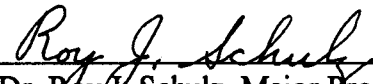


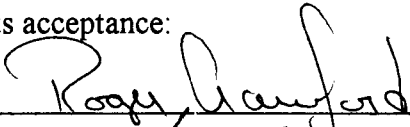
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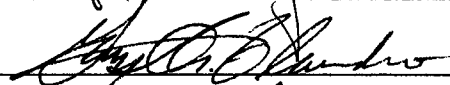
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Dr. Roy J. Schulz, Major Professor

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THE FORMATION OF CARBON IN A
MAGNESIUM/ETHYLENE/OXYGEN FLAME

A Thesis
Presented for the
Master of Science Degree
The University of Tennessee, Knoxville

Robert S. Hiers III
August 1993

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ABSTRACT

Carbon dioxide breathing propulsion systems have been proposed for magnesium fueled ramjet engines operating in the Martian atmosphere. The formation of solid carbon in the exhaust of such a system is of interest because of the effects of solid carbon on performance and operating characteristics as well as radiative heat transfer from the exhaust gases. Previous investigators are in disagreement over the formation of carbon in magnesium/carbon dioxide combustion. In the current investigation magnesium ribbon was burned in the exhaust of a fuel-rich ethylene/oxygen rocket motor. The UV spectra obtained during this oxygen-poor combustion confirmed that the magnesium was oxidized to form MgO. Sufficient quantities of soot were formed to coat the test apparatus. X-ray dispersive microscopic examination indicated the presence of micron-size magnesium oxide spheres coated with solid carbon. The formation of soot is shown to be consistent with equilibrium chemistry calculations which take into account the stoichiometry of the mixing region which forms over the magnesium surface. Equilibrium calculations for a typical aluminized solid propellant formulation are also presented. These calculations show that the equilibrium behavior of aluminum is expected to be very similar to magnesium. The disagreements between previous investigators are resolved through the experimental and theoretical results of the current study.

TABLE OF CONTENTS

CHAPTER	PAGE
1. INTRODUCTION.....	1
2. APPARATUS	4
3. EXPERIMENTAL PROCEDURE	6
4. ANALYSIS.....	9
5. ALUMINUM CALCULATIONS.....	18
6. CONCLUSIONS.....	22
LIST OF REFERENCES	24
APPENDIX.....	27
VITA	64

LIST OF TABLES

TABLE		PAGE
I.	Equilibrium Rocket Chamber Conditions.....	4
II.	Equilibrium Stagnation Region Conditions	6
III.	Global Magnesium Reduction Reactions Ranked by Exothermicity	9
IV.	Global Magnesium Reduction Reactions Ranked in Order of Occurrence	13
V.	Global Aluminum Reduction Reactions Ranked by Exothermicity.....	18
VI.	Global Aluminum Reduction Reactions Ranked in Order of Occurrence	20

LIST OF FIGURES

FIGURE	PAGE
1. Performance of Magnesium Slurry Ramjet.....	28
2. Copper Sample Holder with Magnesium; PreFire	29
3. Experiment Schematic.....	31
4. Chamber Pressure Trace.....	32
5. Video Frames of Sample Holder	
(a) At Motor Ignition	33
(b) At Magnesium Melt-Point.....	35
(c) At Magnesium Ignition	37
(d) At Motor Shutdown	39
6. Experimental Spectrum at $t + .5$ sec.	41
7. MgO 4970 Å Feature Radiance Trace.....	42
8. Copper Sample Holder with Magnesium; PostFire.....	43
9. Closeup PostFire Photograph of Sample Holder with Magnesium.....	45
10. SEM Photomicrograph of Deposition on Sample Holder.	47
11. Control Copper Sample Holder; PreFire.....	49
12. Control Copper Sample Holder; PostFire	51
13. Stagnation Region Mixing Layer Schematic	53
14. Mixing Layer Equilibrium Chemistry; Mass Fractions	54
15. Mixing Layer Temperature.....	55
16. Mixing Layer Equilibrium Chemistry; Adjusted Mass Fractions	56
17. Heats of Reaction for Magnesium Reduction Reactions.....	57
18. Gibbs Free Energy of Reaction for Magnesium Reduction Reactions	58

19.	Aluminum, Mixing Layer Equilibrium Chemistry, Mass Fractions	59
20.	Aluminum, Mixing Layer Temperature	60
21.	Aluminum, Mixing Layer Equilibrium Chemistry, Adjusted Mass Fractions ..	61
22.	Heats of Reaction for Aluminum Reduction Reactions.....	62
23.	Gibbs Free Energy of Reaction for Aluminum Reduction Reactions.....	63

CHAPTER 1

INTRODUCTION

Carbon dioxide breathing propulsion systems have been proposed for magnesium fueled ramjet engines operating in the Martian atmosphere (Ref. 1). Previous investigators are in disagreement over the formation of carbon in magnesium/carbon dioxide combustion. The sooting characteristics of any fuel/oxidizer combination are always of interest to system designers, since they impact material selection as well as indicate performance characteristics and can have a major effect on radiative heat transfer from the exhaust. The burning characteristics of metallic fuels are also of interest in solid propellant rocket combustion, slurry-fueled ramjets, and ducted rocket combustion.

Magnesium was considered as a high energy additive to standard ramjet fuel (JP-3) for terrestrial applications (Ref. 2). An experimental investigation showed substantial performance gains when magnesium was added to the fuel. Figure 1 (reproduced from Ref. 2) (for Figures see Appendix) shows a schematic of the magnesium slurry fueled ramjet as well as various performance curves. The design of the Martian ramjet will be similar to that indicated in Figure 1. A mix of magnesium powder and a carrier gas or liquid will be injected into the high pressure region of the combustor. The magnesium powder will then react with the high pressure high temperature CO₂ generated through ram compression. The current design concepts (Ref. 1) have not proceeded far enough to settle whether a gaseous or liquid carrier will be preferred. In the current analysis, any thermochemical effects of the carrier medium are ignored.

The heterogeneous combustion of magnesium in atmospheres other than air or oxygen has been previously investigated in several studies. Mellor and Glassman (Ref. 3)

investigated vapor-phase diffusion flames utilizing an electrically-heated magnesium wire in low pressure mixtures of carbon dioxide-oxygen, carbon dioxide-argon, and oxygen-argon. In their experiment, the flame would not ignite in the carbon dioxide-argon mixture. In the carbon dioxide-oxygen mixture, an ignition flash was observed but combustion was not sustainable. Carbon particles were observed in the remaining ash.

They comment:

Since successful combustion was obtained if the carbon dioxide was replaced with argon with all other experimental conditions held the same, it can be concluded that the presence of carbon dioxide, and not the apparatus, is the cause of the impossibility of ignition. If indeed magnesium carbide, in addition to the oxide, forms on the surface of the ribbon ... (this) may prevent any gas-phase reaction from occurring.

Yuasa and Isoda (Ref. 4) investigated the combustion of thin magnesium foils in a low speed carbon dioxide stream utilizing a resistively-heated furnace.

They comment:

It should be noted that, for all the metals, the reactions with carbon dioxide mainly produce carbon monoxide and their condensed metal oxides, and that no carbon deposition in magnesium and aluminum flames occurs because appreciable amounts of free oxygen are present at equilibrium" (emphasis added).

Shafirovich and Goldshleger (Ref. 5) burned millimeter size magnesium spheres in a heated bomb filled with carbon dioxide. Although their main interest was in the superheating of the burning droplet, they did report:

A condensed deposit of a complicated structure formed during combustion. The deposit consisted of two shells with a porous substance between them. The inner shell, black in color, was stronger and contained carbon as well as magnesia. Its size was close to the initial size of the sample. The outer white part of the deposit consisted of magnesia only.

These authors are in seeming disagreement concerning the formation of carbon in the combustion of magnesium in carbon dioxide. The intent of the current investigation is

to reconcile the seemingly contradictory reports of carbon formation by the previous investigators. This is accomplished through a new experiment as well as equilibrium calculations that consider the stoichiometry of the flame front that forms over the magnesium surface.

CHAPTER 2

APPARATUS

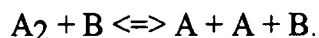
The current study utilizes a small gaseous fueled rocket engine exhausting into a steam-ejector pumped vacuum cell to provide a high enthalpy flow over a magnesium sample. The rocket engine is approximately 6 inches in overall length, operates at 100 psia chamber pressure, and expands to an area ratio of 28.7 with an exit diameter of 1.75 inches. The rocket exhausts into a 3 foot diameter by 4 foot long vacuum cell pumped by a six stage steam ejector. The cell is equipped with optical access ports for viewing with spectrometers and cameras. For this study, the rocket was fueled by gaseous ethylene/oxygen at the slightly fuel rich equivalence ratio of 1.2. The equilibrium chamber conditions obtained from the NASA equilibrium code (Ref. 6) are tabulated in Table I.

TABLE I
EQUILIBRIUM ROCKET CHAMBER CONDITIONS

		Mass Fractions							
P _{psia}	T,K	[CO ₂]	[CO]	[H ₂ O]	[H ₂]	[H]	[OH]	[O ₂]	[O]
100.0	3725.	0.197	0.479	0.086	0.004	0.004	0.069	0.102	0.059

All compositions are expressed as mass fractions. This will simplify the analysis of the theoretical results presented later in the paper. Mass fractions are the most convenient expression of composition whenever chemical change is at issue. Consider a reaction such

as



The mole fraction of species B changes from 0.5 on the left hand side of the reaction to 0.33 on the right hand side, even though species B remains chemically inert throughout the reaction. However, the mass fraction of species B remains unchanged and identical on both sides of the reaction. Therefore, expressing concentrations in mass fractions is preferred to mole fractions when one wishes to draw conclusions about chemical changes. Mole fractions may be the preferred expression of composition in other situations.

A sample holder was machined to hold magnesium ribbon in the rocket engine exhaust. The sample holder consisted of a 1.75 inch diameter oxygen-free copper rod with a 1.5 inch diameter well 0.75 inches deep bored in one end. Two feet of 0.1 inch wide magnesium ribbon was wrapped in a 1 inch diameter coil and clamped into the well. A photograph of the sample holder is shown in Figure 2. The long spike beneath the magnesium ribbon is a section of magnesium welding rod.

CHAPTER 3

EXPERIMENTAL PROCEDURE

The sample holder was positioned 11 inches downstream of the rocket nozzle exit plane concentric with the nozzle centerline. Upon firing the engine, the magnesium sample was immersed in the stagnation region of a high velocity, high enthalpy flow. A sketch of the experimental configuration is shown in Figure 3. The equilibrium stagnation conditions for this region are tabulated in Table II. The stagnation region on the sample holder forms behind a normal shock in the supersonic exhaust flow. This means that the stagnation pressure on the sample holder will be equal to the free stream pitot pressure. Note the low equilibrium oxygen content in comparison with CO and CO₂. The free stream pitot pressure had been previously measured at this point as 1.0 psia. The engine fired for approximately 10 seconds. A chamber pressure trace is shown in Figure 4. The ratio of pitot pressure to chamber pressure indicates a free stream Mach number of approximately 10 at the sample holder.

TABLE II
EQUILIBRIUM STAGNATION REGION CONDITIONS

		Mass Fractions							
P _{psia}	T,K	[CO ₂]	[CO]	[H ₂ O]	[H ₂]	[H]	[OH]	[O ₂]	[O]
1.0	2985.	0.178	0.491	0.069	0.005	0.006	0.057	0.111	0.083

The combustion process was observed by a standard video camera operating at 30 frames per second. The sequence of frames shown in Figure 5 shows the combustion process including ignition of the rocket engine, melting of the magnesium ribbon, ignition of the ribbon, and finally shutdown of the engine. The stagnation region was also observed by an ultraviolet spectrometer. The formation of magnesium oxide was confirmed by the observation of prominent MgO green system bands in the neighborhood of 4900 Angstroms (Ref. 7). The experimental spectrum obtained at approximately 5 sec. after ignition is shown in Figure 6. The transitions of other constituents of the flow are also identified on this figure. A time history of the intensity of the 4970 Angstrom MgO feature is plotted in Figure 7. The trend clearly indicates that the formation of MgO lags behind the ignition of the engine by approximately 2 seconds. This is equivalent to the time required for the magnesium to melt (as observed on the video) and for the heterogeneous combustion process to begin.

