JOURNAL OF SOLID STATE CHEMISTRY **12**, 72–79 (1975)

The Effect of Crystal Size on the Thermal Explosion of α-Lead Azide

M. M. CHAUDHRI AND J. E. FIELD

Physics and Chemistry of Solids, Cavendish Laboratory, Madingley Road, Cambridge, England

Received August 17, 1973

It is shown experimentally that the critical explosion temperature of α-lead azide crystals in air decreases with increase in size of the crystals. The mode of decomposition of the crystals was examined with optical and scanning electron microscopy, and it was found that surface decomposition took place preferentially at localized regions; crystal breakup also occurred. Calculations of explosion temperature for the case of parallelopiped shaped particles in air were made. The predicted decrease in the explosion temperature for an increase in crystal thickness from 4 to 34 μm (minimum dimension) was 6 K, whereas the experimental value was ~ 30 K. It is suggested that the difference between the experimental and theoretical results is due to the mode of decomposition during the preexplosion period. For crystals of thickness less than ~ 3 μm neither explosion nor melting took place even for temperatures as high as 825 K.

1. Introduction

Lead azide has great technological interest and it is important, therefore, to understand its explosive properties as fully as possible. The thermal decomposition of α-lead azide has been studied by many workers (*1–5*), though most believe that the decomposition is a surface phenomena there are conflicts of detail and magnitude in the published data on the kinetic parameters. When lead azide is heated to a high enough temperature it explodes. This is usually attributed to self-heating, though other ideas involving non-thermal processes have been suggested (*6–7*).

One approach to understanding the explosion of a material on heating is to study the effect of particle size on the critical explosion temperature. Bowden and Yoffe (*8*) give data for several explosives which exhibit a "critical size" for explosion at a particular temperature. For lead azide Hawkes and Winkler (*4*) and Bowden and Singh (*9*) have shown that the minimum dimension of a crystal controls its explosion temperature and that this temperature decreases with increasing crystal dimension. A size effect has also been found for pellets of lead azide (*10*). However, in experiments on batches of lead azide crystals in vacuum Groocock (*11*) found no significant size effect. Groocock also analysed the explosion conditions for a particle of lead azide decomposing in conditions of restricted heat transfer; the analysis predicted no variation of explosion temperature with particle diameter.

Here we describe experiments on the influence of the size of α-lead azide crystals on their thermal explosion temperature in air. The minimum dimension (i.e., thickness) of the crystals was varied down to micron dimensions. Lead azide has advantages for this kind of study since it does not melt before explosion even up to 825 K: many other azides (for example, silver azide) melt before their explosion (*8*). Calculations were also made to predict the critical explosion temperature for these crystals under different heat transfer conditions (air and vacuum). In air the heat transfer coefficient between a crystal and its surroundings is dependent on crystal size, and this results in a predicted

Printed in Great Britain

dependence of critical explosion temperature on thickness.

2. Experimental

Experiments were performed on fresh individual single crystals grown in the laboratory by slowly neutralizing hydrazoic acid with lead nitrate solution. The crystals were stored in the dark and in a dry atmosphere.

The determination of the critical temperatures was made in a furnace shown schematically in Fig. 1. It consisted of a silver cylinder 36 mm long and 20 mm in diameter, in one end of which a 14 mm diameter and 4 mm deep hole was drilled along the axis. A calibrated alumel–chromel thermocouple was placed at the centre of the hole at a distance of 2 mm from its lower surface. The block was heated by a regulated electric current through nichrome wire wound round it. The whole system was carefully insulated and thermally stable within ± 1 K up to ~ 850 K. This set-up was made a stage of an optical microscope working at a magnification of 60× and with a field of view of about 1 mm diameter. The specimen under test was placed on a small thin sheet of freshly cleaved mica which in turn was placed in a stainless steel boat of dimensions $0.2 \times 2 \times 2$ mm^3. The boat was attached to a drive unit and could be brought into the furnace and close to the thermocouple junction in a fraction of a second. A stop watch was started as soon as the crystal came near the thermocouple and the subsequent behaviour of the crystal until explosion was observed in reflection. Explosion of the crystal produced an audible click. The time to explosion was measured. It was found that if a crystal did not explode in about 15 s then it would not explode at all. Some partially decomposed crystals were taken out of the furnace after a total period of ~60 s, and examined by scanning electron microscopy. In order to avoid charge accumulation on the crystal a thin film of silver was deposited on the crystal surface.

