two titanium wires at oxygen percentages above 85 can be explained by an increase in the combustion temperature for the thinner wire at these high percentages, since $v \propto 1/(\theta_f - \theta_a)$. Such an increase in temperature explains the much more frequent falls of the globules observed with the thinner wire at these percentages. A higher temperature means a lower surface tension and thus a lower maximum possible weight for the hanging globules. The distance travelled by a globule along the wire before it falls off would therefore be smaller.

This paper has given only a preliminary account of the work now being done on the combustion of titanium and zirconium. Investigations are being extended to other metals, especially those that have oxides with appreciably different properties. A study of the part played by the diffusion of oxygen to the surface and the temperatures obtained is also being undertaken.

I would like to express my thanks to Dr. F. P. Bowden for his interest in this work, and my gratitude to Dr. A. D. Yoffe for his advice and encouragement. I also wish to thank the Safety in Mines Research Board for a grant.

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DISCUSSION

H. P. Broida (*Washington, D.C.*) opening the discussion said: A 'Special Fuels' session sounds as if it would be concerned only with new types of fuels that are, or might be, available for aircraft or rocket use. However, the papers under consideration fit two general categories. First of all there are those papers which are of importance in fundamental questions of combustion—the papers of Gerstein and of Berl *et al.* To some extent the investigation of the burning of titanium and of zirconium by Harrison also belongs to this category.

The others are concerned more directly with practical applications. Olson *et al.* have presented important information in their paper. Marsel and Kramer have shown a practical ignition device for combustion chamber use. The papers discussing diborane flames and on the combustion of titanium and zirconium are also of practical interest but not necessarily of immediate importance.

In reading the paper of Gerstein, I was struck by the implications of his concluding remarks in which he says (on p. 905) that 'Unlike hydrocarbon–air flames, large differences in flame velocity are found for flames of similar flame temperature and identical products of combustion. Since chemical factors appear to have a more pronounced effect on the flame properties of the alkylsilanes than on hydrocarbons, it seems likely that these fuels may prove useful in establishing relationships between chemical structure and flame properties.' In view of such a promising conclusion, I should like to ask Gerstein why it is that so little effort has so far been put into this type of study, considering that some work of this sort started at least as early as 1951?

Berl's paper brings up a similar question. Why are there not more reports at this Symposium of investigations on the combustion of the boron compounds? However, this question ought rightly to be directed to the audience at large, and in fact, might more appropriately be rephrased: Why does this Symposium on combustion put such a large effort into the oxidation of carbon-containing fuels?

In addition to these general questions, I should like to ask Harrison if he would elaborate on a remark in the conclusion of his paper in which he states 'that the combustion of titanium and zirconium takes place at the surface of the molten metal'. Does he consider this to be a gas phase or liquid phase reaction?

One further point of inquiry for Marsel. The possibilities appear great for the use of metal alkyls for combustion chamber ignition. What are some of the difficulties and problems connected with their use?

C. F. Marsel (*New York*), replying to the question 'What are some of the difficulties and problems connected with their use?', asked by Broida in opening the discussion, said: I would like to broaden the context of the question to include the use of the material for the main fuel as well as for auxiliary ignition purposes. This is because the self-igniting properties of the fuels make them of considerable interest for certain practical propulsion systems.

The problems may be subdivided as follows:

Handling—This is not difficult when one becomes accustomed to their special properties: they must be stored under a protective atmosphere of nitrogen; ordinary carbon steel can be used for the construction of containers; organic materials are readily attached, but plastics of the Teflon family are satisfactory.

Thermal stability—This is a more serious problem than with hydrocarbons. There can be considerable pressure build-up in a closed system with storage at elevated temperatures. When subjected to very high heat fluxes, as in regenerative cooling, solid build-up can occur. We are at present studying this problem intensively.

Danger to personnel—Some objections have been raised to the use of these materials for manned vehicles. It is our feeling that this would not be a major problem given the proper type of storage tanks. Naturally this problem would not occur with unmanned missiles.

W. G. Parker (*Birmingham*): Is it feasible to design an aircraft combustor to consume either a hydrocarbon or a boron-type fuel?

W. T. Olson (*Cleveland*): Design features aimed at minimizing boron oxide deposits, such as eliminating or reducing the re-circulation zone in high-speed combustors, for example, would limit the combustor operation on hydrocarbons to low altitude. Such compromises are, however, perfectly feasible.

S. T. Griffiths (*Bletchley*): Broida has suggested further work on alkyl silanes, and this prompts me to draw attention to some work carried out by Wilson and myself which has direct bearing on Gerstein's paper. We have determined the spontaneous ignition temperatures of a number of silanes with alkyl groups ranging from ethyl to *n*-amyl, representing the types, R_4Si, R_2SiH, R_2SiH_2 and $RSiH_3$.

The influence of Si-H bonds upon the ease of ignition depends markedly on the length of the alkyl chain; e.g. the effect of Si-H bonding is pronounced in the ethyl series (which accords with Gerstein's findings for the methyl series), whilst with the *n*-amyl series, the influence of Si-H bonding is offset by the ease of oxidation of the alkyl side chain.

I would agree with Gerstein that combustion studies employing alkyl silanes offer an alternative route to methods employing tagged carbon and deuterium atoms used for investigating hydrocarbon/oxidation mechanisms. As an example I would cite results that we have obtained employing isomeric alkyl silanes containing 6 carbon atoms. These results clearly show that the ease of ignition depends markedly upon the position of the silicon atom in the chain. The more symmetrical the molecule is about the silicon atom the greater is the molecule's resistance to oxidation.

A full report of this work appears in *Combustion and Flame* 2 (1958) 244.

P. L. Harrison (*Cambridge*): In reply to Broida's question, I would first like to draw his attention to work carried out on the combustion of magnesium by K. P. Coffin, and reported by him in the *Fourth* (*International*) *Symposium on Combustion*. Coffin concluded from his experimental observations that the magnesium burns in the vapour phase above the surface of the metal, a conclusion that I entirely agree with. A very obvious characteristic of burning magnesium is the formation of large quantities of oxide smoke, and this is undoubtedly due to the formation of the oxide being from the vapour phase reaction between the metal and the oxygen in the atmosphere.

In none of my experiments with titanium and zirconium was there any appreciable formation of oxide smoke. I conclude from this, and from the fact that the photographic images of the burning material are so sharp, that these metals burn in the liquid phase in my experiments