After engine shut-down, in situ photographs were taken of the sample holder. Figure 8 shows a photograph of the sample holder in the test cell. Note the extremely heavy black coating visible on the leading edge of the sample holder as well as throughout the well. Figure 9 provides a close-up view of the sample holder. Samples of the black deposit were analyzed by wavelength dispersive x-ray spectrometry (Ref. 8) and found to contain mostly micron-sized spheres of magnesium oxide coated with 5-10% solid carbon. A scanning electron photomicrograph of the coating indicating both the small MgO spheres as well as a large (approximately 20 micron diameter) magnesium sphere is shown in Figure 10.

A control experiment was run to investigate the possibility that the solid carbon accreted on the sample holder was merely carbon condensing out of the rocket exhaust plume onto the cold copper surface. Another sample holder was machined out of the same oxygen-free copper stock used for the original sample holder. This new bare sample

holder was then installed in the vacuum cell in the same position as the original sample holder without the magnesium ribbon. The rocket engine was then fired at the same equivalence ratio and chamber pressure, and for the same duration as the original experiment. Figures 11 and 12 show pre- and post-test photographs of the control sample holder. Note the complete absence of carbon deposition on the leading edge of the sample holder. This region was coated with copious quantities of carbon in the original experiment. The sample well, however, is seen to be lightly coated with a soft black sticky substance. This deposition is of a completely different character than the hard coating formed in the original experiment which could only be removed with difficulty. This new black substance is theorized to be fuel fragments condensing on the cool copper surface. No chemical analysis of this deposit was performed. It is expected that a higher temperature boundary condition, achievable with a simple change of the sample holder material from copper to stainless steel, would prevent this incidental condensation. The lower thermal conductivity of stainless steel should keep the surface temperature sufficiently high to prevent the incidental condensation of fuel fragments. Regardless, comparing Figures 11 and 12 with the photographs of the magnesium sample holder (Figs. 2 and 8) it is obvious that the bulk of the carbon formation on the leading edge was due to the presence of the magnesium, since that was the only variable in the experiment. Therefore, the control experiment was partly successful in ruling out the possibility of free carbon condensation as the major cause of carbon deposition in the original experiment.

CHAPTER 4

ANALYSIS

The data acquired during the test indicate that magnesium combustion occurred. The appearance of the MgO bands and the microscopic carbon-coated MgO particles are evidence of the oxidation of magnesium. The carbon deposited on the sample holder indicates that some of the oxygen for this oxidation came from the reduction of either CO₂ or CO to solid carbon (C(s)). Some overall reactions with magnesium in the ethylene/oxygen exhaust and their heats of reaction (Q) at standard conditions are tabulated in Table III (in order of decreasing exothermicity).

Table III

GLOBAL MAGNESIUM REDUCTION REACTIONS RANKED BY EXOTHERMICITY

	Reaction	Q (per mole Mg)
1)	$\text{Mg} + .5\text{O}_2 \Rightarrow \text{MgO(s)}$	-143.7 kcal
2)	$\text{Mg} + \text{CO} \Rightarrow \text{MgO(s)} + \text{C(s)}$	-117.3 kcal
3)	$\text{Mg} + .5\text{CO}_2 \Rightarrow \text{MgO(s)} + .5\text{C(s)}$	-96.7 kcal
4)	$\text{Mg} + \text{H}_2\text{O} \Rightarrow \text{MgO(s)} + \text{H}_2$	-85.9 kcal
5)	$\text{Mg} + \text{CO}_2 \Rightarrow \text{MgO(s)} + \text{CO}$	-76.1 kcal

These enthalpies are based on the heats of formation of Reference 9. Note that the

reactions leading to solid carbon are the most exothermic. Therefore, according to the rule of thumb that states that more exothermic reactions are more likely to occur, thermodynamics (Refs. 3, 10) favors the overall reaction which reduces CO_2 to solid carbon rather than to CO. The overall reaction which reduces CO to solid carbon is even more energetic. Accordingly, Mellor and Glassman propose that CO_2 is more likely to be reduced to soot than to CO.

Mellor and Glassman attributed the failure of magnesium to achieve steady combustion in CO_2 to the formation of an inhibiting carbide layer. However, in the current experiment, the velocity behind the bow shock is high enough to sweep the sample well clear at a high rate. If (as indicated by Ref. 3) a magnesium carbide coating forms over the molten magnesium surface, the aerodynamic forces in the stagnation region will continually remove it, exposing a new magnesium surface. Unfortunately, at this time, standard flame spectra references (Refs. 7, 11) make no mention of magnesium carbide spectra measurements, nor the molecular constants which would allow the calculation of the spectra. If the spectra were known and within the bandpass of the spectrometer used in this experiment, direct confirmation of the formation of magnesium carbide would be possible. It can be concluded, however, that even if the carbide coating is formed, in the current experiment it would not interfere with the combustion of the magnesium. Therefore, the experimental difficulties of Mellor and Glassman (Ref. 3) are avoided.

The bluff body geometry of the sample holder moves the bow shock away from the body, providing a relatively large stagnation region. The shock standoff distance was observed to be approximately 0.20 inches. The large stagnation region provides a region of high static temperature, relatively high static pressure in comparison to the Mellor and Glassman experiment (Ref. 3), high concentrations of carbon dioxide and carbon monoxide, and a relatively low concentration of oxygen.

A mixing region forms in front of the magnesium sample, as sketched in Figure 13. The stoichiometry changes throughout this mixing layer, going from pure plume gases to pure magnesium vapor and then terminating at the solid magnesium surface. The precise definition of the spatial structure and extent of this mixing layer is beyond the scope of the current investigation. The soot-producing layer noted on Figure 13 will be addressed below. Equilibrium chemistry is assumed to describe the composition throughout the mixing layer. A constant static pressure equal to the measured pitot pressure of 1.0 psia is also assumed for the mixing process. Since the stagnation enthalpy is known from the rocket chamber calculation shown in Table I, the measured pitot pressure provides the second independent thermodynamic property required to specify a thermodynamic state point. A series of specified enthalpy-pressure solutions were executed using the NASA equilibrium code (Ref. 6) varying the percentage of liquid magnesium in the mixture from 0 to 100%. This describes the overall variation possible in the chemical composition of the mixing layer without addressing the spatial distribution of the chemistry. Figure 14 presents the results of these equilibrium calculations by plotting the mass fractions of MgO(s) , O_2 , C(s) , CO , CO_2 , and H_2O as functions of the total magnesium concentration. As stated above, the total magnesium concentration ranges from 0-100% through the mixing layer.

The equilibrium chemistry in the mixing layer reveals several interesting features. Most significant is the formation of solid carbon (C(s)) in a magnesium-rich region close to the magnesium surface. This is the soot-producing layer noted on Figure 13 and alluded to above. Magnesium oxide is formed first through the consumption of the small amount of free oxygen present in equilibrium. Moving towards the magnesium surface, the lack of additional molecular oxygen forces the magnesium to reduce the CO and CO_2 to form MgO and solid carbon. The behavior of the CO and CO_2 mass fractions is clearly

inversely related to the mass fraction of C(s). The C(s) mass fraction shows a peak at a total magnesium concentration of approximately 85%. The carbon production then tails off as the magnesium concentration approaches 100% at the magnesium surface. Figure 15 shows the temperature distribution through the mixing layer. The temperature drops from the stagnation temperature of about 2800 K to the fixed temperature of the magnesium at 300 K. The temperature of the magnesium was varied from 300 K up to the melting point of magnesium (923 K) without substantially changing the behavior of the mass fractions.

The mass fractions of the gaseous species shown in Figure 14 all fall off with increasing magnesium percentage. This is due partially to chemical consumption (i.e. the consumption of H₂O to form H₂) and partially to the mass displacement of all species by magnesium. In order to separate these effects, the species mass fractions were re-normalized by the sum of the mass fractions of all species excluding magnesium. That is

$$Y'_i = \frac{Y_i}{(1 - \%Mg/100)}$$

where Y_i is the original mass fraction, Y'_i is the new adjusted mass fraction, and %Mg is the initial mass percentage of magnesium. This new quantity has the units of pounds per pound of oxidizing mixture. The variation of this adjusted mass fraction with magnesium mass fraction is shown in Figure 16. Note that the effect of mass displacement has been completely removed and that the remaining effects of chemical consumption are clearly visible. The small amount of oxygen is consumed first, followed by the reduction of CO₂ to CO with no production of carbon. Occurring almost concurrently is the reduction of water to hydrogen. After all the CO₂ is reduced to CO, the CO is then reduced to carbon. This suggests a new ranking of reactions in order of occurrence, shown in Table IV.

TABLE IV
GLOBAL MAGNESIUM REDUCTION REACTIONS RANKED
IN ORDER OF OCCURRENCE

	Reaction
1)	$\text{Mg} + .5\text{O}_2 \Rightarrow \text{MgO}$
2)	$\text{Mg} + \text{CO}_2 \Rightarrow \text{MgO(s)} + \text{CO}$
3)	$\text{Mg} + \text{H}_2\text{O} \Rightarrow \text{MgO(s)} + \text{H}_2$
4)	$\text{Mg} + \text{CO} \Rightarrow \text{MgO(s)} + \text{C(s)}$

Note that the reduction of CO_2 to CO and solid carbon is not observed to occur in this equilibrium calculation. Instead, CO_2 is reduced solely to CO. This is in direct conflict with the reaction ranking by exothermicity, which predicts that the reduction to CO and solid carbon is more favored than the reduction to only CO. This seeming contradiction may be explained by contrasting the behavior of the Gibbs free energy of reaction and the heat of reaction for each of the reactions. These quantities were calculated using the thermodynamic property curve fits provided with the NASA equilibrium code (Ref. 6).

Figure 17 presents the behavior of the heat of reaction for each of the five global reactions with temperature. Note that, of course, the reactions are in the same ranking of exothermicity as in Table III, and that the curves do not cross with increasing temperature. The discontinuities in the curves occur at phase change temperatures of the various condensed species.

Figure 18 presents the behavior of the Gibbs free energy of reaction for each of the global reactions. Note that, at low temperatures, the reactions rank the same as with the

heat of reaction. This is to be expected since the Gibbs free energy (G) is defined as

$$G = H - TS$$

where H is the enthalpy and S is the entropy. From this relation it is obvious that at low temperatures, the Gibbs free energy and the enthalpy should be approximately the same. More importantly, however, is that these Gibbs free energy curves cross with increasing temperature. At higher temperatures the reaction ranking changes to that shown in Table IV. The only exception is the addition of the reaction that reduces CO_2 to solid carbon and CO . Now it can be seen that the reason this reaction does not occur is that the reaction that reduces CO_2 to only CO has a lower Gibbs free energy and therefore will occur before the soot-producing CO_2 reduction reaction. That is, all the CO_2 is reduced to CO before the CO_2 soot-producing reduction reaction can occur. Since chemical equilibrium is the state of minimum Gibbs free energy, it is not surprising that the results of the equilibrium calculations can be explained by examining the behavior of the Gibbs free energy for each of the proposed global reactions. Therefore, the rule of thumb stating that reactions can be ranked by exothermicity should be used cautiously, especially at elevated temperatures characteristic of combustion processes. The Gibbs free energy of reaction will control the equilibrium state. The formation of a distinct soot-producing layer is a direct consequence of the fact that, in equilibrium at higher temperatures, soot is being produced solely by the reduction of CO .

The appearance of solid carbon in the equilibrium combustion of magnesium in this analysis is clearly in conflict with the conclusions of Yuasa and Isoda (Ref. 4) who performed independent equilibrium calculations. They present equilibrium mole fractions of MgO(s) , O_2 , CO , and CO_2 as functions of equivalence ratio for a magnesium/carbon dioxide flame. The equivalence ratio was varied from 0.25 to 1.5. This corresponds to a magnesium mass percentage ranging from 10 to 45%. As seen on Figure 14, the formation of carbon would not be expected in this range. Therefore, it is concluded that

Yuasa and Isoda stopped their calculations at an insufficiently magnesium-rich equivalence ratio to correctly model the combustion process over the magnesium surface. Additionally, they seem to have ignored their own experimental evidence for the formation of carbon. They report:

The flames did not appear uniformly but sporadically over the sample surface as if several volcanoes were bursting into eruptions. This shows that during the combustion the surface was coated with a somewhat protective layer. In fact, after the test run, a black crust with white powder was found to cover the sample receptacle.... CO was found in the measured combustion products. The combustion time estimated from the measured CO concentration is in agreement with the measured combustion times. Consequently, the results indicate that in the CO₂ stream all the Mg sample burned in gaseous phase to produce CO and MgO. (emphasis added).

