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EFFECT OF REDUCED ATMOSPHERIC PRESSURE ON THE PERFORMANCE CHARACTERISTICS OF PYROTECHNIC COMPOSITIONS CONTAINING ALUMINUM

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INTRODUCTION

Attempts have been made several times in the past to use aluminum (Al) as a fuel in pyrotechnic compositions. Because of the high heat of reaction for Al-oxidant compositions, it was thought that these systems would produce acceptable output. In fact, tests by this group have shown this to be the case for some applications. However, tests have also shown that these systems are totally unacceptable at high altitudes. In the latter environments, the burning rate and intensity are greatly reduced, although the intensity-time integral remains about the same (fig. 1). It has long been thought that the difficulty with the combustion of Al was due to the essentially monomolecular protective oxide coating, but recent experiments indicate that this may not be the case. This report presents the work done to determine the cause of the problem of combustion of Al containing compositions at high altitudes.

EXPERIMENTAL PROCEDURES

The compositions of interest were hand blended, then pressed caseless at 10,000 psi, with a cap of igniter composition on top and a plug of fireclay on the bottom. The pellets were wrapped with two layers of Kraft paper tape to form a case and prevent side burning. They were 0.95 cm in diameter and approximately 1.5 cm long (actual lengths varied with the composition and were individually measured).

The burning rates of the compositions were obtained by burning the pressed pellets in an evacuable window bomb or in an environmental chamber¹. The bomb was 7.6 cm inside diameter and 38 cm long with 1.9 cm thick stainless steel walls. Two observation windows 5.1 cm in diameter were located opposite each other in the center of the bomb. The chamber was a cubic structure 100 cm on a side with a 20-cm diameter window in the center of the door. For both setups, the pellets were set in a holder which positioned them in the center of the window and ignited with an electric match. Because the window became coated with carbon or ash, it was not possible to measure the intensity accurately. Only the burning time was measured, either from a time-intensity curve or by a hand-operated electric timer. Burning rates were calculated from burning times and pellet length and reported as cm/s.

Thermal analysis was performed on a Dupont 900/951 thermal analyzer. Both differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were performed on loose powders of selected compositions.

¹The large chamber was used for studies in air to ensure enough oxygen to burn the excess fuel. The bomb contained sufficient volume to burn the excess metal in pure oxygen, even at reduced pressure.

DISCUSSION AND RESULTS

Performance of Compositions Containing Metal Fuel with Various Oxidants

To ascertain that the component responsible for the poor performance at reduced atmospheric pressure (simulated high altitude) was the Al, compositions using this fuel and several different oxidants were tested. The results are listed in table 1. For all compositions, the burning rate was reduced at reduced pressure. Since compositions listed using sodium nitrate (NaNO_3) and Teflon (TFE) were not appreciably affected with magnesium (Mg) as the fuel, it is obvious that the use of Al fuel is the responsible agent for the deterioration at reduced pressure.

Performance of Compositions Using Iron Oxide as an Additive

It had previously been found that iron oxide (Fe_2O_3) has a beneficial effect on the combustion of Al, reducing sparking and producing a smooth burning flame (ref 1). Using this information as a basis, compositions of Al-TFE and 3/1 Al/Mg-TFE were made with 0 to 6% Fe_2O_3 additive. The results of the burning tests are given in table 2. It appears that at these low concentrations, the amount of Fe_2O_3 made little difference, although the altitude degradation still occurred.

The true thermite composition, however, contains 75% Fe_2O_3 , while the percentages used in this study were extremely low. To test the effect of a composition more like thermite, one made with TFE and equal parts of Al and Fe_2O_3 was burned. The results from table 2 indicate that while there was still some deterioration at low pressure, it was not as large as that for the other compositions containing this additive.

Performance of Compositions Containing Al Fuel with Other Additives

It has been postulated that the undesirable effect of low pressure on burning rate may be related to the presence of the protective oxide coating on the Al particles. Several methods for removing or disrupting this coating, either before or during the burning process, have been suggested. The following approaches were tried:

1. Abrading the Al with silicon carbide to either wholly or partially remove the coating
2. Use of 1% or less of titanates, which are thought to react with the oxide and form a hydrophobic coating which disappears around 200°C
3. Adding a small amount of a flux used to solder Al, which could remove the oxide coating

4. Use of 5% zinc fluoride (ZnF_2), which had previously been found to react with Al at low temperatures

5. Use of 5% KBF_4 , which combines the effect of fluorides and borates, both of which are contained in fluxes

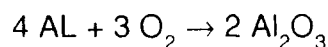
6. Use of a 50-50 mixture of Al and Mg powder

