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Ignition and Combustion of Metals in a Carbon Dioxide Stream

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Abstract

In the prospect of using metals as fuel of breathing combustion engines in carbon dioxide rich planet atmospheres without oxygen such as those of Mars and Venus, a fundamental study was performed experimentally on the ignition and combustion of metals in an impinging pure CO₂ gas stream. Metals selected were lithium, magnesium, boron and aluminum, because of their high heats of reaction with CO₂. To help the understanding of combustion processes of the metals in CO₂, the chemical equilibrium compositions of reaction products and flame temperatures were calculated, and compared with the experimental results.

Li and Mg could ignite spontaneously in the CO₂ stream. The ignition process of Li in the CO₂ stream had two distinct steps, first a surface reaction and then a gas phase reaction. This process was found to be similar to the those of Mg and Na in air streams, but was different from that of Li in an air stream. The spontaneous ignition temperature of Li in the CO₂ stream was much lower than that in the air stream. It was also found that Li burned in vapor-phase at first and then on the metal surface. At the ignition in the CO₂ stream, the Mg surface was covered with a protective film against further oxidation, resulting a higher spontaneous ignition temperature than that in the air stream. Mg could burn in vapor-phase. B could not ignite in the CO₂ stream, but the reactions occurred appreciably on the surface. The reaction rate was quite slow, compared with that in an oxygen stream, and the molten boron oxide appeared on its surface. Al could not ignite within the temperature limits of our apparatus. However, the possibility of its ignition and combustion in the CO₂ stream was demonstrated in a different experiment allowing the attainment of somewhat higher temperatures.

Introduction

In the future an aircraft type vehicle could be used to do the surveys of the planets Mars and Venus. For the purpose, a propulsion engine which can work in the planet atmospheres of the interest, consisting of carbon dioxide, must be developed. Earlier, we proposed a CO₂-breathing engine using metals as fuel¹. The attractive metals for this purpose are lithium, magnesium, boron, and aluminum, because of their high heats of reaction with CO₂¹. As the first step to develop a combustor for the engine, the ignition and combustion characteristics of these metals in CO₂ atmosphere must be made clear.

Up to the present, only limited studies have been made on ignition and combustion of metals in CO₂-inert mixtures or pure CO₂^{2,3}, though numerous experimental studies have been done on the metal ignition and combustion in O₂ containing atmospheres. Mellor and Glassman² and Merzhanov et al.³ ignited Al wires by electrical heating in CO₂-A mixtures and in pure CO₂ streams. They found that Al burned in those atmospheres. However, details of the phenomena involved in the ignition and combustion have not been made clear so far. Mellor and Glassman² also heated Mg ribbons in the same mixtures, and observed that Mg did not burn in the mixtures. The result may be attributed to a disadvantage of the wire heating method that the metal will break before ignition, unless a reaction product film over the metal surface supports the metal after the melting point of the metal is attained. For the ignition and combustion of B, there is no experimental study in CO₂ atmospheres except for the single-particle work of Macek and Semple⁴. They observed that single particles (~45μ) burned even in a hot gas containing very low O₂ and high CO₂. Some phenomena concerning the

ignition and combustion were described in the report, but they were not well defined. To our knowledge, no work has been reported on ignition and combustion of Li in CO₂ atmospheres.

The purpose of the present study is to obtain some fundamental information on the ignition and combustion of Li, Mg, B and Al in pure CO₂ atmosphere. The calculation of equilibrium compositions and flame temperatures of the metal-CO₂ systems was performed, and an experimental investigation on the spontaneous ignition and on the combustion of the metals in a pure CO₂ stream was carried out. A stagnation region of the CO₂ stream was used to make the flow field and physicochemical processes as simple as possible, and to facilitate the experimental observation. For comparison purposes, an air stream was also used as an oxidizer.

Equilibrium Compositions and Flame Temperatures

The equilibrium compositions, involving condensed species, and flame temperatures of the metal-CO₂ systems may help to understand the combustion processes of the metals. Calculations were made at atmospheric pressure for Li and B by the NASA-SP-273 computer program⁵, and for Mg and Al by our simple program¹ developed for a personal computer. (The results calculated by the simple program were compared with those by the NASA program, and they were confirmed to agree within the accuracy of thermochemical data⁶.) Metal carbides were not considered in the calculations by both programs because of their insufficient thermochemical data (see Ref. 5 and 7).

The calculated flame temperatures are shown in Fig. 1, and the equilibrium compositions in Fig. 2 against equivalence ratio, where a stoichiometric reaction is defined as the reaction in which a

stable metal oxide and CO are formed. The flame temperatures of Mg and Al with CO₂ are much higher than those of ordinary hydrocarbons with air⁸. The flame temperatures of Li and B, on the other hand, are similar or lower than those of hydrocarbons with air. The reason for these differences is that, on a mass base of CO₂ or air, Mg and Al liberate more heat than B and hydrocarbons. The low flame temperature of Li, though it has a high heat of reaction, is due to latent heats of vaporization of Li and fusion of Li₂O. It should be noted that, for all of the metals, the reactions with CO₂ mainly produce CO and their condensed metal oxides, and that no carbon deposition in Mg and Al flames occurs because appreciable amounts of free oxygen are present at equilibrium⁹. For Li and B, on the contrary, the deposition occurs on the rich side of the metal-CO₂ systems as there hardly exists free oxygen. The flame temperatures of Li and B on the rich side vary only slightly with the equivalence ratio, because of carbon deposition and condensation of metal vapors. When the melting points of oxides are reached, phase transitions occur and flame temperatures remain constant. These can be seen on the lean side of Li-CO₂ system in Fig. 2(a) and on the lean and rich sides of Al-CO₂ system in Fig. 2(d).

Experimental Apparatus and Procedure

Figure 3 shows a schematic of the experimental apparatus used in this study. A combustion chamber had a horizontally mounted resistance heater with a depression at the center, an axially symmetric converging nozzle, and quartz windows, through which the Xe beam passed, to allow photographic and emission spectrum observations. CO₂ gas, after passing through a rectifying screen, issued from the nozzle with an exit diameter of 30 mm into a

spherical part of the chamber with a uniform velocity distribution. Throughout the present study, the nozzle exit velocity of the CO₂ gas was kept constant at 0.5 m/s. The CO₂ gas impinged on a sample holder (20 mm in diameter, 10 mm in height), which was situated at 25 mm downstream of the nozzle exit to produce a stagnation flow over it. The holder was made of MgO, and had a depression (10 mm in diameter, 3 mm in depth) in which a metal sample was just fitted through an exchangeable receptacle, made of very thin molybdenum or stainless steel (0.02 mm thick) to avoid reactions between the holder and the metals. The sample was heated through the sample holder by the heater (75 mm long, 20 mm wide, and 0.3 mm thick), made of molybdenum which does not react appreciably with CO₂. (When air was used as an oxidizer, a heater made of Kanthal with the same dimensions was used.) The Xe arc lamp with an elliptical reflecting mirror (400 mm in diameter) was also used for additional heating.