The "protective layer" observation is directly in line with the observations of Mellor and Glassman, and supports their conclusion asserting the formation of a magnesium carbide crust.

Apparently, the CO₂ jet velocity of 0.5 m/sec in the Yuasa and Isoda experiment was sufficient to remove this layer in patches, causing the sporadic combustion they observed. The "black crust with white powder" observation is in agreement with the observations of Shafirovich and Goldshleger, quoted previously, in which they observed an outer layer of magnesium oxide over an inner layer of carbon mixed with magnesium oxide. Yuasa and Isoda did not report a chemical analysis of the "black crust", and based their conclusion about the absence of carbon formation on combustion time estimates and the formation of CO. Their conclusion was supported by their equilibrium calculations which, for the range of equivalence ratios they chose, showed no carbon formation. Based on this analysis, and in light of the other experiments discussed above, it is concluded that, in their experiment, Yuasa and Isoda probably formed solid carbon but did not recognize it.

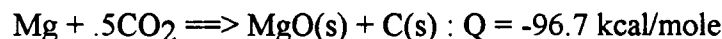
Also, additional, very recent experimental and analytical work published by

Shafirovich and Goldshleger (Ref. 12) indicates the formation of carbon in magnesium/carbon dioxide combustion in the same equivalence ratio range as the current study. In this experiment, magnesium pellets were injected into a furnace held at 1000 K filled with CO/CO₂ mixtures at a pressure of 1 atm, in contrast with the 1 psia, 2985 K conditions of the current experiment. The agreement between their results and the results of the current study using two completely different experimental techniques, different enthalpies, and different pressures indicates that the formation of carbon in magnesium combustion is a robust phenomena and is not extremely sensitive to experimental conditions.

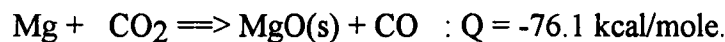
Therefore, if Yuasa and Isoda formed solid carbon in their experiment, all the previous experiments and the current work are in agreement; the heterogeneous combustion of solid magnesium with carbon dioxide in magnesium-rich (greater than 70% by mass) environments produces solid carbon. This hypothesis is supported by direct experimental observations of carbon formation as well as chemical equilibrium calculations that consider the complete stoichiometry of the mixing layer that forms above the magnesium surface. However, in contradiction to the work of Mellor and Glassman, equilibrium calculations reveal that CO₂ must be completely reduced to CO before any soot is formed.

This has an obvious impact on the calculation of the performance of the ramjet engine. Yuasa and Isoda (Ref. 1) indicate that the specific thrust (total thrust/total weight flow of fuel and oxidizer) is directly proportional to the heat of reaction of the fuel and oxidizer. Additionally, they show that the specific fuel consumption (weight flow of fuel/total thrust) is inversely proportional to the heat of reaction. Obviously, the more energy released when the fuel and oxidizer react, the better the performance characteristics; e.g. higher thrust, longer range, more payload, etc. Therefore, it is important to choose the appropriate reaction when calculating the potential energy release of the particular fuel and oxidizer combination. Table III shows that, for a ramjet

operating in the Martian CO₂ atmosphere, there are two possible reactions:



and



Obviously, for maximum performance, the former reaction would be preferred. That is, in contrast to more typical operations, the formation of soot indicates maximum energy release, i.e. maximum performance. This is because the oxidizer contains the carbon, rather than the fuel. So, instead of the usual hydrocarbon fuel/oxygen combustion where soot indicates incomplete combustion, in the magnesium/carbon dioxide system the presence of soot indicates complete combustion and maximum energy release from the fuel. However, as the previous equilibrium analysis has shown, equilibrium favors the reaction leading to CO rather than C(s). This means that performance estimates should use the heat of reaction of the latter reaction, i.e. -76.1 kcal/mole. The difference in energy release between these two reactions is nearly 25%. This impacts directly on the calculated performance of the ramjet engine. Obviously, conservative performance estimates should use the lower heat release in combination with some assumed combustion efficiency. Once again, this shows the importance of considering the Gibbs free energy (i.e. equilibrium) when choosing reactions.

CHAPTER 5

ALUMINUM CALCULATIONS

Aluminum powder is used in solid rocket motor propellant formulations to raise chamber temperature and thereby enhance performance characteristics. The calculations and experiments described above suggest that each metallic particle in a solid rocket motor becomes a soot producing site as it burns. Since most current solid rocket motor systems utilize aluminum in the propellant formulation, calculations similar to those performed with magnesium were carried out.

Global reactions and the heats of reaction at standard conditions for aluminum reacting with CO_2 and H_2O are presented in Table V (in order of decreasing exothermicity).

TABLE V

GLOBAL ALUMINUM REDUCTION REACTIONS RANKED BY EXOTHERMICITY

	Reaction	Q(per mole Al)
1)	$\text{Al} + .75\text{O}_2 \Rightarrow .5\text{Al}_2\text{O}_3$	-200.2 kcal
2)	$\text{Al} + 1.5\text{CO} \Rightarrow .5\text{Al}_2\text{O}_3 + 1.5\text{C(s)}$	-160.6 kcal
3)	$\text{Al} + .75\text{CO}_2 \Rightarrow .5\text{Al}_2\text{O}_3 + .75\text{C(s)}$	-129.7 kcal
4)	$\text{Al} + 1.5\text{H}_2\text{O} \Rightarrow .5\text{Al}_2\text{O}_3 + 1.5\text{H}_2$	-113.6 kcal
5)	$\text{Al} + 1.5\text{CO}_2 \Rightarrow .5\text{Al}_2\text{O}_3 + 1.5\text{CO}$	-98.8 kcal

These reduction reactions are in the same order of exothermicity as the magnesium reduction reactions in Table III.

A typical solid propellant mixture composition (Ref. 13) was used in this study. The propellant formulation is a 90-percent solids-loading composite consisting of 58-percent ammonium perchlorate (AP), 8.5-percent hydroxyl-terminated polybutadiene (HTPB), 12-percent HMX, 1.5 percent-plasticizer, and 20-percent metallic aluminum by weight. This propellant mixture (sans aluminum) was used as the oxidizing mixture for aluminum in the same manner as the ethylene/oxygen exhaust products were used as the oxidizing mixture for magnesium.

Figure 19 presents the distribution of species mass fraction for Al_2O_3 (irrespective of phase), CO_2 , CO , H_2O , O_2 , and C(s) as a function of percent metallic aluminum. This represents the mixing layer surrounding a burning aluminum particle in the rocket chamber. These calculations were performed at a pressure of 865 psia, a representative solid rocket motor chamber pressure. On the figure, 100-percent aluminum represents the particle surface, while 0-percent aluminum represents solely the combustion products of the HTPB/AP/HMX mixture. Note the obvious similarity to the magnesium calculations in Figure 15. The only striking difference is the lack of any free molecular oxygen in the gaseous mixture. Figure 20 presents the temperature distribution within the mixing layer. The aluminum surface was held fixed at 300 K. As before, this temperature was varied up to the melt point of aluminum (933 K) without substantially changing the equilibrium results.

Once again, in order to separate the effects of mass displacement and chemical consumption, adjusted mass fractions were calculated and are presented in Figure 21. The effect of consumption is now clearly visible. The CO_2 is reduced to CO , as evident from the initial decrease of CO_2 and the increase of CO with no production of solid carbon. Concurrently, H_2O is reduced to H_2 . Only after all the H_2O and CO_2 are consumed does

the aluminum reduce the remaining CO to soot. This process was first proposed by Wolfhard (Ref. 14). The behavior of the mass fractions implies the reaction ranking in Table VI (in order of occurrence).

TABLE VI
GLOBAL ALUMINUM REDUCTION REACTIONS RANKED IN ORDER OF
OCCURRENCE

	Reaction
1)	$\text{Al} + 1.5\text{CO}_2 \Rightarrow .5\text{Al}_2\text{O}_3 + 1.5\text{CO}$
2)	$\text{Al} + 1.5\text{H}_2\text{O} \Rightarrow .5\text{Al}_2\text{O}_3 + 1.5\text{H}_2$
3)	$\text{Al} + 1.5\text{CO} \Rightarrow .5\text{Al}_2\text{O}_3 + 1.5\text{C(s)}$

Note the similarity of Table VI with Table IV and the obvious contradiction with Table V. The ranking by exothermicity implies that solid carbon should be preferentially formed through the reduction of CO₂ to CO and soot whereas this reaction is not observed to occur in the equilibrium calculations. As before, the discrepancy between ranking the global reactions by exothermicity and by the results of equilibrium calculations can be explained through the examination of the Gibbs free energy of reaction and the heat of reaction for each of the proposed global reactions.

Figure 22 presents the heat of reaction as a function of temperature for each of the reactions in Table V. Note that the reactions rank the same as the ranking by exothermicity in Table V. As with the magnesium reactions, the curves do not cross. The discontinuities occur at phase change temperatures.

Figure 23 presents the Gibbs free energy of reaction for each of the proposed global aluminum reduction reactions. Note the similarity with the magnesium reactions in Figure 18. The low temperature reaction ranking agrees with the ranking in Table V, while,

because the curves cross, the high temperature ranking agrees with Table VI. The aluminum preferentially reduces the CO_2 to just CO at higher temperatures. The reduction of CO_2 to CO and soot does not occur because of the previous conversion of all the CO_2 to CO. Only after the reduction of H_2O and CO_2 will aluminum reduce CO to soot. As with the magnesium calculations, the ranking of the reactions by Gibbs free energy necessarily agrees with the ranking observed in the equilibrium calculations.

The local stoichiometry about the burning metallic aluminum results in the formation of soot in a localized zone close to the surface of the burning particle. Therefore, aluminum and magnesium have been shown to have similar equilibrium combustion characteristics in carbon dioxide. In the heterogeneous combustion process, both first reduce local concentrations of carbon dioxide to carbon monoxide before reducing the carbon monoxide to solid carbon.

CHAPTER 6

CONCLUSIONS

The formation of soot in the combustion of magnesium in an ethylene/oxygen flame has been experimentally confirmed. Spectral observations indicated that the magnesium was oxidized, and post-test examination confirmed the formation of soot. A control experiment was partly successful in ruling out the possibility that the soot was formed from fuel fragments. A new set of experiments using stainless steel rather than copper for the sample holder would help address this issue. The formation of solid carbon is further supported by equilibrium chemistry calculations that consider the local stoichiometry through the mixing layer. The consideration of local stoichiometry in heterogeneous combustion offers a more complete picture of the combustion process than relying solely on the overall oxidizer/fuel ratio. Local stoichiometry calculations of the reaction of a typical HTPB/AP/HMX solid propellant formulation with aluminum suggest that the mechanism is also valid for aluminum oxidation in a solid rocket motor. Further experimentation with aluminum is required to confirm this assertion. The rule of thumb which states that reactions can be ranked in order of exothermicity is shown to be invalid at high temperatures in equilibrium. Exothermic rankings of reaction mechanisms should be used as a guide, not as a rule. The experimental and analytical results of previous investigators have been reconciled.

Although no direct observations have been made, there is also mounting evidence for the formation of a protective carbide layer over the molten magnesium surface. In the absence of sufficient aerodynamic forces to remove this layer, combustion can be inhibited. This effect may impact the design of combustion systems. Systems designers

considering the use of magnesium as a fuel in carbon dioxide breathing ramjets or as a fuel additive for solid propellant rockets will also have to contend with solid combustion products that form combustion-inhibiting crusts on the fuel surface, as well as exhausts containing solid carbon.