7. Use of an alloy containing 70% Al and 30% Mg

8. Use of an Al/Si powder with and without Fe_2O_3 ; composition of Al/Si had performed satisfactorily in an item previously, but had not been tested at altitude

9. Adding a small amount of Ti-B which would produce a large amount of heat, aiding in the vaporization of Al

The technique selected to test the effectiveness of these methods for removing the oxide coating was to heat the treated Al powder or alloy in a Dupont 951 TGA in an atmosphere of oxygen. Removal or disruption of the oxide coating should result in an increased reactivity of the Al powder with oxygen. For Al powder alone, the reaction began at $600^\circ C$; the reaction gradually accelerated, and at $1000^\circ C$, the Al had gained 28% of its original weight. Aluminum reacts with oxygen according to the equation



Therefore, for complete reaction, the weight increased would be 89% of the weight of Al; therefore, in this experiment, 32% of the Al had reacted with oxygen at $1000^\circ C$.

The effectiveness of removing the oxide coating by abrasion was investigated by grinding the "as received" Al powder with carborundum in a mortar and pestle for 20 minutes under an inert atmosphere, and then heating the abraded Al in the TGA in oxygen. In this experiment, the Al began to gain weight at $600^\circ C$, and the reaction increased at a greater rate than in the case of the original Al. At $1000^\circ C$, the abraded Al had undergone 50% reaction with oxygen.

Six samples of organic titanates were obtained from Kenrich Petrochemicals, Incorporated. The thermal stability of each of these compounds was determined by heating the titanates in the TGA at $10^\circ C/min$ in a helium atmosphere and also by heating at a constant temperature of $75^\circ C$. Al powder was then treated with the most thermally stable titanate (designated KR38S) in two ways: (1) mix the dry Al powder with the liquid titanate in a mortar and pestle, (2) dissolve the titanate in ethyl acetate and disperse the Al throughout the solution, then evaporate the ethyl acetate. Both

samples of Al were heated to 1000°C in the TGA. They both showed a reaction beginning at 600°C with 27.6% reaction having occurred by 1000°C, or about the same as with "as received" Al.

Various materials considered to be fluxing agents were mixed with Al powder. Al mixed with ZnF_2 showed oxidation beginning at 600°C with 78% reaction having occurred by 1000°C. When KBF_4 was mixed with Al, the reaction with oxygen began at 450°C, and 83% of the Al had reacted by 1000°C. Al powder mixed with a commercial silver soldering flux called "Handi-flux" showed reaction with oxygen at 450°C and 75% reaction by 1000°C. A special flux intended for use in soldering Al designated "Neptune G flux" was obtained from Nassau Research Corporation. This material had the most dramatic effect on the reaction of Al with oxygen. Al mixed in a mortar and pestle with 5% by weight of this flux and heated at 10°C/min on the TGA began to lose weight at 450°C and then ignited with complete combustion occurring at 595°C. Just prior to ignition, only 5% of the Al had reacted.

Another method of mixing the Neptune G flux with the Al was tried. The flux was dissolved in water and stirred with the Al, which was then dried in an oven. The powder treated in this manner ignited at 605°C when heated in the TGA.

Mixtures of Al treated by these various methods and TFE were then made by blending in a mortar and pestle and subjecting it to differential thermal analysis. In these experiments, approximately 30 Mg of the composition were heated in the Dupont 900 DTA at 15°C/min in an ambient air atmosphere while the various thermal reactions were recorded. A composition of untreated Al and TFE showed little exothermal reaction when heated to 750°C under these conditions, and examination of the residue showed no evidence of an ignition or propagative reaction. Similar behavior was noted for compositions containing Al treated with organic titanates, ZrF_2 , or KBF_4 ; however, when a composition using Al mixed with Neptune G flux was heated under the same conditions, ignition and propagative reaction took place at 465 to 480°C. Even when the DTA was performed under vacuum, ignition, and propagative reaction of this composition occurred.

When an alloy of 30/70 Mg/Al was heated in oxygen on the TGA, reaction with oxygen began at 500°C and culminated in ignition and complete combustion at 770°C. However, while a composition of this alloy and TFE showed a strong exothermal reaction at 500°C, there was no evidence of ignition and propagative reaction. An alloy of 50/50 Mg/Al was heated in oxygen on the TGA and showed oxidation beginning at 400°C with ignition and combustion occurring at 500°C after about 5% reaction. This

alloy is considerably more reactive than the 30/70 alloy and is as reactive as the Al treated with the Neptune G flux.