Li, Mg, B and Al used in this study have the purities of 99.0%, 99.9%, 99.5%, and 99.85%, respectively. Li and Mg were obtained in rod form, and Al in plate form. They were all cut to the sample shape. However, B was obtained in crystal lump form (3~5 mm), and the lump itself was used without cutting because B was too hard and breakable to make a shape. Just prior to a test run, Li sample was washed quickly in acetone, and the others in carbon tetrachloride to remove oil on the surfaces. In a test run, after the chamber was evacuated, it was filled with an inert gas, usually helium, sometimes argon, at the atmospheric pressure. Then, the sample was heated in the inert gas stream. The Li and the Mg samples were heated by the heater only, and the B and the Al samples by both of the heater and the Xe lamp to obtain much higher temperature. When the sample temperature became uniform at a predetermined value, the test run was started by feeding the CO₂ gas to sweep the inert gas

away and expose the sample to the CO₂ stream. The flow rate of the inert gas was adjusted so as to equalize the sample temperature before and after the gas replacement.

The sample temperature was measured by a thermocouple inserted in the sample from the backside. Chromel-alumel (0.1 mm wire diameter) thermocouples were used for the Li and the Mg samples, and a Pt/Pt-13%Re (0.2 mm wire diameter) or a W-5%Re/W-26%Re (0.25 mm wire diameter) thermocouple for the B and the Al samples. They were calibrated beforehand by measuring the melting points of the samples and other standard metals. Emission spectra were photographed with a grating spectroscopy via a quartz fiber light guide. Gaseous combustion products were checked by sampling during combustion at the combustion chamber exit, and analyzed by a gas chromatograph.

In the present study, the definitions of ignition and several temperatures were essentially the same as in previous studies^{10,11}: i.e., ignition is defined as the instant when a flame appears on the surface, the initial sample temperature T_{in} is the sample temperature at the instant when the sample is exposed to the CO₂ stream, the critical ignition temperature T_{cr} is the lowest T_{in} at which the sample heats up by itself to ignition, and the ignition temperature T_{ig} is the sample temperature at the instant of ignition.

Experimental Results and Discussion

(1) Lithium

Li could be spontaneously ignited in the CO₂ stream. To determine an ignition limit, the ignition delay time t_d was measured as a function of T_{in} . Here t_d was defined as the time elapsed from the instant when CO₂ was introduced into the chamber to the instant

of ignition. Figure 4-(a) shows the observed t_d plotted against T_{in} in the CO_2 stream. The value of t_d increased with decreasing T_{in} , and when T_{in} was decreased below a critical value of $340^\circ C$, the ignition did not occur at least in twenty minutes. This value was identified as T_{cr} . For the comparison, t_d in the air stream with the same nozzle exit velocity as the CO_2 stream is shown in Fig. 4-(b). It can be seen that t_d varied little with T_{in} , always being a few seconds. With decreasing T_{in} , the ignition limit suddenly occurred. T_{cr} in air, $710^\circ C$, was much higher than in CO_2 .

Figure 5-(1) shows a typical example of time variation of the sample temperature for Li from the instant of the exposure to the CO_2 stream to the beginning of combustion. The sample appearances at the instants designated by letters "a" to "d" on the temperature curve are shown in the photographs of Fig. 5-(2). In the inert gas stream, the sample was observed to have a metallic luster surface, and actively ejected its reddish vapor. (Vapor was visible at the sample temperatures above $400\sim 440^\circ C$, much lower than the boiling point of Li ($1347^\circ C$.) At the instant when it was exposed to the CO_2 stream, its surface was immediately covered with a gray film, and vapor was no longer observable (Fig.5-(2)-(a)). On the other hand, the sample temperature started to increase. This indicates that the exothermic surface reactions occur in the CO_2 stream. As the surface reactions proceeded, the gray film began to turn black and several wrinkles appeared on the surface about time "b". About time "c", the wrinkles began to increase in number until the sample was completely covered with them. Corresponding to this, the sample temperature began to increase rapidly. This situation will be termed "transition". The sample temperature at the instant of "transition" was $470\sim 550^\circ C$. As the temperature increased further, the wrinkles suddenly disappeared, and immediately after that, at

"d", a bright yellow-reddish flame appeared over the surface, indicating ignition. T_{ig} was observed to be 840-890 °C. The average heat release rate was estimated from the temperature increase rate of the sample between "transition" and ignition by assuming that the reaction surface area was kept constant. It was about 40 J/(cm².s), insensitive to T_{in} . This rate was two orders of magnitude larger than that prior to "transition". This suggests that the surface reaction mechanism changes drastically after "transition", even though there is evidence that the reaction surface area also increases substantially due to the development of the unevenness of the sample surface. The observed ignition process of Li in the CO₂ stream was found to be very similar to those of Mg and Na in the air streams^{10,11}, which belong to the same group as Li¹². This fact implies that the ignition mechanisms of Mg and Na in the air streams and that of Li in the CO₂ stream followed similar ignition processes. The ignition mechanism proposed in the previous papers for the ignition of Mg and Na in the air streams^{10,11} is that "transition" occurs at the instant when the rate limiting step changes from the surface reaction to O₂ diffusion through the boundary layer over the sample surface. This mechanism could be also true in the case of Li in the CO₂ stream. In the air stream, on the other hand, the sample appearances and the sample temperatures of Li during the ignition process were observed to be rather different from those in the CO₂ stream. In the case of ignition, no film was apparent on the sample surface, while it was exposed to the air stream. Besides, the sample temperature increased very rapidly from the beginning. The facts, that t_d was nearly insensitive to T_{in} and that T_{cr} in the air stream was much higher than "transition" temperature in the CO₂ stream, suggest that, in the air stream at below T_{cr} , surface reactions form a

protective film against further oxidation at the beginning, but when T_{in} exceeds T_{cr} , the film immediately becomes non-protective or disappears, resulting in directly exposed Li surface. Consequently, the O_2 diffusion through the boundary layer becomes the rate limiting step for the ignition process.

Duration of flaming combustion in the CO_2 stream was about two seconds, during which time only small quantities of white smoke were generated. After that, however, the sample continued to be heated red over a period of 20~30 sec. The final products were black and hard, sticking to the sample holder, differing from the grayish brown powder products in the case of combustion in the air stream. Figure 6-(a) shows the emission spectrum of the Li flame with the identified characteristic lines. The presence of Li lines indicates that Li was burning in the gaseous phase. CO was found in the measured gaseous combustion products leaving the chamber. This agrees with the calculation of equilibrium compositions. However, the measured CO concentration was one or two orders of magnitude lower than the value expected if the whole sample had burned out in two seconds in gaseous phase. These results suggest that most of the sample reacted in solid phase to produce solid products, including Li_2C_2 or C.

(2) Magnesium

Figures 7-(b) and (a) show the observed t_d plotted against T_{in} for the Mg sample in the CO_2 stream and in the air stream, respectively. In the case of CO_2 stream, t_d hardly varied with decreasing T_{in} , and when T_{in} decreased below $T_{cr}=851^\circ C$, the ignition did not occur. On the other hand, in the air stream, t_d increased substantially with decreasing T_{in} , and T_{cr} was $628^\circ C$, which was close to the previously obtained value in the hot air stream¹⁰. The

observed value of T_{cr} in the CO_2 stream was much higher than that in the air stream. This suggests that the reaction film formed during the ignition process in the CO_2 stream had properties different from that in the air stream.