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LIST OF REFERENCES

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APPENDIX

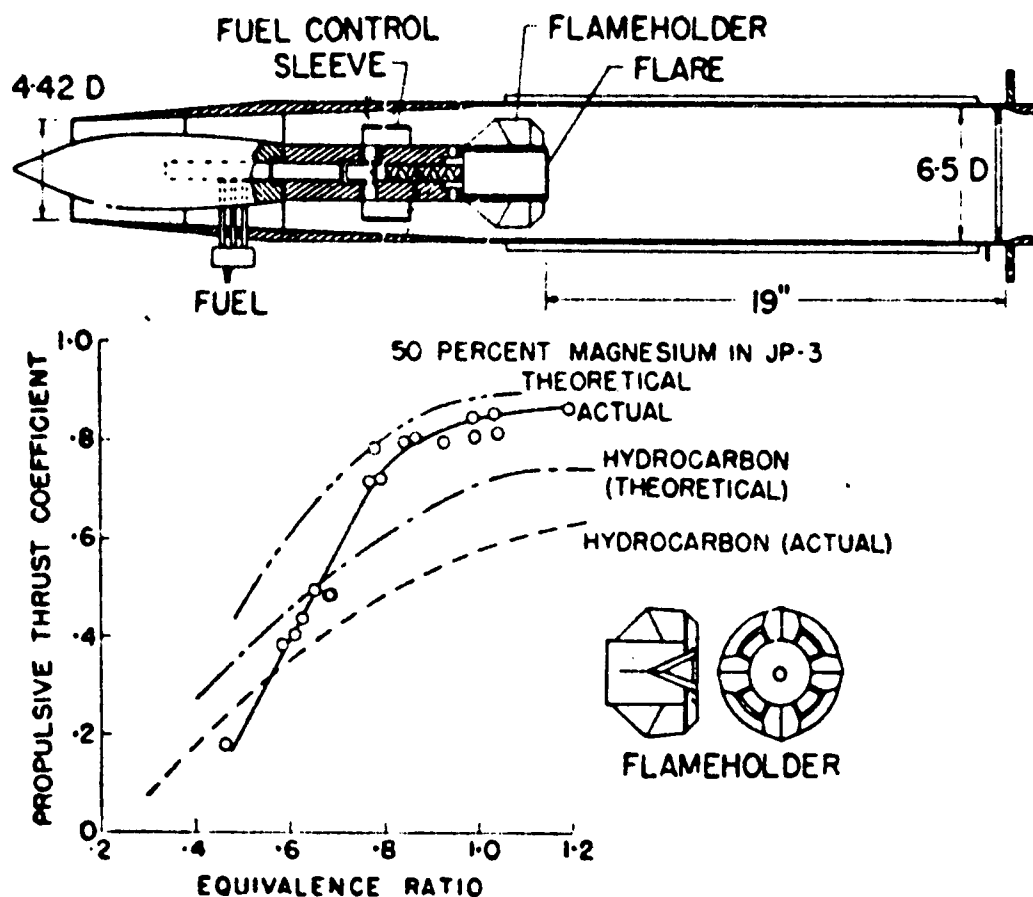


Figure 1. Performance of a Magnesium Slurry Ramjet

Source: Olson, W. T., and Setze, P. C. "Some Combustion Problems of High-Energy Fuels for Aircraft", Seventh Symposium (International) on Combustion, London and Oxford, 28 August - 3 September 1958, The Combustion Institute, London, 1959.