Compositions chosen on the basis of the thermal studies were then made and burned in air at ambient and reduced pressure. The results are summarized in table 3. The rather startling finding was that only the composition containing Mg:Al alloy was not greatly affected by reduced pressure. Especially surprising was the result for the Neptune G additive. This composition, which ignited before the Al melted in the DTA, would not burn propagatively at 40,000 ft. Even at 25,000 ft. complete combustion was difficult to achieve. However, even though this composition ignited in a vacuum in the DTA, when it did burn, the burning rate was slowed down as much as it was for the composition containing untreated Al. The increased oxidation at lower temperature exhibited by Al with several of these additives in the TGA indicated that the oxide coating was being removed or disrupted, but the burning rate for compositions containing these additives were still strongly affected by reduced pressure. It appears that a different cause other than the oxide coating for the problem must be found.

Performance of Compositions Containing Al Fuel in Various Atmospheres

Two possibilities come readily to mind as causes of the altitude degradation: (1) the lack of oxygen to support combustion at the reduced pressure, and (2) the lack of heat feedback from the flame to the solid composition caused by pulling the flame away from the surface at reduced pressure.

To test the effect of oxygen (or lack of it) on the burning of these compositions, the Al-TFE compositions were burned in air and in atmospheres of pure argon, helium, and oxygen. The results are listed in table 4.

The unexpected result of these experiments was that the content of the atmosphere had essentially no effect on the burning rate. A composition burned in argon, helium, and oxygen burned at about the same rate as in air, both at ambient and at reduced pressures. It therefore appears that atmospheric oxygen does not participate in the process controlling the burning rate of these compositions. The light output would be affected by the amount of oxygen in the atmosphere, but that effect is not being addressed in this study. However, this behavior has been studied for Al-NaNO₃ compositions (ref 3). The data for the combustion in helium and air also provided the answer to the possibility of reducing heat feedback by pulling the flame away from the burning surface. The use of a helium atmosphere should cool the flame significantly since the thermal conductivity of helium is six and nine times greater than that of air and argon respectively (ref 2). However, the burning rate at both ambient and reduced pressure, indicating that this cooling does not affect the burning rate. Consequently, the lifting of the flame from the surface should not affect it either. In fact, the flame appeared smaller at reduced pressure, contrary to expectations of enlargement, and no lifting of the flame from the surface could be observed.

Performance of Compositions Containing Different Fuels in Various Atmospheres

Since the atmospheric content does not affect the burning rate, it is believed that the problem is caused solely by processes occurring in the body of the flare near the burning surface. Since the major difference between Al and Mg (other than the oxide coating) is their very different boiling temperatures and heats of vaporization, the effect of reduced pressure on the burning rate of compositions containing other fuels with very different boiling point and heats of vaporization was examined. Some pertinent thermal data for the fuels are listed in table 5; the burning rate data for compositions containing these fuels is presented in table 6.

Al, Ti, and B are all high boiling fuels, while Mg, Ca, and Zn are low boiling ones (table 5). The Pilling-Bedsworth ratio² indicates that the oxide coating on B would spall off and not be protective, but that the coating on Al and Ti would be protective. On the other hand, the coating on Zn is extremely protective [this is the reason it is chosen for galvanizing metal (ref 4)] while Mg and Ca have coatings which are not totally protective (ref 5). Since the burning rates of composition containing Mg, Ca (ref 6), and Zn are minimally affected by altitude³ this information again indicates that the oxide coating is not the problem at reduced pressure. It was noticed that all compositions containing high boiling fuels are strongly affected, with the highest boiling one most affected of all.

If the problem with the burning time is caused by the high boiling point of the fuel, it would be aggravated by the excess fuel contained in the compositions. The excess fuel becomes a product of the reaction. Reaction temperatures are calculated by the Shidlovskiy equation (ref 7):

$$T = \frac{\Delta H_{rx} - \sum \Delta H_{tr}}{\sum C_p}$$

where

- T = maximum reaction temperature in °C
- ΔH_{rx} = heat of reaction
- $\sum \Delta H_{tr}$ = sum of the heats of transition of products
- $\sum C_p$ = sum of heat capacities of products

² Pilling-Bedsworth ratio calculated by $P-B \text{ ratio} = \frac{d \text{ metal}}{d \text{ oxide}} \times \frac{MW \text{ oxide}}{MW \text{ total metal}} = \frac{V \text{ oxide}}{V \text{ metal}}$

³ While the burning rate of the composition containing Ca would appear to be affected, the data is for 100,000 ft altitude. The effect, if any, is greatly reduced at lower altitudes, so it would be very small at 40,000 ft.