Figure 8-(1) shows a typical example of time variation of the sample temperature for Mg from the instant of the exposure to the CO_2 stream to the time when steady combustion was attained. The sample appearances corresponding to letters "a"~"d" of Fig. 8-(1) are shown in Fig. 8-(2). Prior to the CO_2 exposure, the Mg sample also ejected its vapor actively. (Vapor was visible above the melting point of Mg ($650^\circ C$.) As soon as it was exposed to the stream, the sample surface was uniformly covered with a gray reaction film (Fig.8-(2)-(a)). This was followed by the appearance of a black reaction film (Fig.8-(2)-(b)), with a corresponding increase in the sample temperature. In the case of non-ignition, no change from a gray film to a black film occurred. As the temperature increased due to the exothermic surface reactions with CO_2 , wrinkles appeared over the surface about time "c", and then the surface as a whole became red hot (Fig.8-(2)-(c)). Finally one or more incandescent flames appeared locally, which produced ignition. ^{(Fig.8-(2)-(d))} This ignition process was different from that observed in the air stream; i.e., just prior to the ignition, the surface unevenness disappeared suddenly to yield a smooth flat surface of liquid metal, and then a reddish purple emission spread over the whole surface leading to the uniform ignition with an incandescent flame. T_{ig} in the CO_2 stream was $950\sim 990^\circ C$, which was higher than $T_{ig}=840\sim 870^\circ C$ in the air stream. The average heat release rate between "transition" and ignition was about $12 J/(cm^2 \cdot s)$, which was insensitive to T_{in} over the range tested. The value was lower than that of about $20 J/(cm^2 \cdot s)$ in the air stream. The difference in heat release rate

is approximately explained by the difference in heat of reaction with CO_2 and O_2 . This implies that Mg can react with CO_2 as fast as with O_2 . In addition, the results suggest the ignition mechanism of Mg in CO_2 as follows. When T_{in} is lower than T_{cr} , surface reactions proceed initially to form a protective film on the sample surface, inhibiting further oxidation. (In the present study, the composition of the film was not determined.) On the contrary, when T_{in} is higher than T_{cr} , the film formed in early reaction stages becomes non-protective. One of the reasons for this may be high enough pressure of Mg vapor (for example, about 60 mmHg at 850°C). Once Mg vapor permeates through the film, which is probably porous, CO_2 diffusion through the boundary layer over the sample surface becomes the rate limiting step because it is considered to be much slower than gas phase reactions. This is supported by the observed insensitivity of t_d to T_{in} in the CO_2 stream. While the film is not perfectly broken, the flames appear locally (as will be shown below).

After ignition, the Mg sample continued to burn with several incandescent flames and with a large amount of white smoke for a period of 30~40 sec, during which the sample temperature remained $1000\sim 1050^\circ\text{C}$ close to the boiling point of Mg (1107°C). 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, inside of which no residue existed. The corresponding flame spectrum is shown in Fig. 6-(b). The atomic lines of Mg and the bands of MgO were visible, in agreement with observations of several other investigators^{10,12,13} for Mg flames in oxidizing atmospheres. CO

was found in the combustion products by the gas analysis of the 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 of the Mg sample burned in gaseous phase to produce CO and MgO.

(3) Boron

For B, ignition, which was characterized by a rapid increase of the sample temperature and followed by self-sustained combustion, did not occur in the CO₂ stream at T_{in} up to the theoretical stoichiometric flame temperature (1684°C). However, exothermic surface reactions were observed. Figure 9 shows a typical example of sample appearances during the reaction process at $T_{in}=1670^{\circ}\text{C}$. Figure 9-(a) represents the sample (weight: about 0.35 g) just before the exposure to the CO₂ stream, showing a clean and rough metal surface. As soon as the sample was exposed to the CO₂ stream, some white smoke was produced from its surface with a change of color from black to white, with a small attending temperature increase of the sample. The smoke was found to appear when the sample temperature exceeded about 1130~1160°C. The analysis of gaseous reaction products showed that CO was generated during the process, suggesting that the smoke was B₂O₃ condensed in the surrounding open space. Therefore, it is clear that surface reactions proceed in the CO₂ stream. This is supported by subsequent observations. As the reactions proceeded, the sample surface became smooth (Fig.9-(b)); this suggests that the sample surface was raised to its melting point due to the exothermic surface reactions. The photograph shows also that there existed many droplets on the sample surface. They were probably molten B₂O₃ failing to evaporate from the surface. They had agglomerated to make a pool on the

surface (Fig.9-(c)). It may be inferred that the thickness of the molten boron oxide layer covering the metal surface remained almost constant due to removal by agglomeration and evaporation. Besides, it should be noted that even at this time the sample was almost identical in size and shape with the original one. It took about ten minutes until all of the sample was consumed. This is in approximate agreement with the time estimated from the measured CO concentration, indicating that the overall reaction of B with CO₂ through the B₂O₃ layer proceeded very slowly.

The low reaction rate in CO₂ was found to increase in air or in oxygen. Figure 9-(d) shows a typical sample appearance during the reaction process in the O₂ with the same nozzle velocity. It can be seen that large quantities of green-white smoke consisting of condensed B₂O₃ were generated surrounding the sample. The B sample was also melted perfectly and had a metallic surface. The consumption time in the stream was about one minute. The observations suggest that in the O₂ the B sample burned in the vapor-phase, which implies attainment of extremely high sample temperature. Unfortunately, the sample temperature could not be determined, because of melting of the thermocouple wires. However, assuming that its vapor pressure is similar to that of Li or Mg at ignition with a flame, the temperature of B may be estimated to be above 2600°C.

(4) Aluminum

The Al sample was not ignited in the CO₂ stream. The reason for this was that the sample temperature could not be raised high enough by radiation due to high reflectivity of Al. However, we tried an additional experiment, heating an Al sample directly in a depression of a small tungsten heater as high as possible. As a

result, the Al ignited and then burned with a very bright-white flame for a short period. Unfortunately, the sample temperature could not be determined due to the breaking of the thermocouple used as a result of an alloy reaction with Al and the extremely high temperature (probably above 2000°C).

Conclusions

The present study has revealed the ignition and combustion characteristics of lithium, magnesium, boron and aluminum in an impinging CO₂ stream as follows.

(1) Li and Mg could ignite and burn in the vapor phase in the CO₂ stream. B did not ignite, but could considerably react with CO₂ on its surface. (2) The spontaneous ignition temperatures of Li was much lower in CO₂ than in air. On the contrary, the ignition temperature of Mg was much higher in CO₂. (3) Al burned also, but the ignition temperature could not be determined. (4) For all the metals, condensed metal oxide and CO were the main products of combustion. (5) The stoichiometric theoretical flame temperatures of Mg and Al, nearly 3000 K, are much higher than those of Li and B, which are about 2000 K.