Figure 2. Copper Sample Holder with Magnesium; PreFire



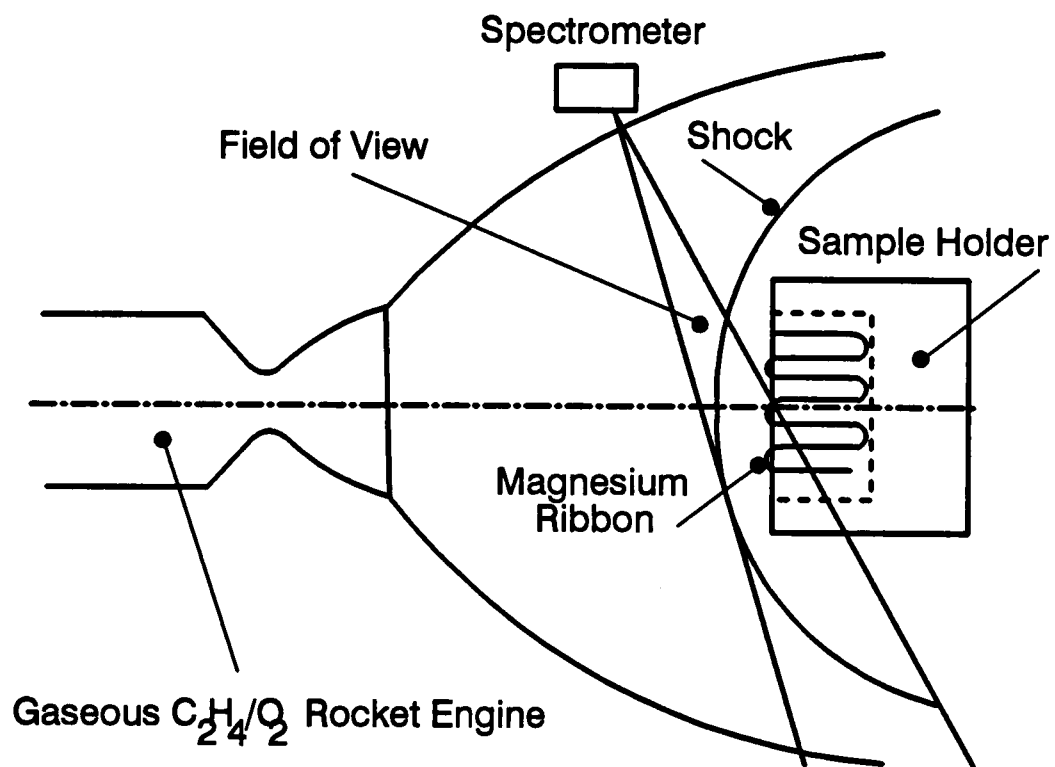


Figure 3. Experiment Schematic

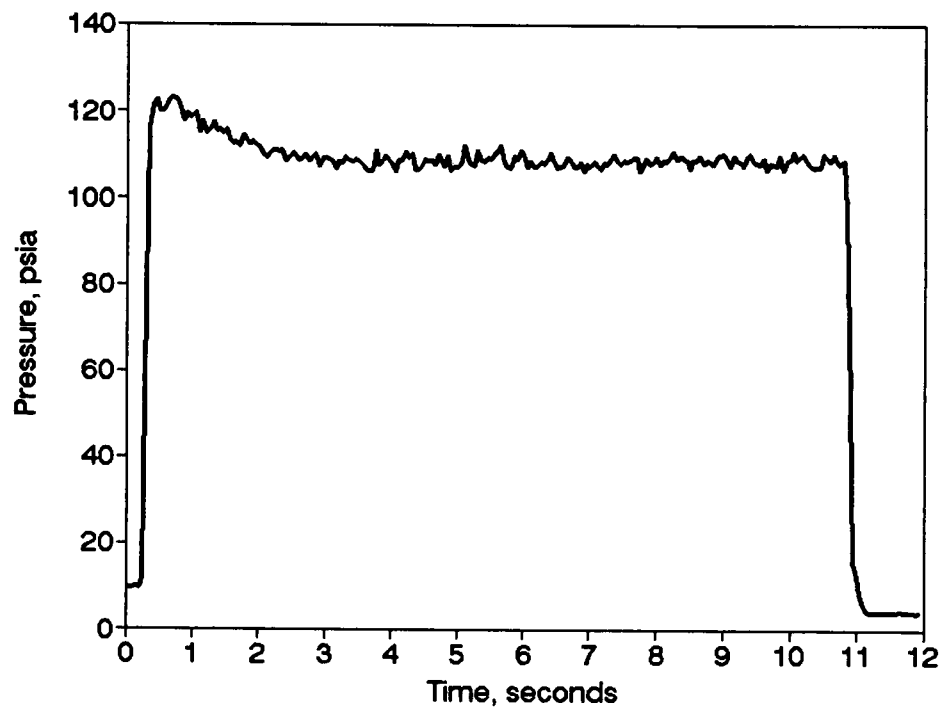


Figure 4. Chamber Pressure Trace

Figure 5. Video Frames of Sample Holder
(a) At Motor Ignition

⇐ FLOW



Figure 5. (continued)
(b) At Magnesium Melt-Point

↙ FLOW ↘

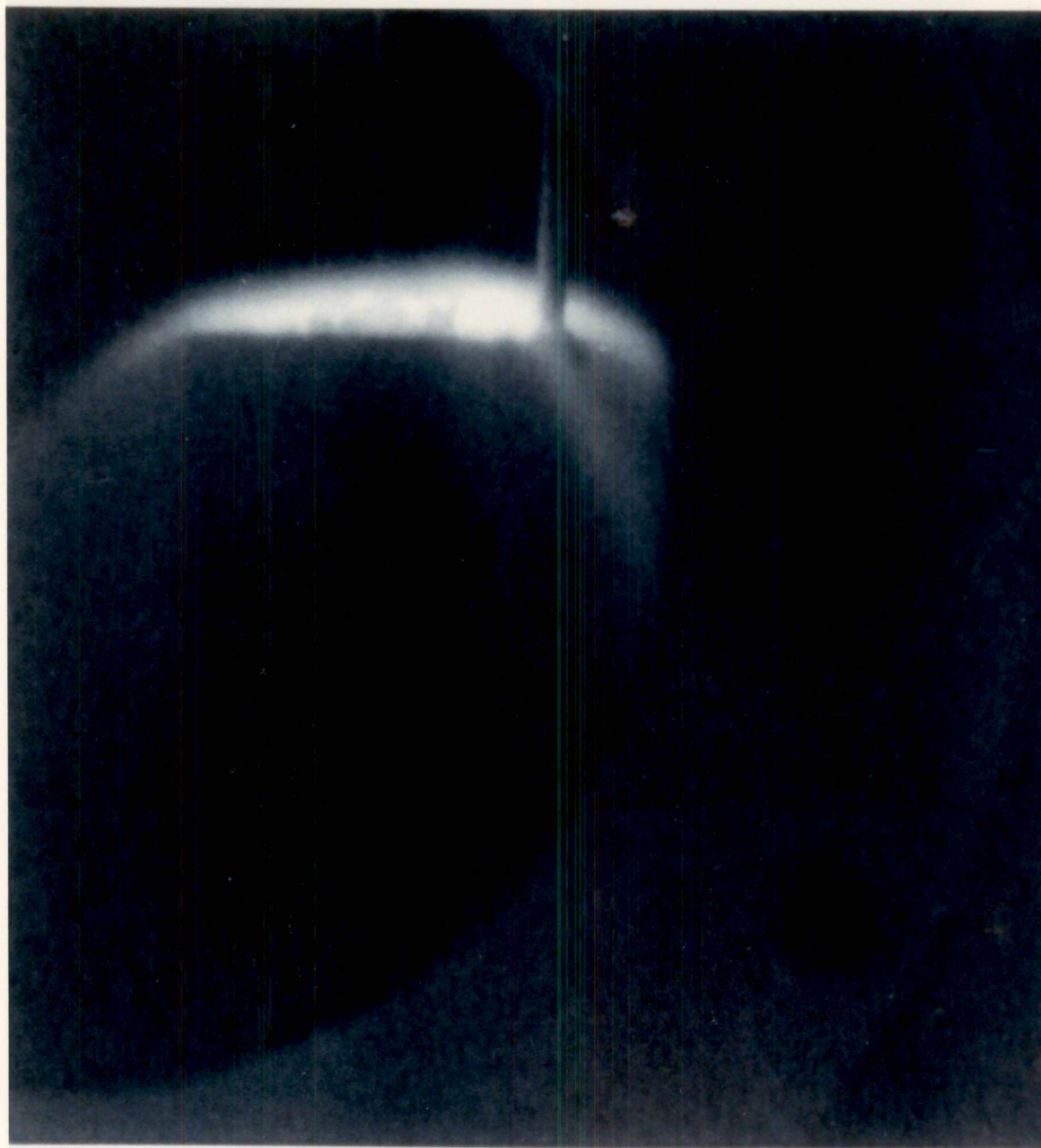


Figure 5. (continued)
(c) At Magnesium Ignition

↙ FLOW ↘

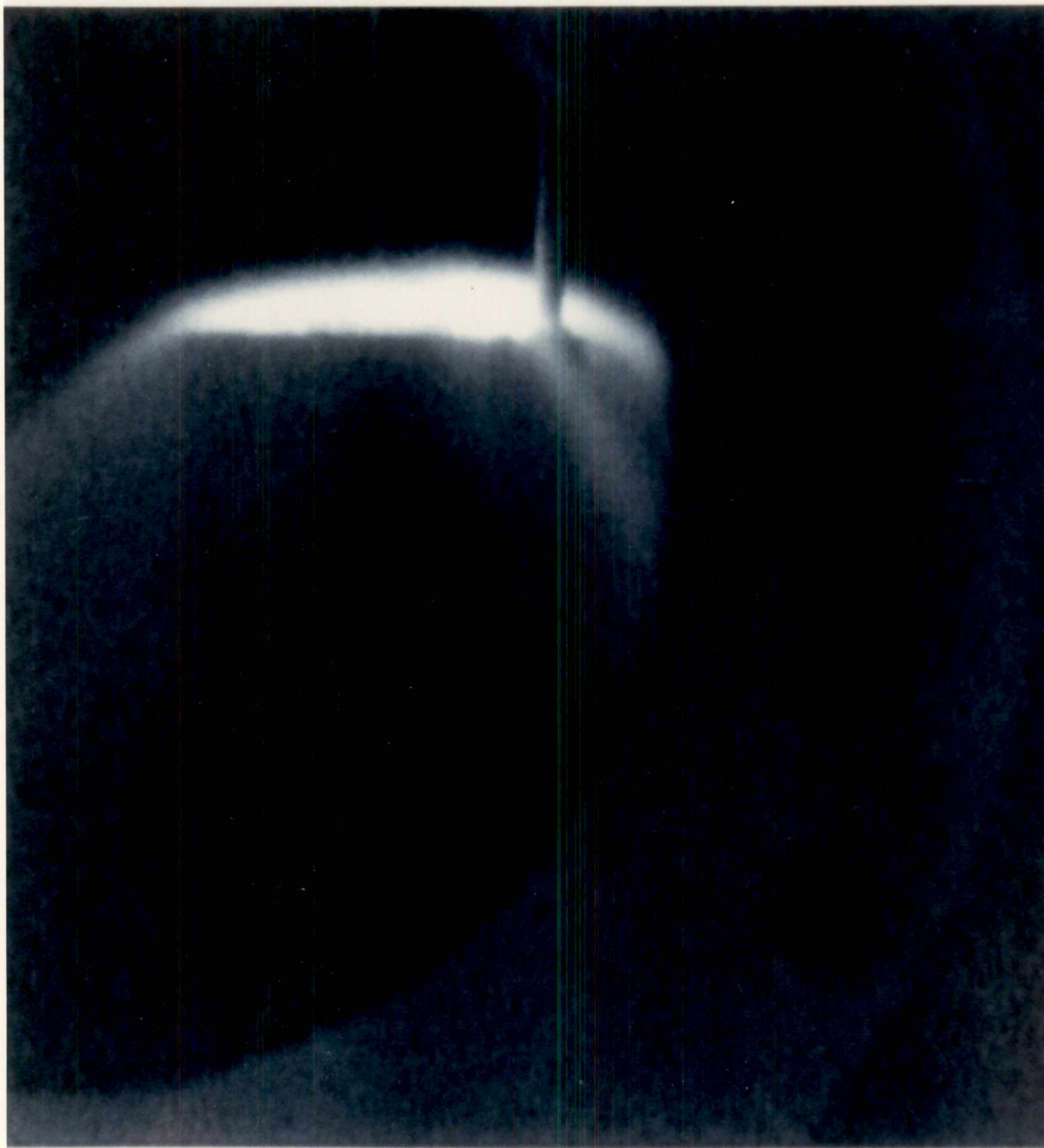
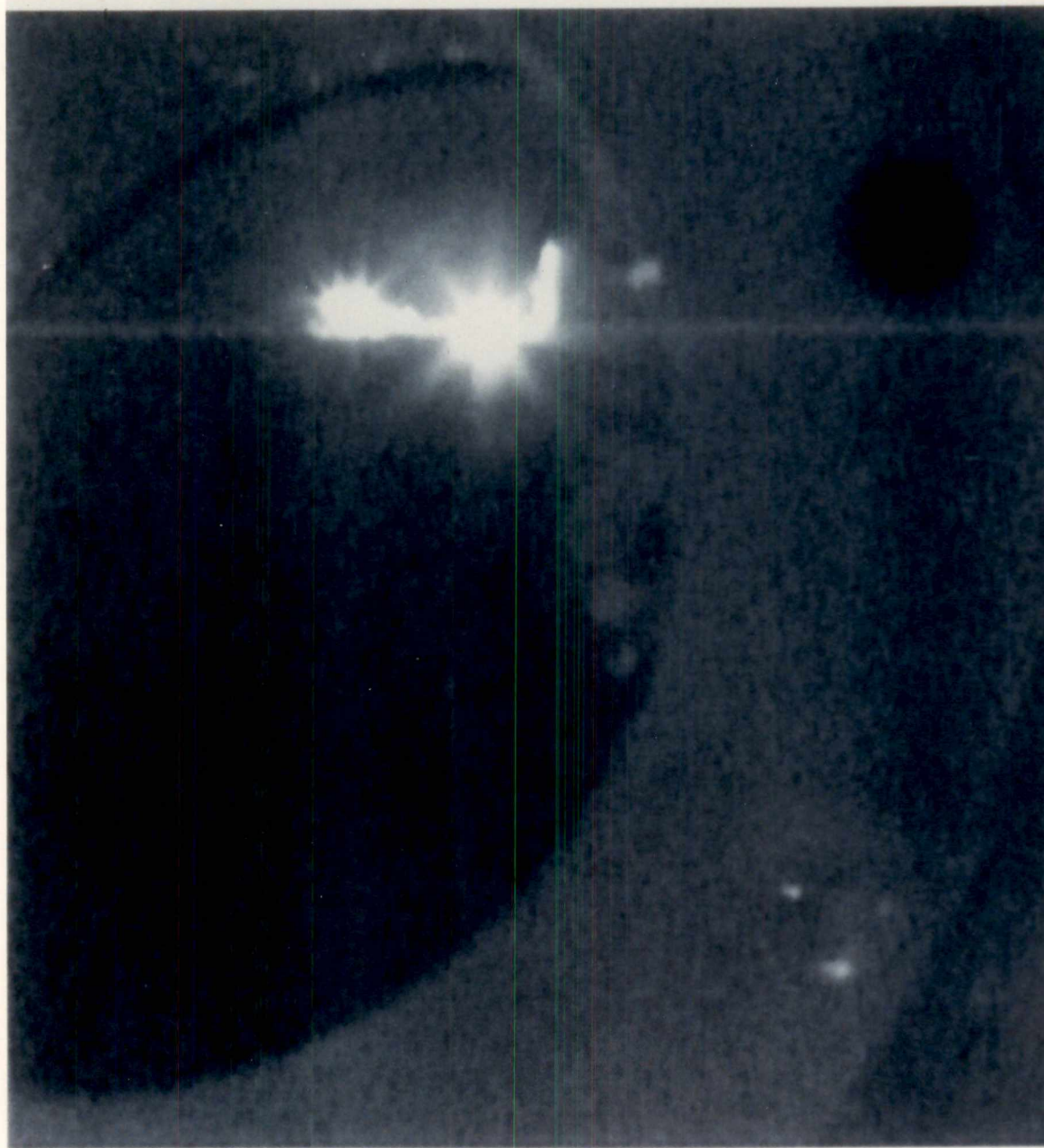


Figure 5. (continued)
(d) At Motor Shutdown

FLOW



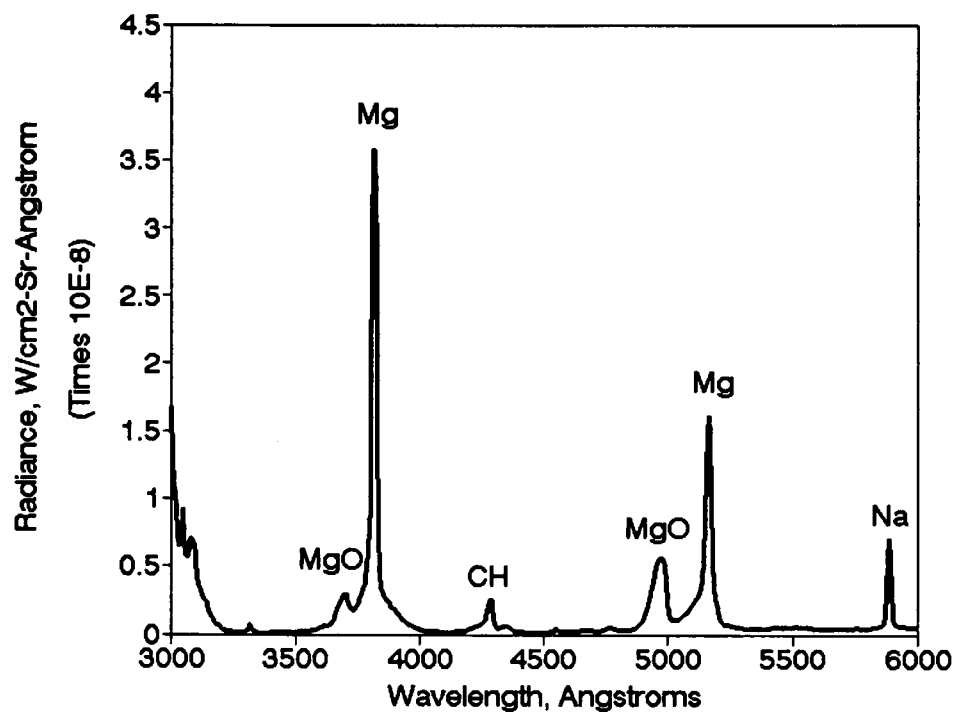


Figure 6. Experimental Spectrum at $t + .5$ sec.