The results of calculations made by estimating the reaction temperature and inserting the values for ΔH_r and C_p for that temperature into the equation are listed in table 7. If the estimate is far away from the calculated value, a new estimate is made and new values used until estimate and calculation are about the same. The temperatures calculated are maxima, and the actual reaction temperatures would probably be lower than the calculated values. However, the calculations show that, except for the Al-NaNO₃ composition, the temperatures for the compositions with high boiling fuels were lower than the fuel boiling point, while those for compositions with low boiling fuels were higher than the boiling points of the fuels (or, as in the case for Ca, limited by the boiling point of the metal⁴).

The above calculations are for ambient pressure, but what happens at reduced pressure? The heat of vaporization increases (about 1%), but the boiling point of the metal is reduced considerably (table 5). This phenomenon would not appreciably affect the compositions with low boiling fuels since the reaction temperature is already equal to or higher than the boiling point of the fuel at ambient pressure. However, for the compositions with high boiling fuels, the lowering of pressure at altitude and consequent lowering of boiling point would result in more of the excess fuel being vaporized and consequent removal of heat from the burning surface (needed as heat to vaporize the fuel). The resultant lowering of temperature would cause a reduction of the burning rate at reduced pressure.

To test this hypothesis, a composition containing only 40% Al was burned. The temperature calculated for this composition (the second reaction in table 7) is much higher than that for the composition with a higher Al content. In fact, it is almost the same as the boiling point of Al. The results summarized in table 8 indicate that the burning rate for this composition was much less degraded by altitude than was that for the composition containing a larger amount of Al.

The seemingly anomalous results of the thermal analysis and burning studies can now be explained. For instance, the composition Neptune G flux ignited in a vacuum in the DTA but would not even propagate at 40,000 ft. The answer is simple: in the DTA, the entire composition is heated, while in the flare pellet, only the burning surface is heated, and the heat must then be conducted back into the bulk of the composition. The excess fuel soaks up the heat in the same manner as for the other Al composition. In fact, the composition was slowed so much that propagation failed at 40,000 ft.

⁴The 85-15 Ca-NaNO₃ composition was used in the calculation since it would give the lowest reaction temperature. Less Ca in the composition would yield a higher calculated temperature.

It is interesting to note that there was a 50% decrease in the burning rate (BR) for a composition containing a physical mixture of 25/75 Mg/Al powder (table 2), while there was only an 18% decrease for one containing an alloy of 30/70 Mg/Al (table 3). There is a large amount of excess Al even if none of the Mg reacts with the oxidant. This should have the effect of lowering the reaction temperature by boiling the excess Al. However, the composition containing the alloy was affected very little. Liddell and Doan state that for two metals of very different boiling points, the boiling point of the alloy is close to the lower boiling one until the percentage of the higher boiling one becomes quite high (ref 8). The melting point of the alloy is depressed from the melting point of either Mg or Al by 200 to 460°C, and figure 2 shows that the boiling point of the alloy is not much higher than that for the Mg unless the alloy contains in excess of 90% Al (ref 8).

It would be expected that the powder mixture of fuels would perform in the same way since there should be no difference between alloy and mixture once the fuel has melted. However, the burning rate of the powder mixture composition (table 2) was affected by altitude almost as much as one containing pure Al fuel. This is caused by the oxide coating on Al, which keeps its form so well, even after the fuel has melted, that there is little effective mixing of the Mg and Al. However, the alloy does not behave as a physical mixture; the metals are already mixed in a lattice and are in intimate contact with each other after melting.

The great reactivity which is characteristic of Mg powder, would explain the puzzling results from burning the Mg composition in oxygen. For this composition, the burning rate was lower in oxygen as compared to those in air and the other gases. In a previous study (ref 9), it was found that the burning rate of Mg-NaNO₃ compositions containing 40% and 50% Mg was the same in air as in oxygen, but that it was lower in oxygen, relative to air, for a composition containing 60% Mg. In fact, the burning rate of the latter composition in oxygen was the same as the burning rate for the composition containing 50% Mg.

It has been determined (ref 10) that the burning rate is dependent on the thermal conductivity of the composition, which in turn varies with the metal content. For both the Mg-NaNO₃ and Mg-TFE compositions, there is a large amount of excess metal; this metal would react rapidly with the oxygen atmosphere, as it melts at the surface. The reaction product, MgO, has a much smaller thermal conductivity than the metal (ref 3). Therefore, less heat would be conducted back into the composition. While oxygen is present in the air, it would not be as readily available for reacting as in the oxygen atmosphere. This phenomenon would not occur with the Al, Ti, and Zn compositions, since all of the metals have protective coatings which reduce their reactivity. For this reason, these compositions display little difference in burning rate for the atmospheres employed.