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References

1. Yuasa, S. and Isoda, H.: J. Japan Soc. Aero. Space Sci. 36, No. 409,(1988).
2. Mellor, A. M. and Glassman, I.: Heterogeneous Combustion (Wolfhard et al, Ed.), Vol. 15, p. 159, Academic Press, 1964.
3. Merzhanov, A. G., Grigorjev, Yu. M. and Gal'chenko, Yu. A.: Combust. Flame 29, 1 (1977).
4. Macek, A. and Semple, J. M.: Combust. Sci. Tech. 1, 191 (1969).
5. Gordon, S and McBride, B.: Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations, NASA SP-273, 1971.
6. Mitani, T.: personal communication.
7. JANAF Thermochemical Tables, 2nd ed., Office of Standard Reference Data, National Bureau of Standards, Washington, D.C., 1971, and 1974-1975-1978 and 1982 Supplement, The Dow Chemical Company, Michigan, 1974, 1975, 1978, 1982.
8. Kanury, A. M.: Introduction to Combustion Phenomena, p. 131, Gordon and Breach Science Publishers, 1985.
9. Penner, S. S.: Chemistry Problems in Jet Propulsion, p. 154, Pergamon Press, 1957.
10. Takeno, T. and Yuasa, S.: Combust. Sci. Tech. 21, 109 (1980).
11. Yuasa, S.: Twentieth Symposium (International) on Combustion, p. 1869, The Combustion Institute, 1984.
12. Brzustowski, T. A. and Glassman, I.: Heterogeneous Combustion (Wolfhard et al, Ed.), Vol. 15, p. 41, Academic Press, 1964.
13. Sullivan, H. F. and Glassman, I.: Combust. Sci. Tech. 4, 241 (1972).

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(d) in an oxygen stream, $T_{in}=1490^{\circ}\text{C}$.

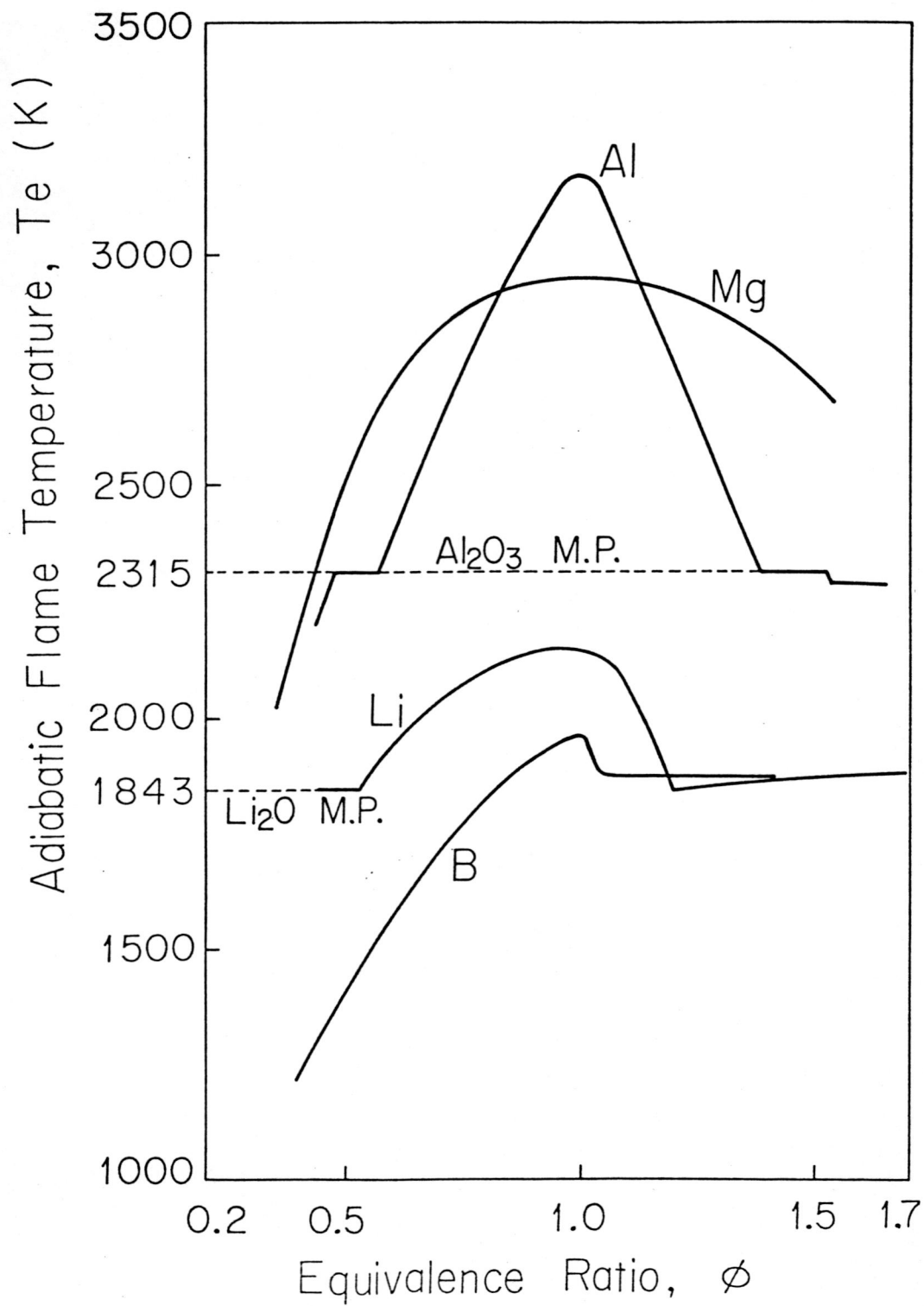


Fig. 1. Calculated temperatures of metal- CO_2 flames at 1 atm against equivalence ratio.