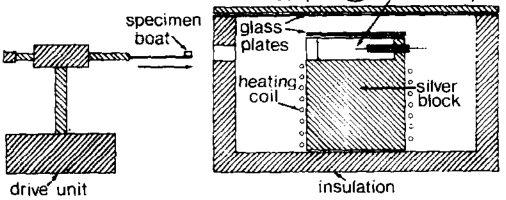

FIG. 1. Schematic diagram of furnace, showing experimental arrangement.

Mass spectrometric studies in ultrahigh vacuum were made on the products of decomposition of crystals from all the batches used to confirm that they were free from impurities.

3. Results

3.1. Explosion Temperature

The results, which are based on the examination of a few hundred crystals are presented graphically in Fig. 2. The procedure for establishing each point was to first select crystals of a particular thickness and to divide these into batches containing 6–10 crystals. With the furnace at a chosen temperature crystals from a batch were then individually inserted. Depending whether more or less than 50% of the crystals exploded the temperature of the furnace was reduced or raised by a step of one degree and another batch tested. When 50% of the crystals exploded reproducibly this temperature was taken as the explosion temperature. It will be seen from Fig. 2 that the critical explosion temperature rises slowly as the crystal thickness reduces from the largest thickness measured (~ 34 μm) to about 18 μm, then at an increasingly faster rate as smaller sizes are reached.

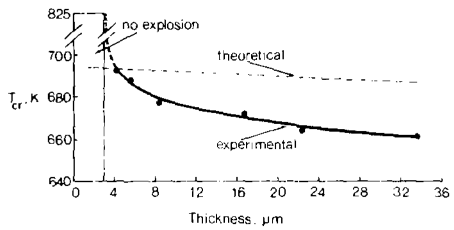

FIG. 2. Critical explosion temperature vs crystal thickness. The dotted line is the theoretical curve. The boxed area is for small crystals which did not explode even up to the highest temperatures tested (825 K). For details of how the experimental points were established see text. Crystal thicknesses were accurate to ± 0.5 μm and temperatures to ± 1 K.

Thus there is an increase of over 30 K in the critical explosion temperature for a decrease in the thickness of the crystal from 34 to 4 μm. Crystals of thickness less than 3 μm did not explode even up to 825 K irrespective of their surface area. It was found that the width of the crystal only affected the crystals' explosive behaviour if it was less than about 10 μm. Typically the lengths and widths of the crystals were in the ranges 100–200 μm. No melting of the lead azide crystals was observed even up to 825 K.

The time of explosion did not appear to depend on the size or the surface area of the crystals: even at one temperature the values of the time to explosion were inconsistent with one another. This observation is contrary to that of Ubbelhode, though there is an experimental difference in that he used batches of crystals while in the present experiments individual crystals were studied. However, generally the time to explosion reduced with increase of the furnace temperature.

3.2. The Mode of Decomposition of the Crystals

An initially transparent crystal when placed in the furnace first became translucent, and then from one or more points on the surface a grey film spread rapidly (within a fraction of a second) over the crystal. This grey colour lasted a very short time and if the crystal did not explode the colour changed to a reddish yellow. A striking feature of the decomposition was that pits formed on the surface of the crystals. These pits were of two types, those which had dimensions in the range 30–100 μm, and smaller ones of 3–5 μm in size. The number of large pits varied from one crystal to another, but it was never greater