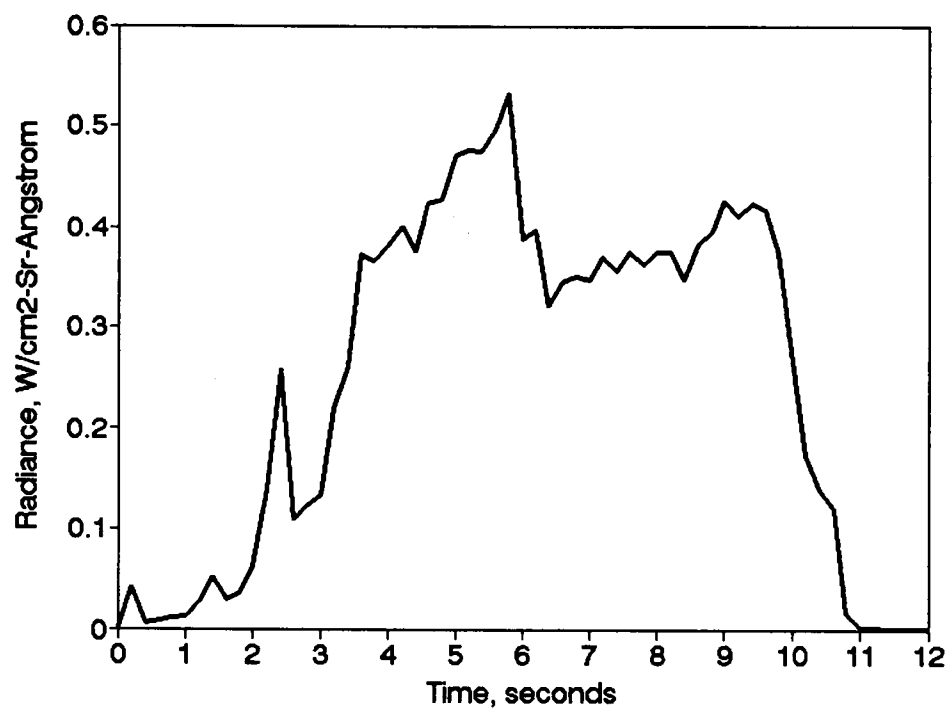


Figure 7. MgO 4970 Å Feature Radiance Trace

Figure 8. Copper Sample Holder with Magnesium; PostFire

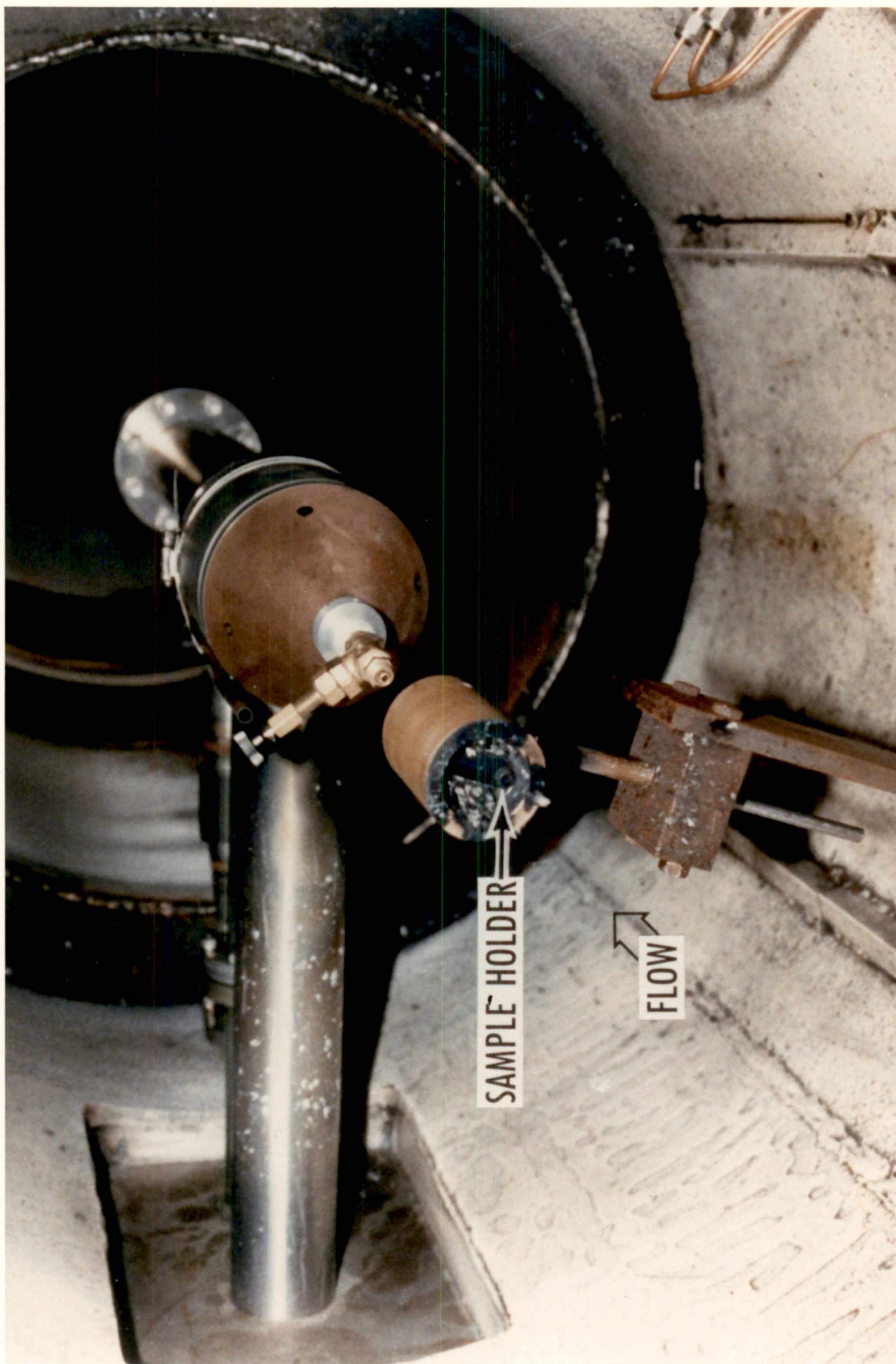


Figure 9. Closeup PostFire Photograph of Sample Holder with Magnesium



Figure 10. SEM Photomicrograph of Deposition on Sample Holder

4NA 1,28KX 20KV WD:29MM S:00000 P:00000