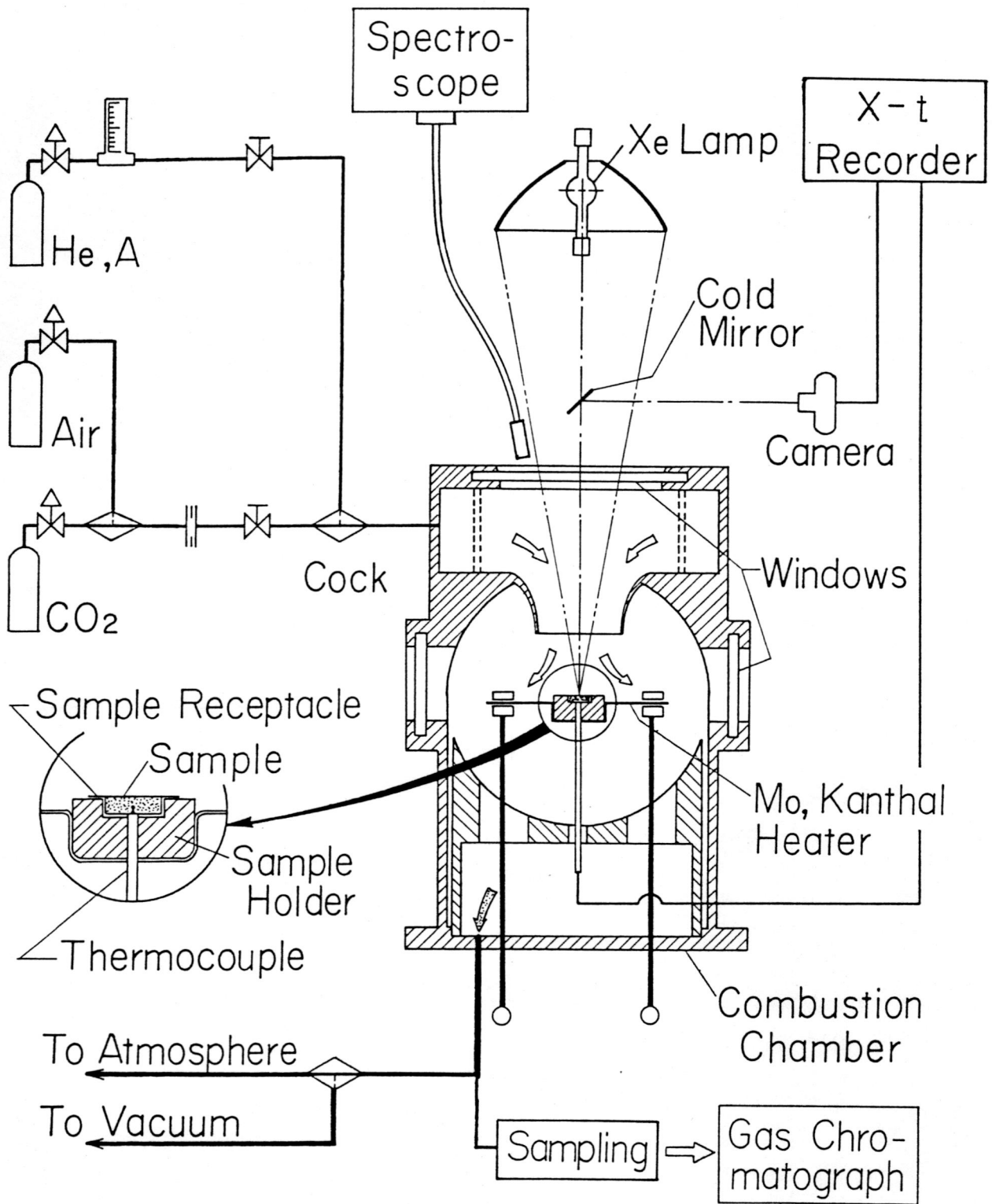


Fig. 3. Schematic of experimental apparatus.

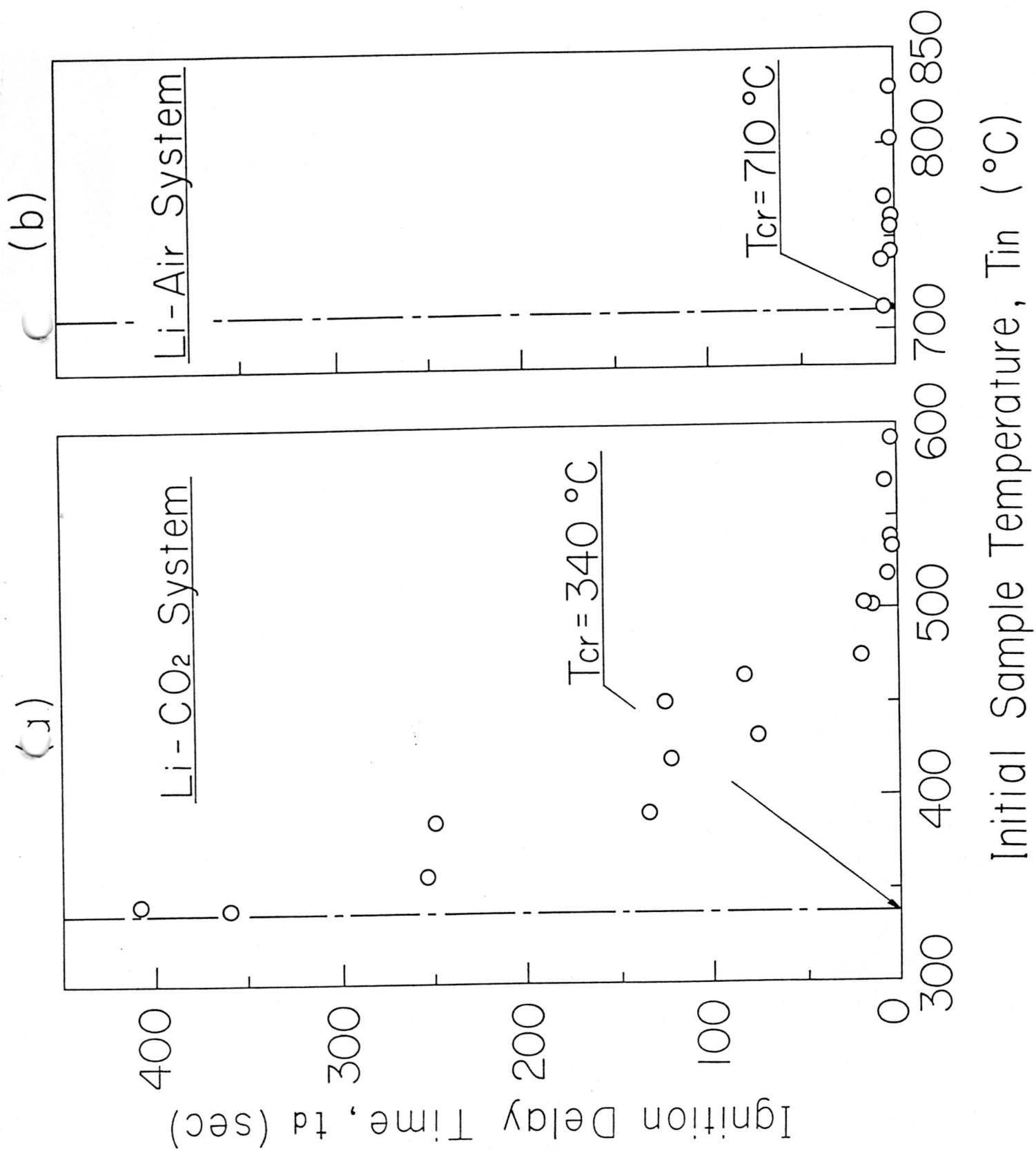


Fig. 4. Ignition delay time of lithium against initial sample temperature: (a) in a CO₂ stream, (b) in an air stream.