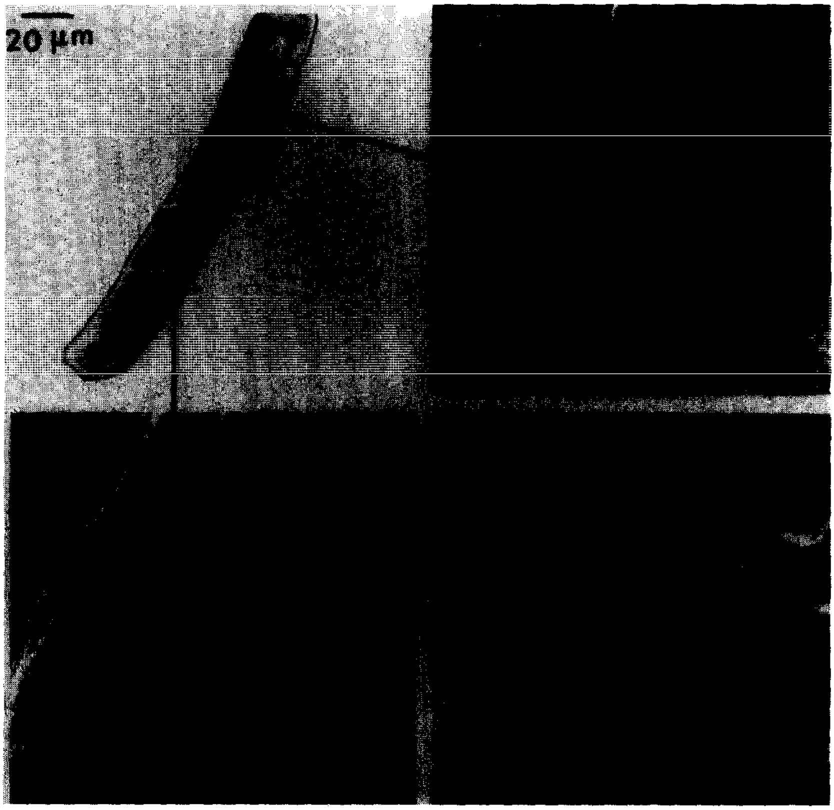

FIG. 3. Scanning electron micrographs of a lead azide crystal partially decomposed in the furnace. Note the large pit, labelled P, the many smaller pits, and the associated fractures.

than ten for the observed surface of the crystal. These pits formed suddenly and appeared to be formed by rapid decomposition at localized sites rather than by fragmentation of the crystal surface.

When crystals of thickness greater than 30 μm were placed in the furnace at temperatures slightly greater than their critical explosion temperatures, small fragments detached from the crystals' surface, the process continuing until the crystals exploded. In some crystals cracks were also observed just before their explosion. Another observation of interest was that some crystals (thickness up to 100 μm) exploded only partially, leaving unexploded fragments, and a few suffered multiple explosions.

Figure 3 shows scanning electron micrographs of a partially decomposed crystal which developed many cracks and pits on its surface. The dimensions of the crystal were $5.6 \times 39 \times 350\ \mu m^3$, and it was placed into the furnace heated to 686 K. At P a large pit formed rapidly, and later (while the crystal was still in the furnace) a crack appeared. Many of the small size pits can also be seen in Fig. 3. These pits go into the crystal along its *b*-axis, and in higher magnification micrographs it can be seen that they are fairly regular in shape. This indicates that the rate of decomposition was preferential on certain planes. It was observed that in general the amount of pitting and cracking was dependent on the thickness of the crystal at a given temperature, and increased as the crystal thickness increased. Crystals having thickness less than 3 μm did not crack or form pits at any temperature up to the highest investigated (i.e., 825 K). This proved useful since it was possible to do thermal decomposition studies