CONCLUSIONS

The oxide coating of Al has long been alleged to be the cause of the poor performance of pyrotechnic compositions containing Al, and this coating was similarly blamed for the slowing of the burning which takes place at high altitudes (reduced atmospheric pressure). However, it has been found that even if the coating was removed or disrupted by the use of additives, the degradation still occurred. In addition, compositions which contained Zn that had a very protective coating were not affected by reduced pressure, while B, on which the coating would spall off and not be protective, made a poor fuel since its compositions were more strongly degraded than those of Al.

Since there was essentially no difference in the burning rate in atmospheres of air, argon, helium, or oxygen (except for the Mg composition), it seemed that the cause of the slower burning was not due to the absence of oxygen or to the reduction of heat feedback from the flame at reduced pressure. It did happen, though, that compositions with low boiling fuels such as Mg, Ca, and Zn were not affected, while those containing high boiling fuels such as Al, Ti, and B were affected.

From this information, it was evident that the cause was the high boiling point and consequent high heat of vaporization of the latter fuels. By reducing the atmospheric pressure, the boiling point was reduced allowing more of the excess fuel to vaporize, removing heat from the surface, and slowing the burning process. Since the reaction temperature is above the boiling point of the low boiling fuels, this occurrence had little or no effect on compositions containing these fuels. The addition of heat by a thermite reaction alleviated the reduction somewhat, as did the reduction of excess fuel achieved by using a less fuel rich composition. While a composition using a mixture of Mg/Al powder as a fuel was degraded by reduced pressure, using an alloy of about the same metal composition was not. This was due to the boiling point of the alloy being closer to that of Mg than Al. The powder mixture, on the other hand, performed as if it were two different fuels and there was still a large excess of Al.

Another unexpected occurrence also took place. The very fuel rich composition containing Mg burned more slowly in oxygen than in air, helium or argon. The reason was the very high reactivity of molten Mg at the burning surface which reacted rapidly with oxygen at the burning surface to form MgO, which had a much lower thermal conductivity. Therefore, the heat cannot be transferred back into the composition as rapidly, and the burning rate was reduced. Al, Zn, and Ti were not as reactive, being covered by protective coatings, so they do not exhibit this behavior.

It appears that the cause of the reduction in burning rate of Al containing compositions is the inherent physical properties of the Al, and the problem cannot be surmounted in any practical way to produce a composition useful at both sea level and high altitudes.

Table 1. Effect of altitude on the burning rate of Al-oxidant and Mg-oxidant compositions

<u>Fuel-oxidant</u>	<u>Burning rate (cm/s)</u>		<u>Percent decrease at altitude</u>
	<u>Ambient</u>	<u>40,000 ft</u>	
Al-NaNO ₃	0.318	0.168*	47
Al-KC10 ₄	0.210	0.101	52
Al-TFE	0.151	0.081	47
Mg-NaNO ₃	0.143	0.125*	12
Mg-TFE	0.218	0.201	8

*20,000 ft

Table 2. Effect of Fe₂O₃ content and altitude on the burning rate of compositions containing Al and Teflon

% Fe ₂ O ₃	<u>Burning rate (cm/s)</u>		<u>Percent decrease at altitude</u>
	<u>Ambient</u>	<u>40,000 ft</u>	
	<u>Al fuel</u>		
0	0.196	0.066	66
2	0.183	0.075	59
4	0.195	0.088	55
6	0.213	0.096	55
	<u>25/75 Mg/Al powder fuel</u>		
0	0.158	0.079	50
2	0.241	0.105	56
4	0.212	0.121	43
6	0.220	0.111	50
	<u>1/1 Al:Fe₂O₃</u>		
	0.086	0.056	35

Table 3. Effect of additives on the burning rate of Al-TFE-binder compositions in air at ambient and altitude

<u>Additive</u>	<u>Burning rate (cm/s)</u>		<u>Percent decrease at altitude</u>
	<u>Ambient</u>	<u>40,000 ft</u>	
None	0.196	0.066	66
Abraded Al ^a	0.128	0.040	68
KA38S titanate	0.173	0.068	61
ZnF ₂	0.185	0.069	63
KBF ₄	0.170	0.049	71
Neptune G flux (no binder)	0.100	0.053 ^b	46
30/70 Mg/Al alloy ^a	0.264	0.217	18
50/50 Mg/Al alloy ^a	0.140	0.165	17 (inc)
Al/Si powder fuel ^a	0.129	0.034	74
Al/Si powder fuel (with Fe ₂ O ₃)	0.173	0.053	75

^aNo additive

^b25,000 ft

Table 4. Effect of various atmospheres and pressure on the burning rate of Al-TFE compositions