20UM

Mg SPHERE

MgO SPHERES
COATED WITH
CARBON

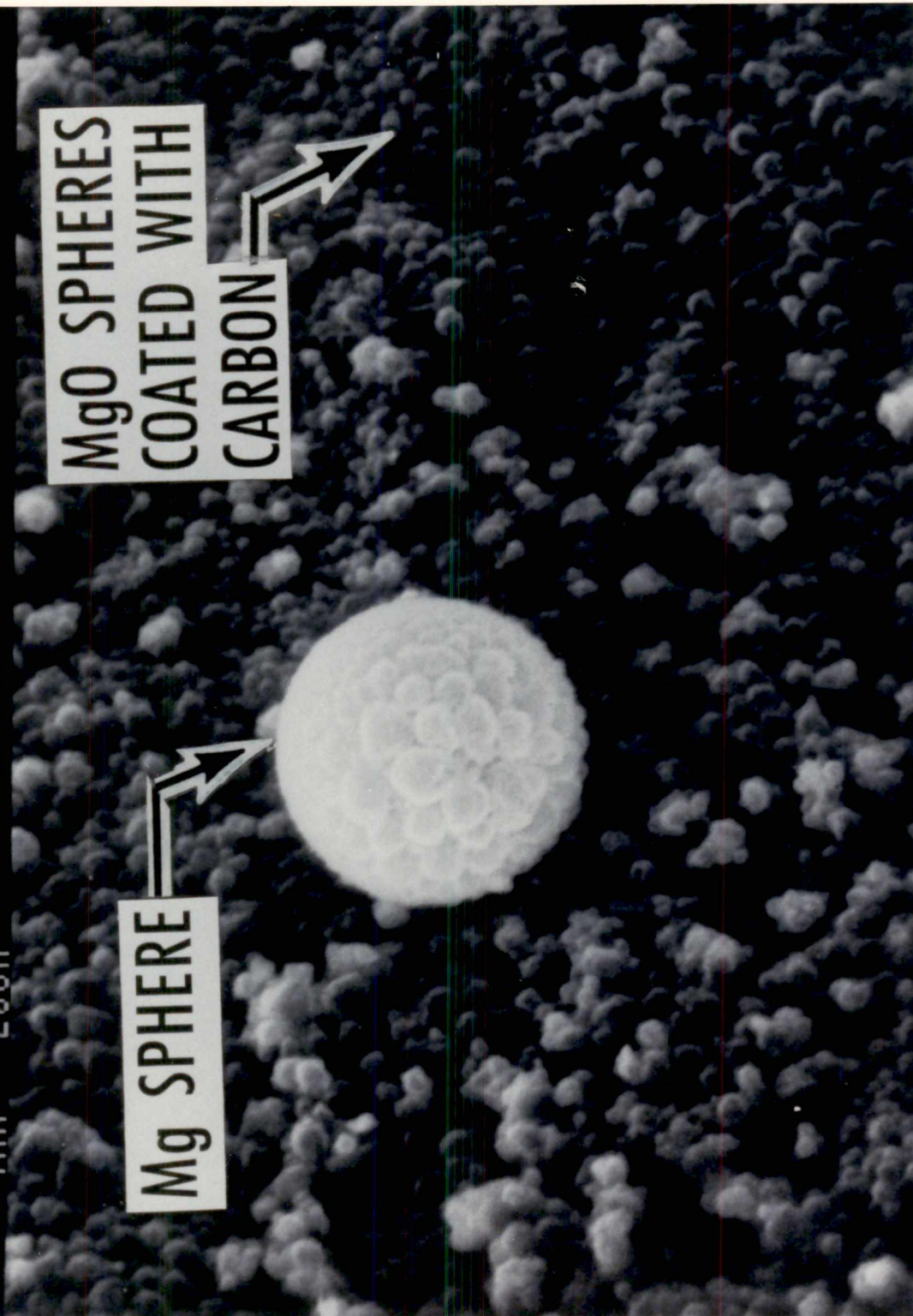


Figure 11. Control Copper Sample Holder; PreFire

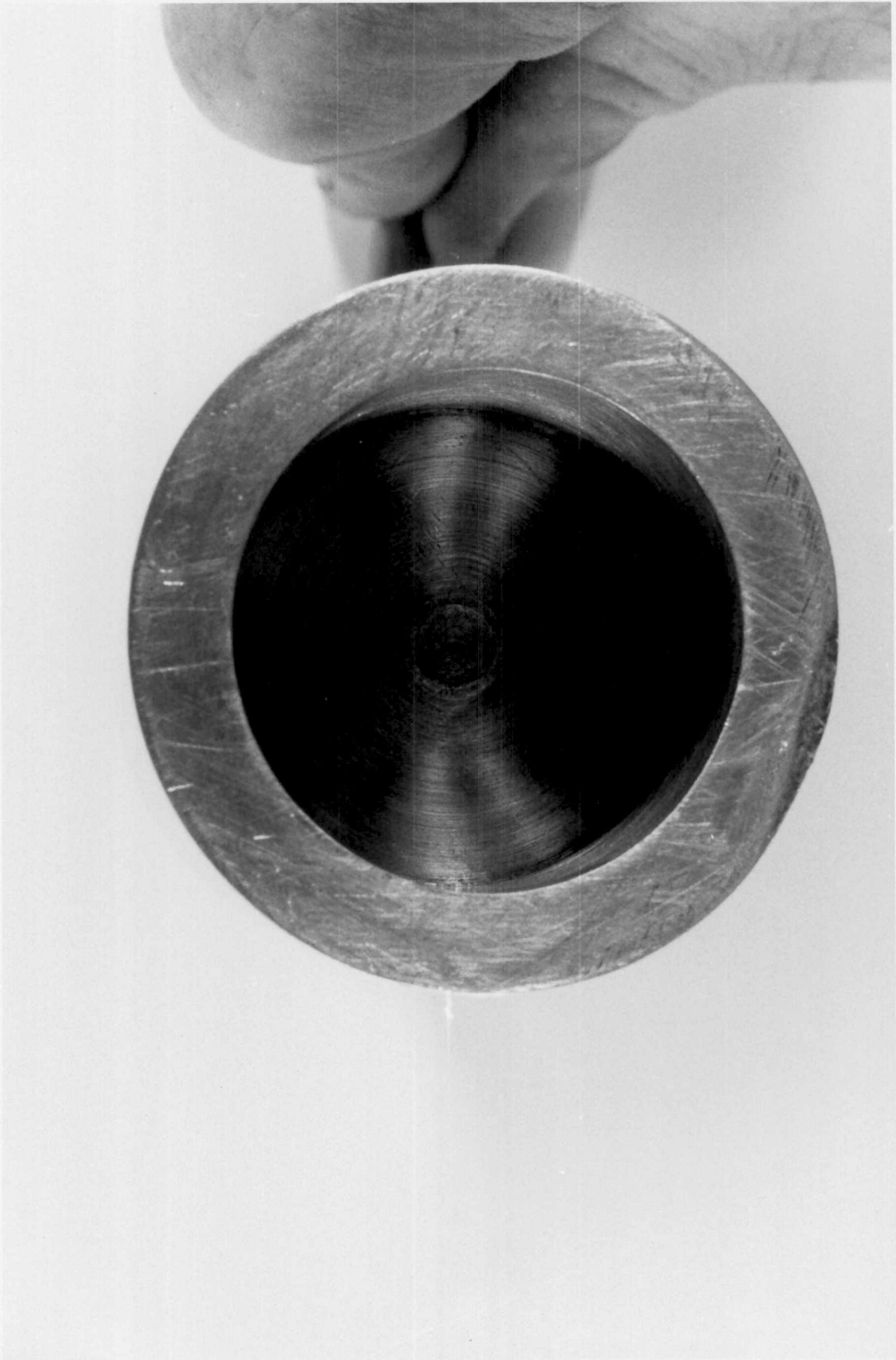


Figure 12. Control Copper Sample Holder; PostFire



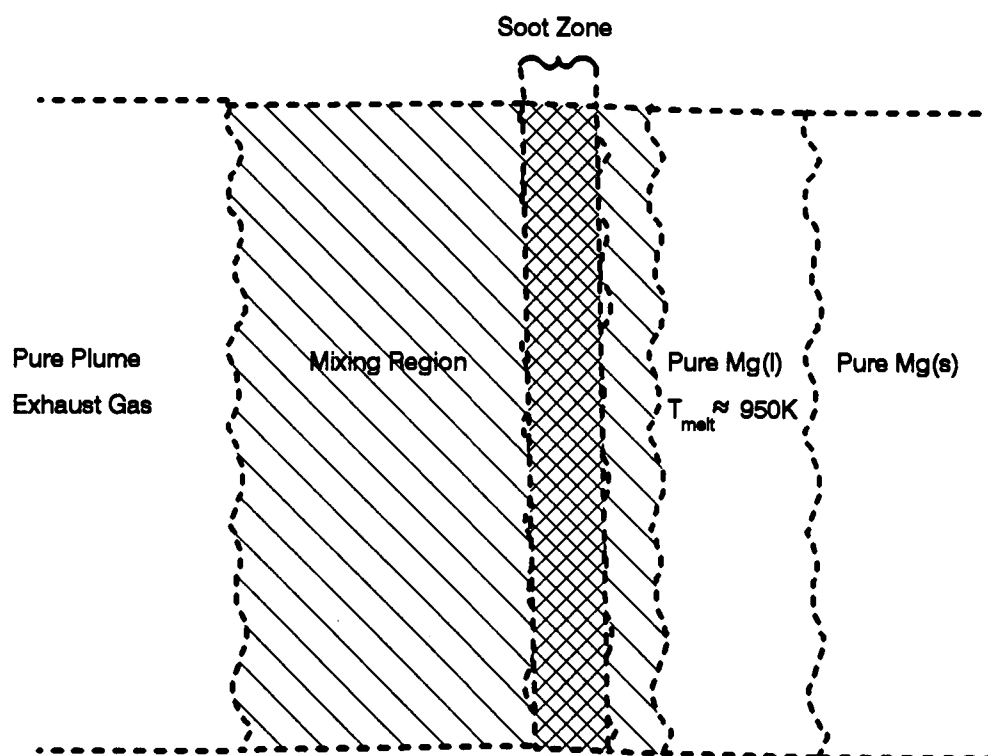
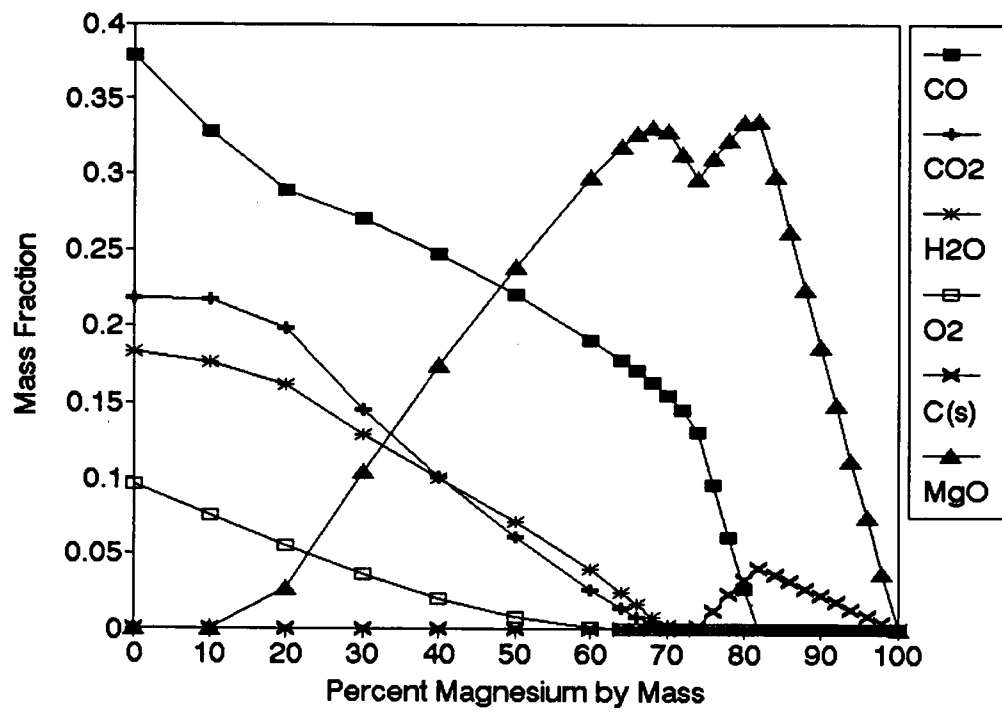
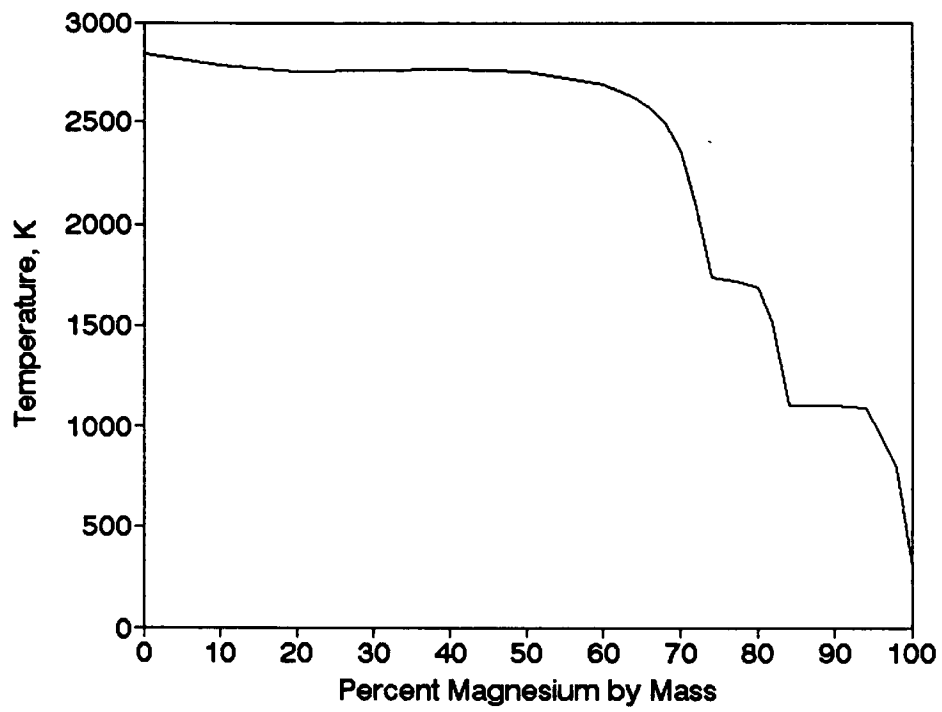