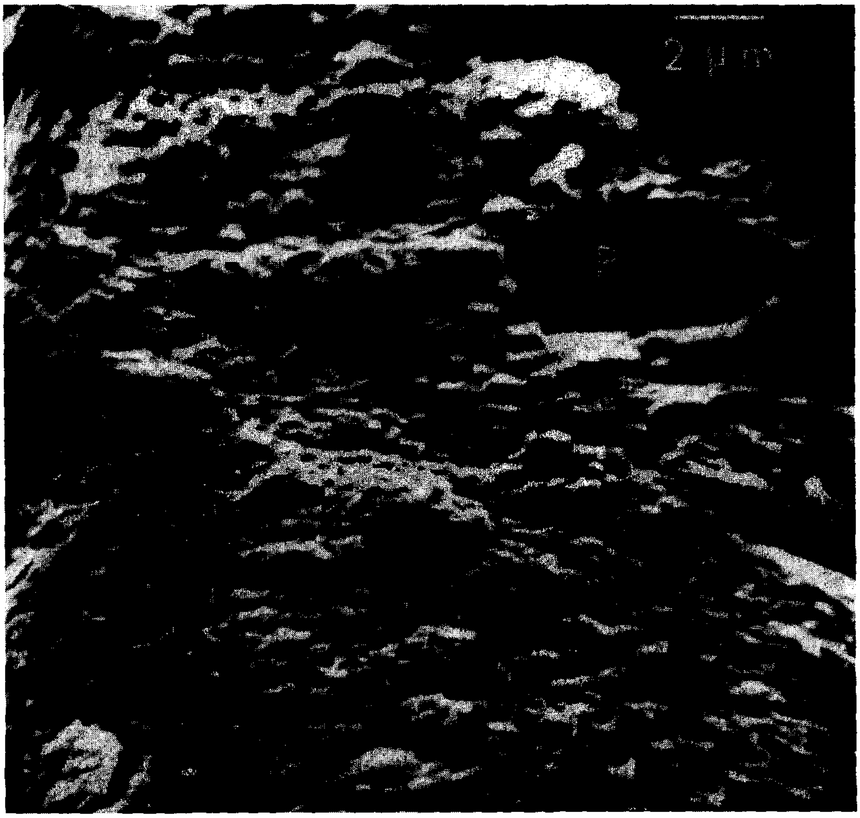

FIG. 4. A lead azide crystal partially decomposed inside the electron microscope by the electron beam. The appearance is similar to that of crystals decomposed in the atmosphere. A pit has formed at P.

on small crystals at temperatures higher than the critical explosion temperature for large crystals. Such experiments were performed in an ultrahigh vacuum system at temperatures up to ~710 K; even at this temperature the decomposition of α-lead azide crystals was a surface phenomenon.

Some crystals were decomposed in vacuum inside the scanning electron microscope using the electron beam of the microscope (10^{-11} A and 30 keV). Decomposition pits were formed and a typical photograph of the decomposed surface of a crystal is shown in Fig. 4. The structure of the pits is very similar to that formed by decomposition in the atmosphere. The conclusion from this and other micrographs is that the atmosphere does not significantly affect the pitting and fracture processes described earlier.

4. Theory

Calculations follow for the critical explosion temperature of parallelopiped and spherical shaped crystals in air and vacuum conditions. In order to analyse the system for air confinement the following assumptions are made

1. At these relatively high temperatures, the decomposition gas produces a film between the crystal and its support so that the particle is effectively suspended (Groocock (*11*, p. 1534), gives arguments supporting this).
2. Material defficiency in the crystal does not occur during its pre-explosion period and crystal dimensions do not change significantly.
3. The temperature of the crystal is uniform throughout: for the crystal sizes used this can be shown to be a reasonable approximation.
4. Only surface decomposition occurs and there is no crystal breakup. (See *Discussion*.)
5. Properties such as density and specific heat remain constant.

When a crystal is placed inside the furnace it will start to gain heat by radiation, convection and its exothermic decomposition. Because of the exothermic nature of the reaction, the crystal temperature will go above that of the furnace. At this stage it will lose heat by convection and radiation while still gaining heat due to its decomposition. The crystal will only explode if the rate of gain of heat is greater than the rate of loss of heat and continues to be so.