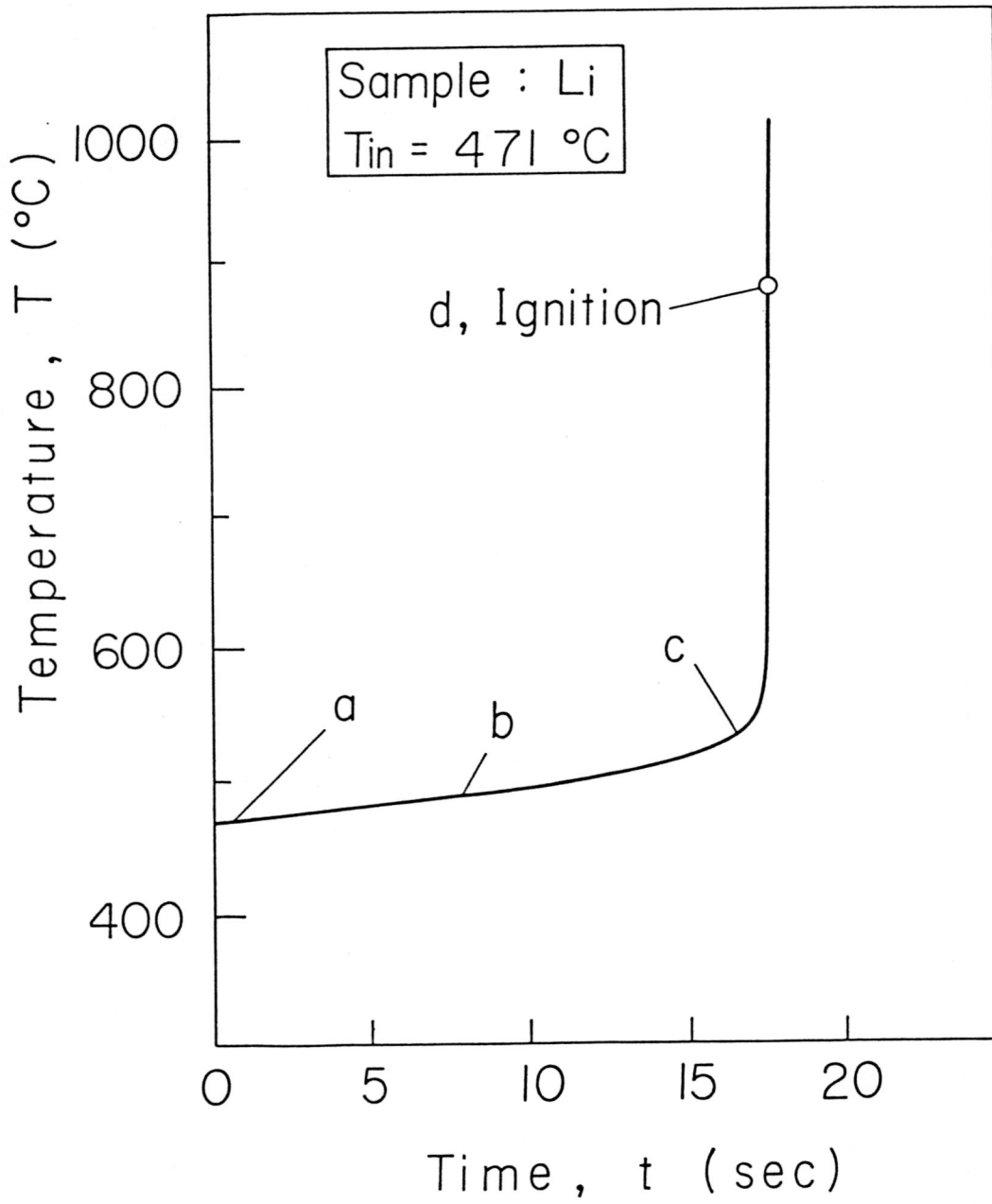


Fig. 5-(1). Time variation of sample temperature of lithium in a CO_2 stream.

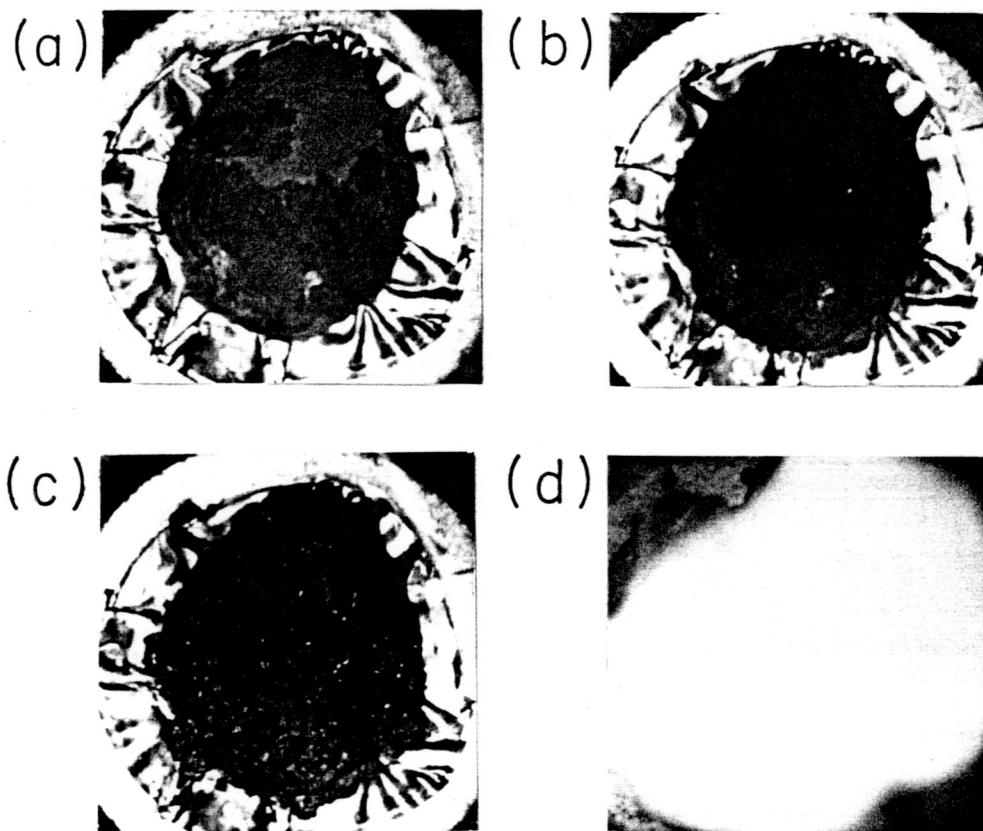


Fig. 5-(2). Direct photographs of sample appearances of lithium
in a CO_2 stream. $T_{\text{in}}=471^\circ\text{C}$.