Figure 13. Stagnation Region Mixing Layer Schematic



Figures 14. Mixing Layer Equilibrium Chemistry; Mass Fractions



Figures 15. Mixing Layer Temperature

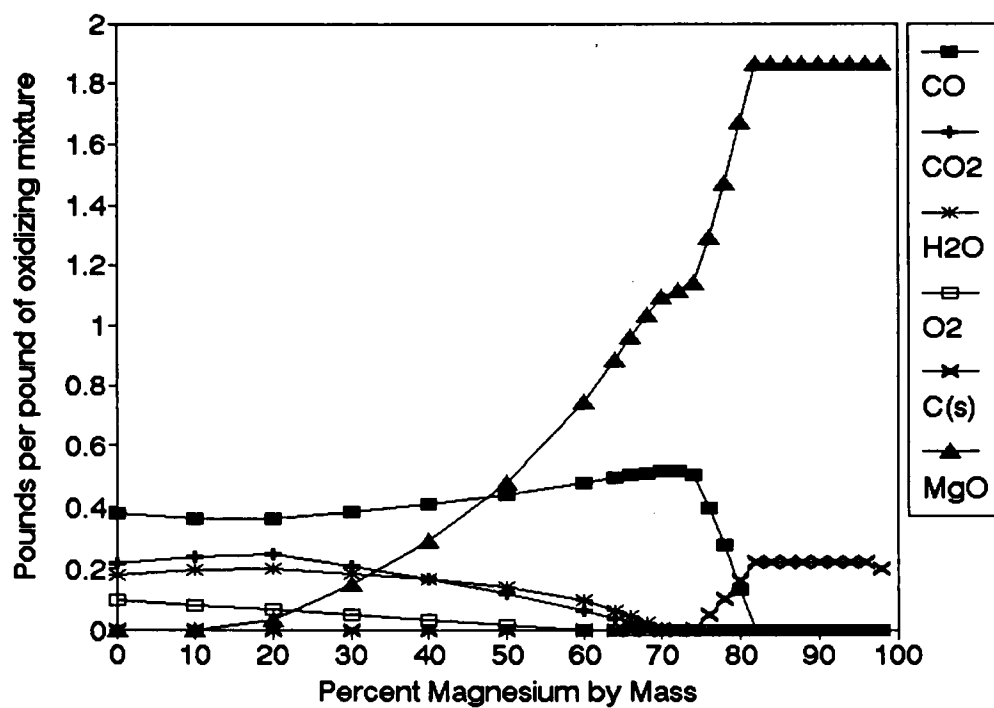


Figure 16. Mixing Layer Equilibrium Chemistry; Adjusted Mass Fractions

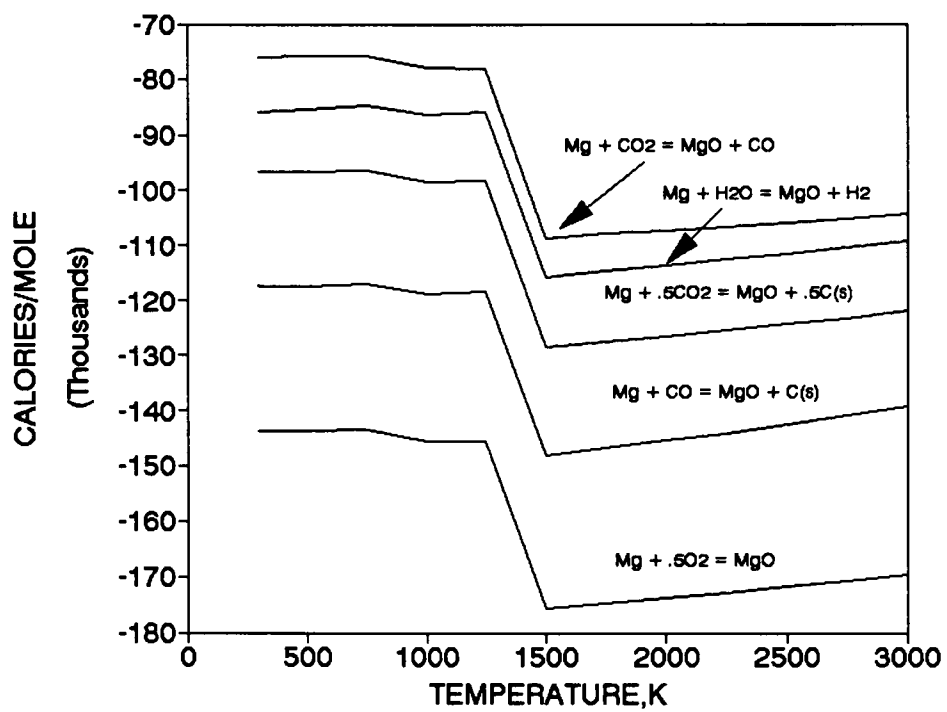


Figure 17. Heats of Reaction for Magnesium Reduction Reactions

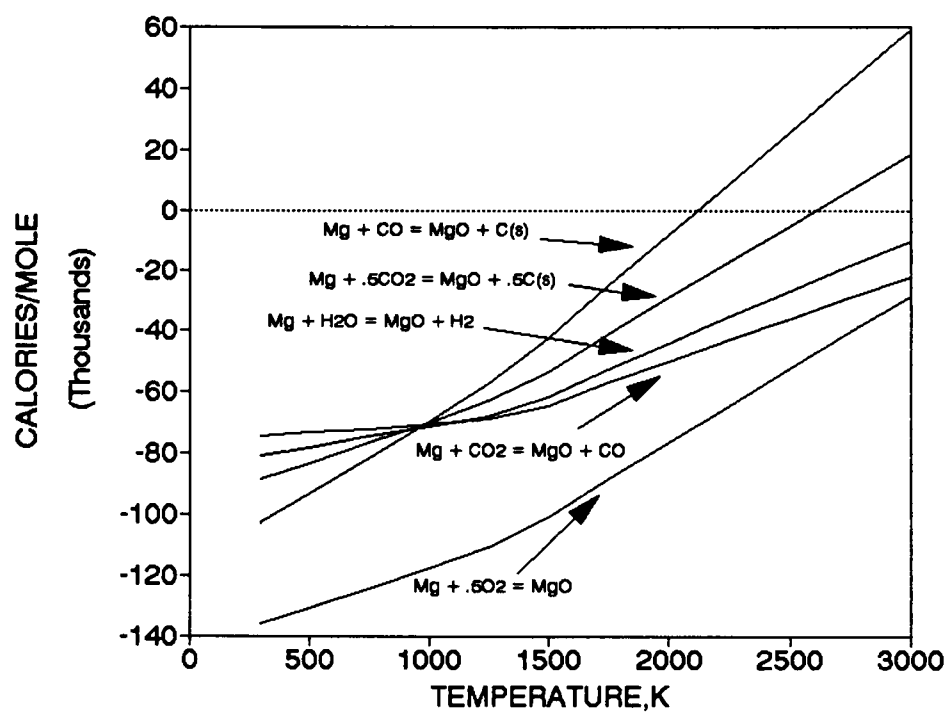


Figure 18. Gibbs Free Energy of Reaction for Magnesium Reduction Reactions

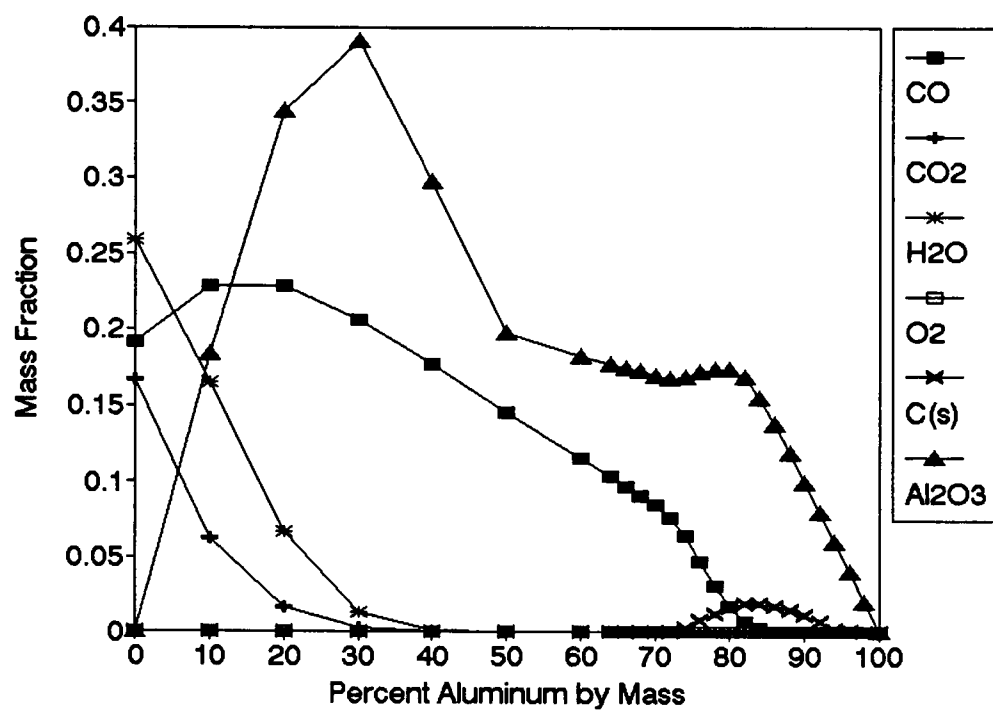


Figure 19. Aluminum, Mixing Layer Equilibrium Chemistry, Mass Fractions

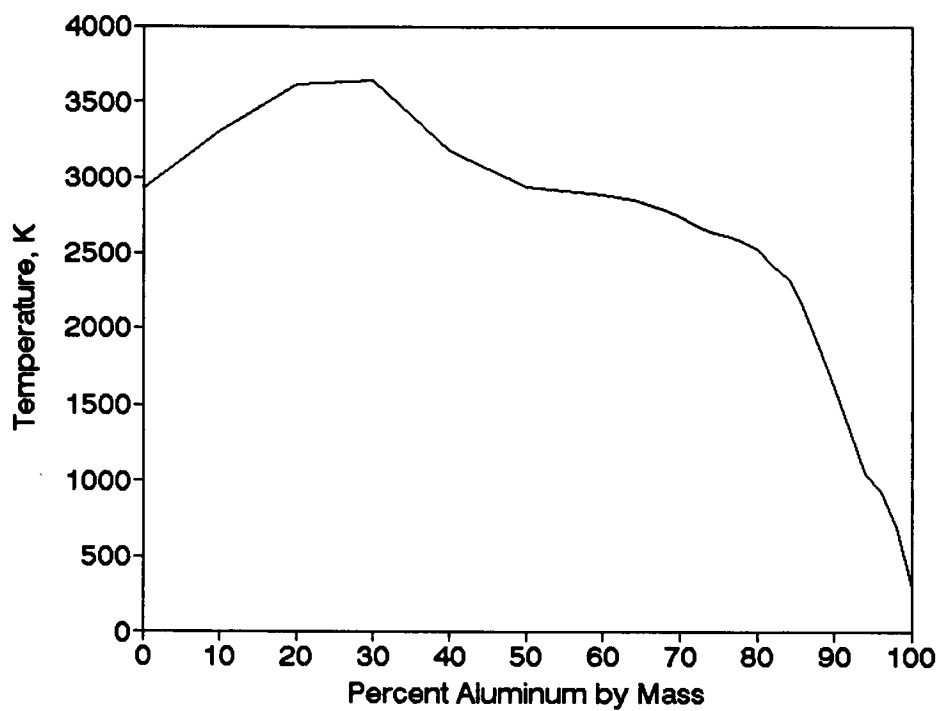


Figure 20. Aluminum, Mixing Layer Temperature

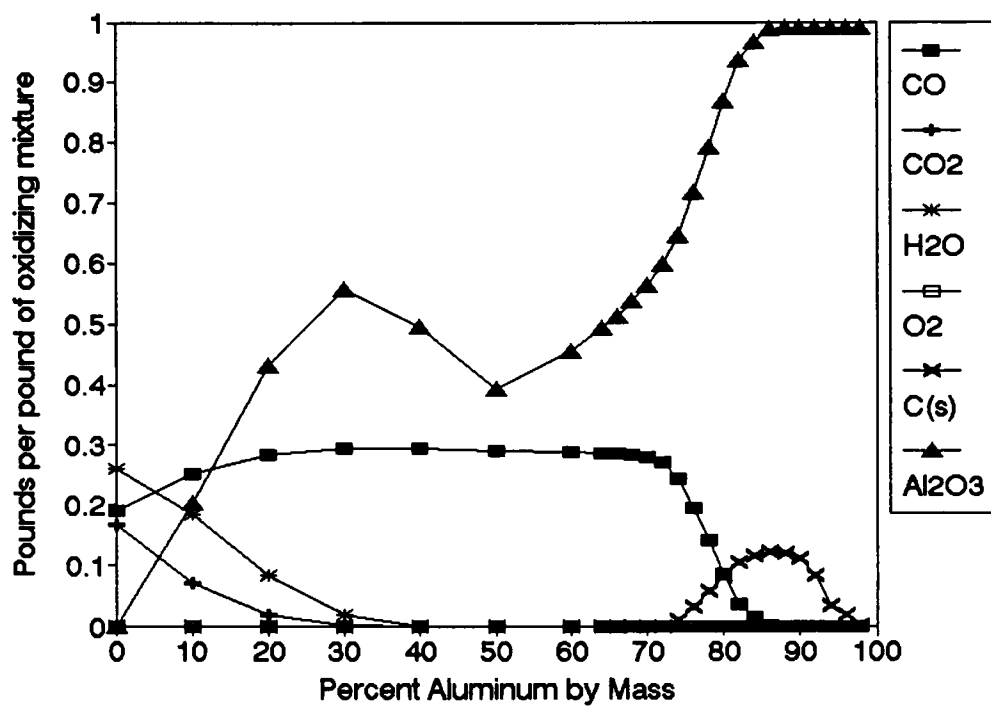


Figure 21. Aluminum, Mixing Layer Equilibrium Chemistry, Adjusted Mass Fractions

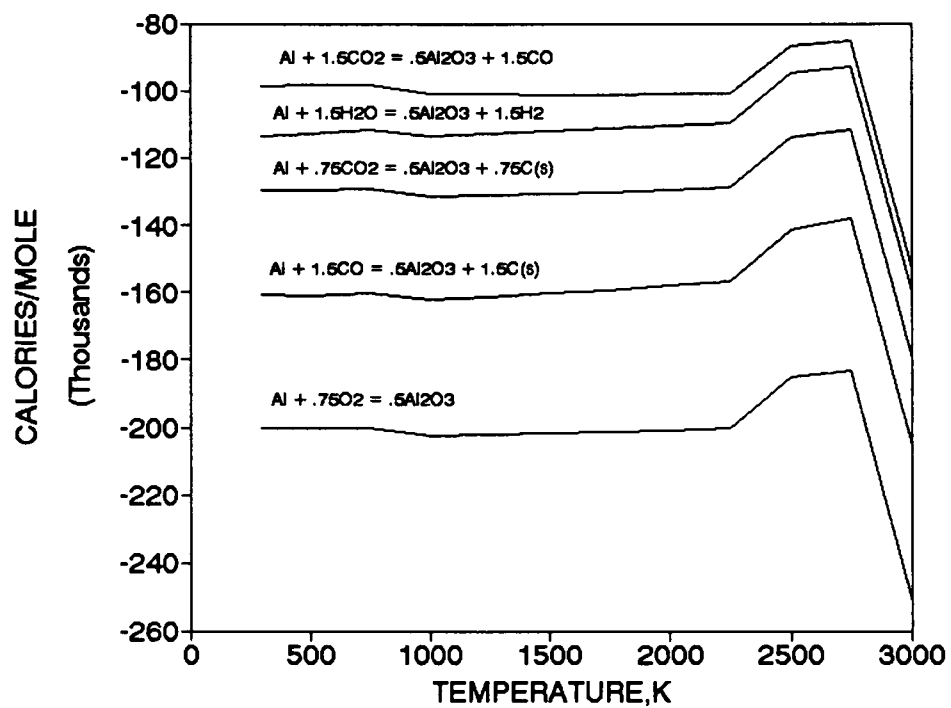


Figure 22. Heats of Reaction for Aluminum Reduction Reactions

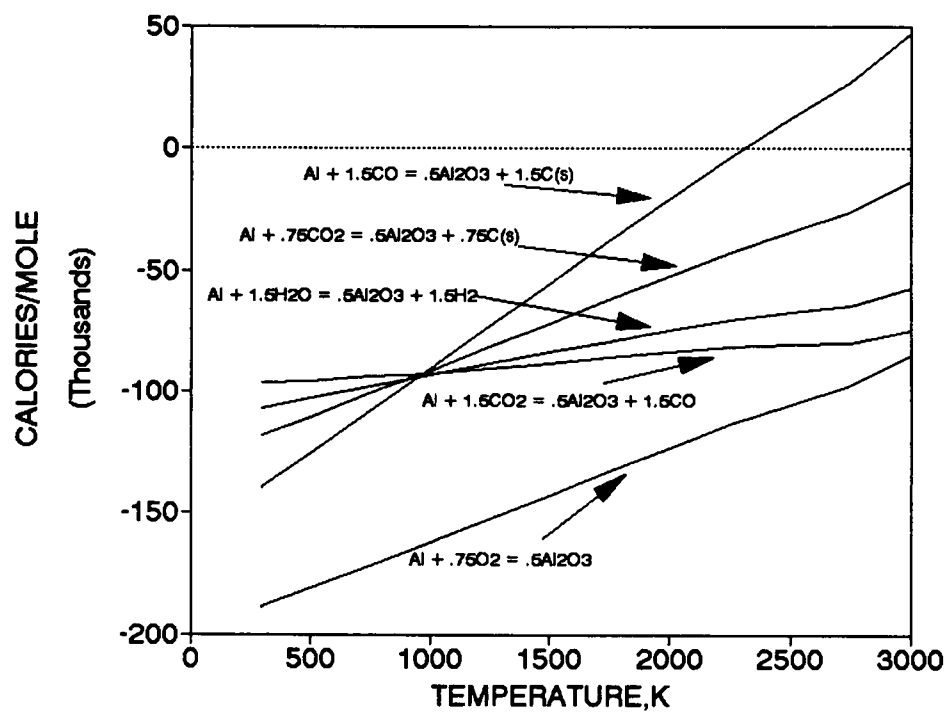


Figure 23. Gibbs Free Energy of Reaction for Aluminum Reduction Reactions

VITA

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