<u>Atmosphere</u>	<u>Burning rate (cm/s)</u>		<u>Percent decrease at altitude</u>
	<u>Ambient</u>	<u>40,000 ft</u>	
Air	0.151	0.081	47
Oxygen	0.145	0.078	46
Argon	0.165	0.099	40
Helium	0.159	0.091	43

Table 5. Physical data for various fuels

<u>Fuels</u>	<u>Boiling point (°C)^a</u>	<u>Boiling point at 40,000 ft (°C)^b</u>	<u>Heat of vaporization (Kcal/mole)^a</u>	<u>P-B ratio</u>
Al	2467	2142	67.9	1.48
Mg	1110	938	32.5	0.81
Ti	3290	2933	107.0	1.73
B	2550 (subl)	2335 (subl)	114.0	3.14
Zn	907	759	27.4	1.59
Ca	1490	957 (100,000 ft)	36.7	0.64

^aTaken from the Handbook of Chemistry and Physics (ref 3)

^bCalculated from equation in Handbook of Physical Chemistry (ref 5)

Table 6. Effect of atmospheric content and altitude on the burning rate of compositions containing fuels with various boiling points

Fuel	Boiling point (°C)	Burning rates				Pressure
		Air	Oxygen	Argon	Helium	
Al	3467	0.151	0.144	0.115	0.159	Ambient
		0.081	0.078	0.099	0.091	40,000 ft
		47	56	50	54	% dec at alt
Ti	3290	0.318	0.318	0.328	0.320	Ambient
		0.146	0.141	0.163	0.141	40,000 ft
		54	56	50	56	% dec at alt
B	2550(subl)	0.131				Ambient
		0.036				40,000 ft
		73				% dec at alt
Mg	1110	0.220	0.148	0.241	0.228	Ambient
		0.201	0.148	0.233	0.225	40,000 ft
		6	0	3	2	% dec at alt
Zn	907	0.78	0.79			Ambient
		0.78	0.77			40,000 ft
		0	2			% dec at alt
Ca	1490	2.68*				Ambient
		1.93				100,000 ft
		28				% dec at alt

*Taken from "Progress Report Covering High Altitude Flare Research" (ref 6)

Table 7. Shidlovskiy temperature calculations

<u>Chemical Reaction</u>	<u>Temperature calculation (°C)</u>
$2.26 \text{ Al} + 0.3 \text{ C}_2\text{F}_4 \rightarrow 0.4 \text{ AlF}_3 + 0.6 \text{ C} + 1.86 \text{ Al}$	Est. = 1427 Calc. = 1357
$1.48 \text{ Al} + 0.51 \text{ C}_2\text{F}_4 \rightarrow 0.68 \text{ AlF}_3 + 1.02 \text{ C} + 0.8 \text{ Al}$	Est. = 2427 Calc. = 2400
$1.85 \text{ Al} + 0.588 \text{ NaNO}_3 \rightarrow 0.588 \text{ Al}_2\text{O}_3 + 0.294 \text{ N}_2 + 0.588 \text{ Na} + 0.674 \text{ Al}$	Est. = 2527 Calc. = 2689
$1.96 \text{ Al} + 0.32 \text{ KClO}_4 \rightarrow 0.43 \text{ Al}_2\text{O}_3 + 0.323 \text{ KCl} + 1.1 \text{ Al}$	Est. = 2527 Calc. = 2462
$1.36 \text{ Ti} + 0.3 \text{ C}_2\text{F}_4 \rightarrow 0.4 \text{ TiF}_3 + 0.6 \text{ C} + 0.96 \text{ Ti}$	Est. = 2227 Calc. = 2204
$2.54 \text{ Mg} + 0.34 \text{ C}_2\text{F}_4 \rightarrow 0.68 \text{ MgF}_2 + 0.68 \text{ C} + 1.86 \text{ Mg}$	Est. = 1427 Calc. = 1390
$1.98 \text{ Mg} + 0.559 \text{ NaNO}_3 \rightarrow 1.68 \text{ MgO} + 0.28 \text{ N}_2 + 0.559 \text{ Na} + 0.3 \text{ Mg}^a$	Est. = 2927 Calc. = 3832
$2.13 \text{ Ca} + 0.18 \text{ NaNO}_3 \rightarrow 0.54 \text{ CaO} + 0.09 \text{ N}_2 + 0.18 \text{ Na} + 1.59 \text{ Ca}$	Est. = 1427 Calc. = 1740
(Ca would vaporize at 1490°C but the total heat of vaporation is greater than the heat of reaction.)	
$4 \text{ B} + 2 \text{ KNO}_3 \rightarrow 2 \text{ B}_2\text{O}_3 + 2 \text{ K} + \text{N}_2 + \text{excess B}$	Est. = 2427 Calc. = 2372

^aSome authorities cite the boiling point of MgO as 3077°C but no heat of vaporation is listed. A heat of only 26 Kcal/mole would be sufficient to lower the calculated temperature to 3077°C.