For a particle in air the rates of gain and loss of heat are as follows. The parameters are defined at the end of the paper.

The rate of production of heat by chemical decomposition is

$$(dQ_1/dt) = 2(l^2 + 2la)AQ\,e^{-E/RT}. \qquad (1)$$

The rate of radiative loss of heat is

$$(dQ_2/dt) = 2(l^2 + 2la)\varepsilon\sigma(T^4 - T_f^4). \qquad (2)$$

The coefficient of heat transfer, h, under conditions when the product of Grashof and Prandtl numbers is less than 10^{-5} (as in these experiments) is given by the relation, $(hL/k) = 0.4$, where L is the characteristic length defined by $1/L = (1/L_v) + (1/L_h)$, L_v and L_h being the appropriate pair of edge lengths, respectively (*12*).

Experimentally, the crystal length and width (both l in the theoretical treatment) were much greater than the crystal thickness, a. Therefore the characteristic lengths for the horizontal and vertical surfaces were $l/2$ and a, respectively. Since for a surface $dQ/dt = h \times \text{area} \times (T - T_f)$, then the rate of loss of heat by all the surfaces (area, $2l^2 + 4la$) is given by

$$dQ_3/dt = 3.2lk(T - T_f). \qquad (3)$$

Combining all these rates the heat balance equation becomes,

$$\begin{aligned} \rho al^2c(dT/dt) = {} & 2(l^2 + 2la)AQ\,e^{-E/RT} \\ & - 2(l^2 + 2la)\varepsilon\sigma(T^4 - T_f^4) \\ & - 3.2lk(T - T_f), \end{aligned} \qquad (4)$$

where the left-hand side of the equation represents the rate of accumulation of heat in the crystal. This equation has been solved numerically to find the change in temperature of the crystal with time, the initial conditions being that at $t = 0$, $T = 300$ K. It was found, depending on the temperature of the furnace, that the crystal temperature either became constant at a temperature above that of the furnace or rose sharply after a certain length of time. Based on the experimental observation mentioned earlier that crystals did not explode for times greater than about 15 s times to explosion in the range 0–15 s were considered. The sharp rise of temperature with time was interpreted as explosion of the crystal, and the temperature of the furnace at which this happened as the critical explosion temperature. Figure 5 shows the temperature–time behaviour of two crystals placed in the furnace at temperatures above and below their explosion temperature, respectively. For the lower curve the furnace temperature was 689.3 K and an equilibrium situation is reached at about 720 K. The upper curve is for a furnace temperature of 689.8 K and after 5.5 s the curve rises sharply (i.e., the crystal explodes). The value of l and a for this particular example were 170 μm and 23 μm, respectively.

By varying the value of a in the same range as in the experiments, keeping l constant at 200 μm and the time to explosion a few seconds, the variation of critical explosion temperature with the thickness of the crystal was computed. The results are given in Fig. 2; when the thickness reduces from 34 to 4 μm an increase of 6 K is predicted. Calculations were also made with a constant and l varied in the range 50–400 μm. The results confirmed the experimental observations that the parameter l, certainly when it is $\gg a$, has an insignificant effect on the critical explosion temperature.

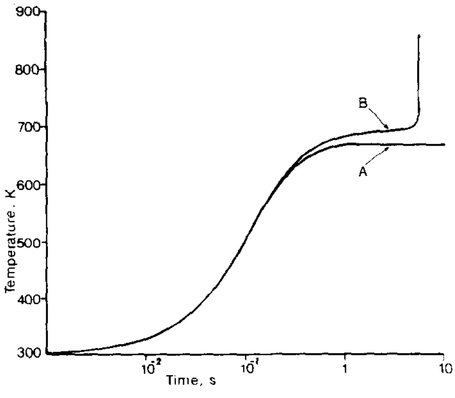

FIG. 5. Temperature vs time for crystals of thickness 23 μm which (A) come to equilibrium and (B) explode when placed in the furnace. Furnace temperatures for A and B are 689.3 and 689.8 K, respectively.