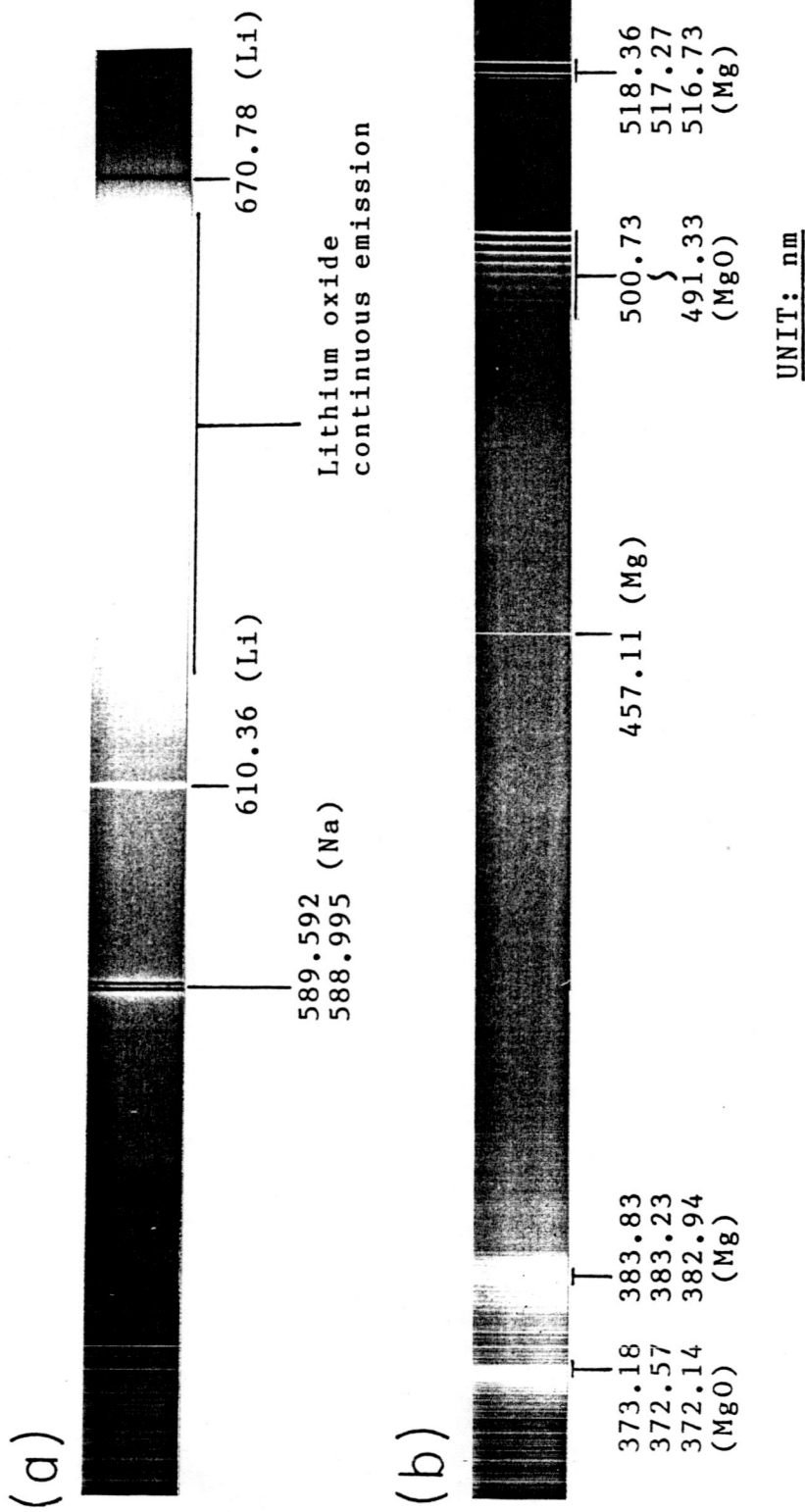


Fig. 6. Emission spectrum of metal-CO₂ flames with identified characteristic lines and bandheads: (a) lithium, (b) magnesium.

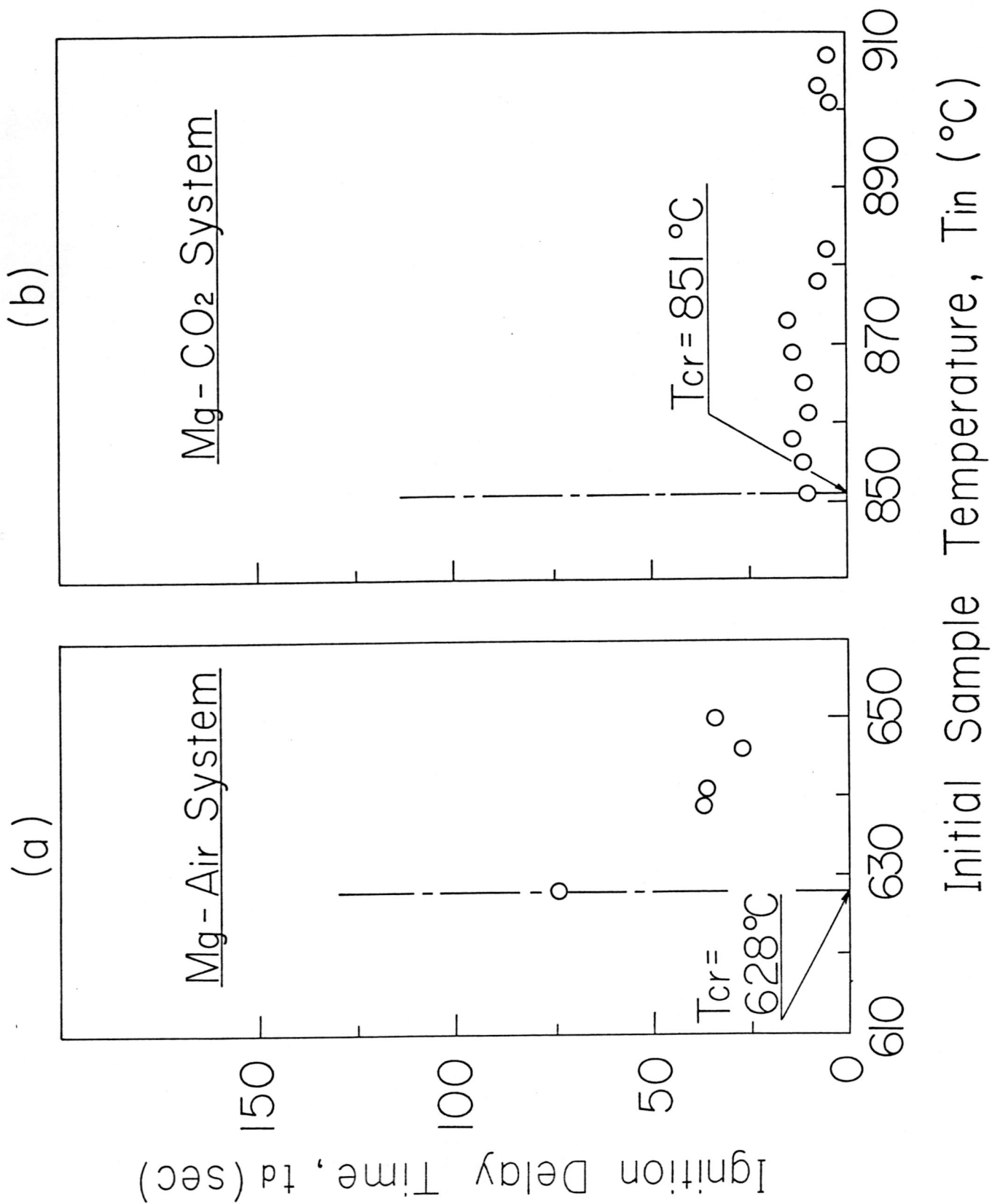


Fig. 7. Ignition delay time of magnesium against initial sample temperature: (a) in an air stream, (b) in a CO₂ stream.