Table 7. (cont)

<u>Chemical Reaction</u>	<u>Temperature calculation (°C)</u>
$1.0 \text{ Zn} + 0.3 \text{ C}_2\text{F}_4 \rightarrow 0.6 \text{ ZnF}_2 + 0.6 \text{ C} + 0.4 \text{ Zn}^b$	Est. = 927 Calc. = 2395

^bNo data could be found for ZnF_2 except that it vaporized around 1500°C . If heat of fusion is assumed as 5 and heat of vaporization as 40.8 Kcal/mole, it is found that the estimate is 1427°C and the calculated is 1455°C .

Table 8. Effect of various atmospheres and pressure on the burning rate of a composition containing a low amount of Al

<u>Atmosphere</u>	<u>Burning rate (cm/s)</u>		<u>Percent decrease at altitude</u>
	<u>Ambient</u>	<u>40,000 ft</u>	
Air	0.076	0.063	17
Oxygen	0.076	0.065	14
Argon	0.078	0.059	24
Helium	0.071	0.058	19

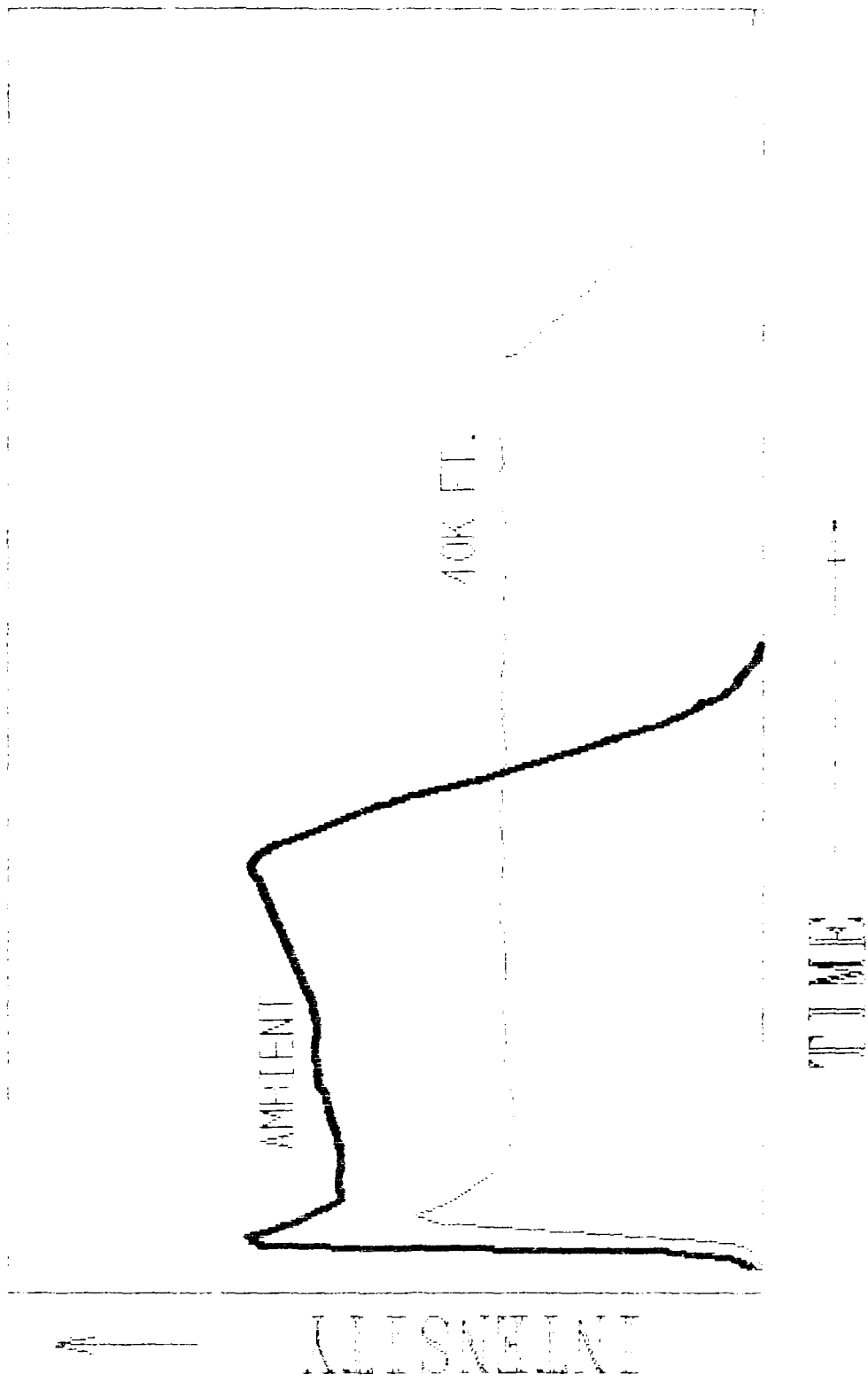
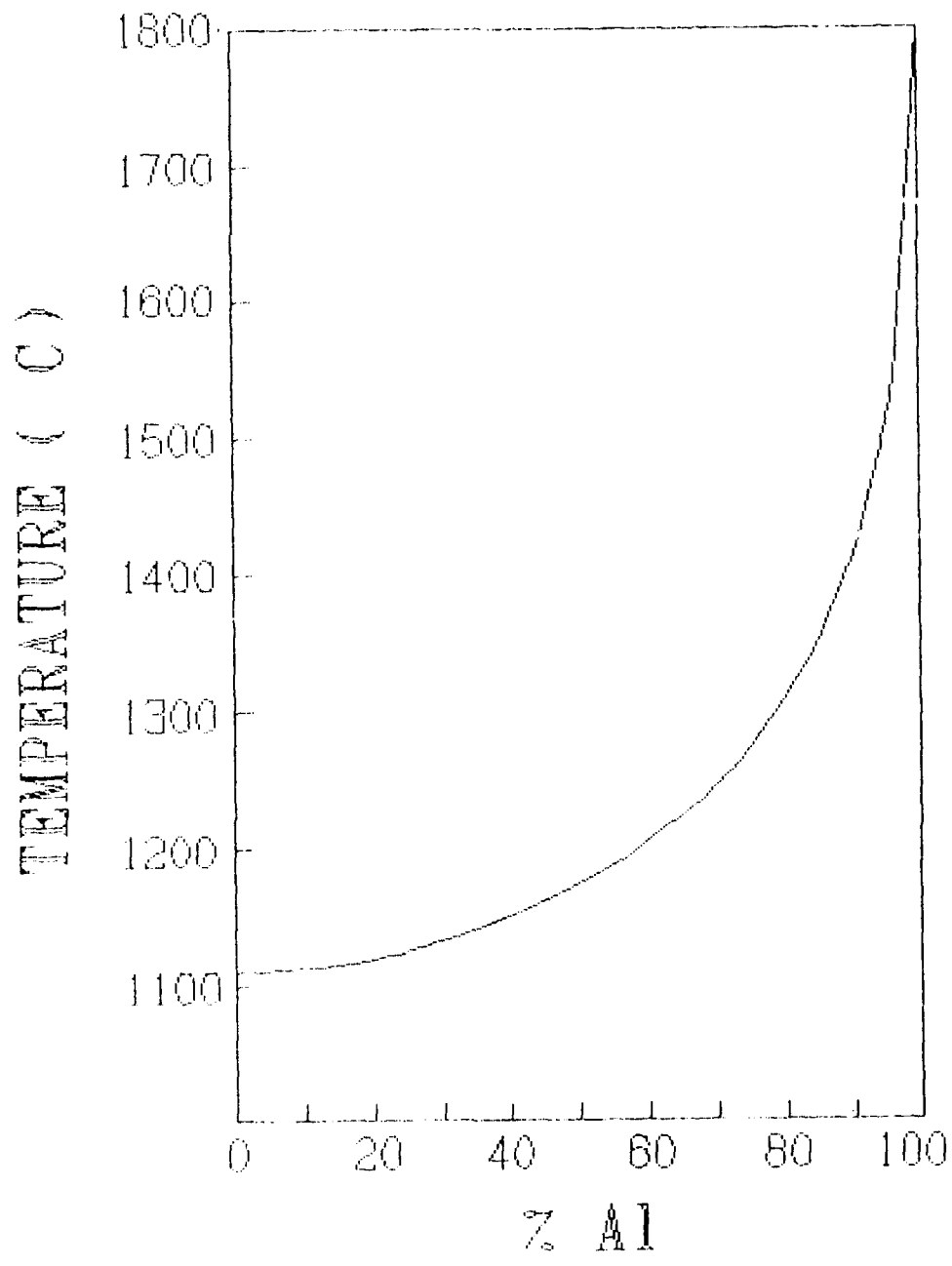


Figure 1. The effect of altitude on the burning time and intensity of an Al-containing composition



NOTE: Liddell, D. M. and Doan, G. E., The Principles of Metallurgy, McGraw-Hill Book Company, Inc., New York, 1933.

Figure 2. Boiling points of magnesium/aluminum alloys

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