These calculations can also be extended to the vacuum situation. In vacuum the last term from the right-hand side of Eq. (4) is removed. The equation then reduces to

$$dT/dT = (2(l^2 + 2la)/\rho a l^2 c)\,[AQ\,e^{-E/RT} - \varepsilon\sigma(T^4 - T_f{}^4)]. \qquad (5)$$

Equation (5) shows that in vacuum there will be no size effect, and this supports the the conclusions of Groocock (*11*). Moreover, the explosion temperature in vacuum as would be expected is lower than in air. For example, for a 34 μm thick crystal the critical explosion temperature in air is 688 K, whereas it is 625 K in vacuum.

5. Discussion

Both theory and experiment show that for parallelopiped shaped α-lead azide crystals in air there is an increase of explosion temperature with decreasing crystal thickness (Fig. 2). However, in the range 34–4 μm the experimental increase is 30 K and this is significantly larger than the predicted theoretical change of 6 K. Crystals of thickness ~ 3 μm and less did not explode, even up to 825 K, irrespective of surface area. Since the curve in Fig. 2 cannot enter the boxed region below ~ 3 μm it indicates that the curve for thicknesses below 4 μm is likely to rise sharply and asymptotically to a point > 825 K (there is already a trend towards a much steeper curve for the points below 8 μm). As regards the theoretical curve its most dependable feature is its slope. The position of the line above the abscissa is dependent on the value taken for the heat transfer coefficient. However, it is difficult to select a precise value for this quantity since published work invariably involves much larger particles (*12*). It could be argued that agreement between theory and experiment should be best for particles of thickness less than ~3 μm since crystal breakup does not take place and assumption 4 of the theory is met. This would suggest a higher value for the heat transfer coefficient than the one used.

The observations made during the preexplosion period showed that preferential decomposition and cracking takes place (see Figs. 3 and 4), the degree of which was found to be greater for thicker crystals. In separate experiments a mass spectrometric study was made on α-lead azide crystals in an ultrahigh vacuum apparatus. No traces of impurities were detected which strongly suggests that crystal breakup during the preexplosion period was not due to impurities in the crystal.

Several workers (see, for example *13*, *14*) have shown that many materials have a dependence of strength on size with a tendency for high strengths (less structural defects) when specimens become of micron size. Others have measured dislocation densities in thin films as a function of thickness (*15*). The observations of little or no pitting or cracking below ~3 μm and an increasing amount for greater thicknesses is not unexpected therefore. Cracking and pitting would help towards a lowering of the explosion temperature by producing fresh surfaces on which decomposition could take place. Decomposition on crack surfaces would also take place in conditions of restricted heat transfer. An observation by Fox and Soria Ruiz (*15*, *16*) could also be important here. They showed that gaseous decomposition products are formed during the fracture of thermally unstable solids, and that the amount of decomposition increases with fracture velocity. It is not fully understood whether this decomposition occurs because of a temperature rise at the crack tip or because of changes of activation energy and preexponential factor which are equivalent to an "effective" temperature rise. However, whatever the detailed mechanisms it supports the view that the rate of thermal decomposition could be enhanced at a fracturing or freshly fractured surface. Factors such as this it is suggested explain the present experimental observations and the divergence from theory. The present theory assumes (assumption 4) that preferential decomposition and crystal breakup did not take place. The "ideal" theory for lead azide would have to take these features into account, but this is likely to be difficult since the relations between defects, strength, reactivity of freshly fractured surface, etc., are only poorly understood at present.

The observation of crystals only partially exploding and leaving unexploded fragments (Section 3) was noted in earlier experiments (*18*) in which initiation was by hot wire. The explanation is that reaction in small crystals of lead azide propagates as a deflagration at a velocity which depends on crystal thickness; these velocities can be less than the stress wave velocity. Thus stress waves can precede the reaction front and cause crystal breakup ahead of it. When the reaction reaches a crack which cuts across the whole crystal reaction stops (*18*).