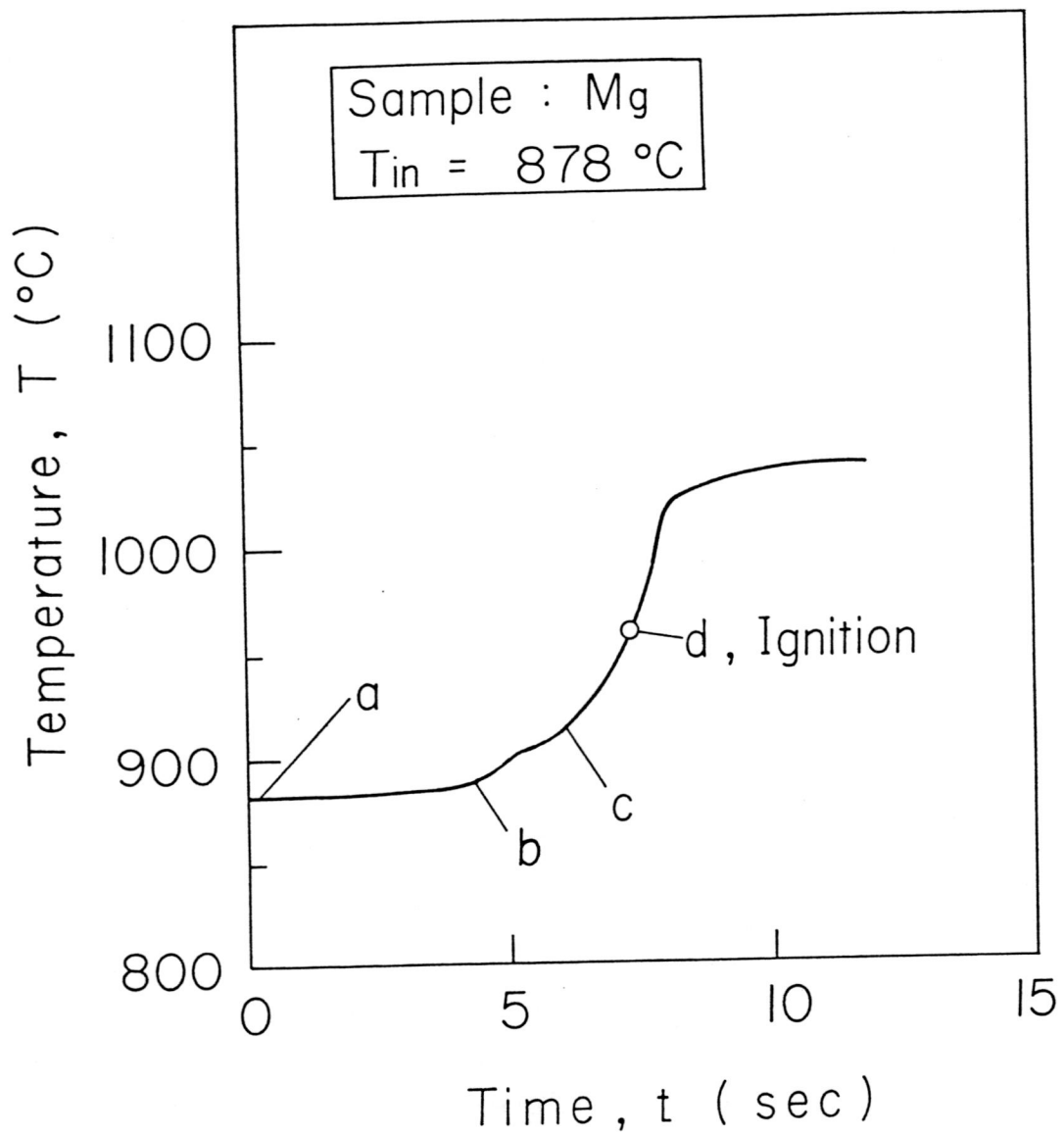


Fig. 8-(1). Time variation of sample temperature of magnesium in a CO_2 stream.

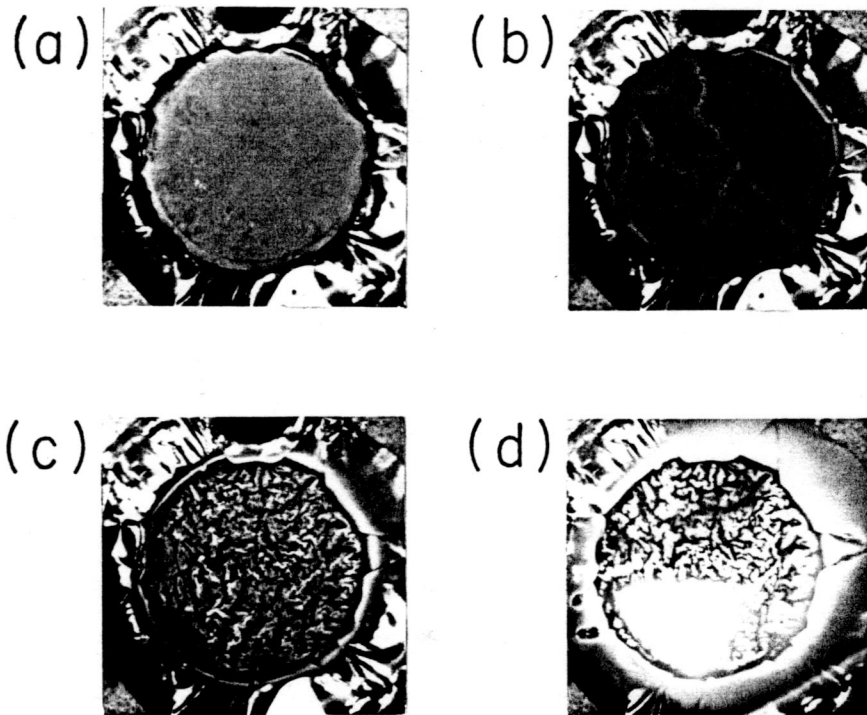


Fig. 8-(2). Direct photographs of sample appearances of magnesium in a CO_2 stream. $T_{\text{in}}=878^\circ\text{C}$.

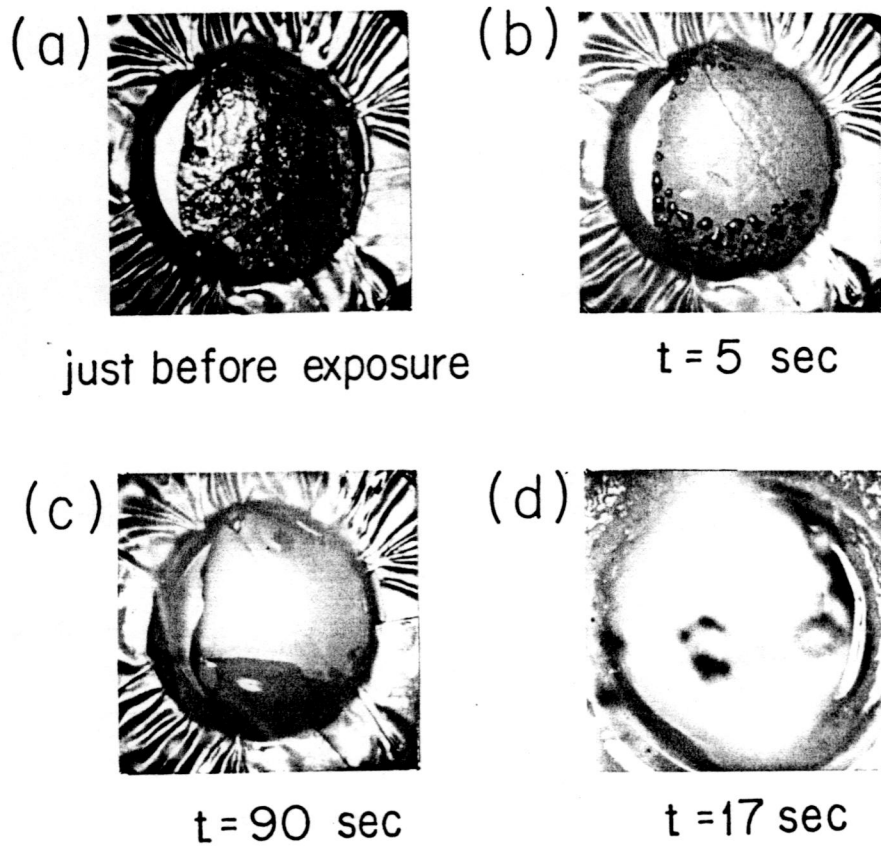


Fig. 9. Direct photographs of sample appearances of boron:

(a)~(c) in a CO_2 stream, $T_{\text{in}} = 1670^\circ\text{C}$;

(d) in an oxygen stream, $T_{\text{in}} = 1490^\circ\text{C}$.