Conclusions

Numerical calculations for parallelopiped shaped α-lead azide crystals placed in hot air show that there is a small size effect on the critical explosion temperature. Experiments on individual crystals showed that there is a significant decrease in explosion temperature with the increase in crystal thickness (minimum dimension). It is suggested that the observations of preferential decomposition pitting, and fracture in the preexplosion period are important and that increased defect concentration with crystal size accounts for the observed experimental fall in explosion temperature. As with many other explosive situations it appears that defects which cause localized high reaction rate affect the critical explosion condition.

Parameters: h: Coefficient of heat transfer $\mathrm{Jm}^{-2}\ s^{-1}\ \mathrm{K}^{-1}$; a: Thickness of slab, M; l: Length and width of the slab, 170 μm; k: Thermal conductivity of air, 2.427×10^{-2} $\mathrm{Jm}^{-1}\ s^{-1}\ \mathrm{K}^{-1}$; R: Universal gas constant, 8.314 J $\mathrm{mole}^{-1}\ \mathrm{K}^{-1}$; σ: Stefan's constant, $5.670 \times 10^{-8}\ \mathrm{Jm}^{-2}\ \mathrm{K}^{-4}\ s^{-1}$; ε: Emissivity of lead azide, single crystal surface 0.9; t: Time, s; T: Temperature of the crystal, K; T_f: Temperature of the furnace, K; ρ: Density of α-lead azide, 4.70×10^3 Kg m^{-3}; c: Specific heat of lead azide, $4.85 \times 10^2 \mathrm{Jkg}^{-1}\mathrm{K}^{-1}$; Q: Heat of decomposition of lead azide, 1.65 MJkg^{-1}; dQ_n/dt: Rate of Production of heat Js^{-1}; E: Activation energy for decomposition, 123×10^3 J mole^{-1} A: Preexponential factor,

3.59×10^6 $kgs^{-1}m^{-2}$. (These values of E and A are for crystals which we have used in our experiments.)

Acknowledgments

We thank Prof. P. Gray for helpful comments, and Dr. K. N. G. Fuller for advice on the value chosen for the emissivity of lead azide at elevated temperatures. Dr. M. M. Chaudhri thanks the Saigol Foundation and the Procurement Executive, Ministry of Defense.

References

1. W. E. Garner and A. S. Gomm, *J. Chem. Soc.* 2123 (1931).
2. P. J. F. Griffiths and J. M. Groocock, *J. Chem. Soc.* 3380 (1957).
3. J. Jach, *Trans. Faraday Soc.* **59**, 947 (1963).
4. A. S. Hawkes and C. A. Winkler, *Canad. J. Research*, **25B**, 548 (1947).
5. P. G. Fox, *J. Solid State Chem.* **2**, 491 (1970).
6. A. R. Ubbelohde, *Phil. Trans. Roy. Soc. London* **A241**, 281 (1948).
7. A. R. Ubbelohde, *Research* **3–5**, 207 (1950).
8. F. P. Bowden and A. D. Yoffe, "Fast Reaction in Solids," Butterworth, London (1958).
9. F. P. Bowden and K. Singh, *Proc. Roy. Soc. (London), Ser. A* **227**, 22 (1954).
10. F. P. Bowden and A. C. McLaren, *2nd ONR Symposium on Detonation*, p. 447, 1955.
11. J. M. Groocock, *Trans. Faraday Soc.* **54**, 1526 (1958).
12. M. Jacob, "Heat Transfer," Vol. I, p. 525, Wiley, N.Y. (1949).
13. N. Gane, *Proc. Roy. Soc. (London), Ser.* A **317**, 367 (1970).
14. K. Steier and K. Schönert, *2nd Int. Symposium on Comminution*, Cannes, Dechema—Monograph **69**, No. 1292, p. 167 (1971).
15. Y. Kawapaki and H. Fujita, *Proc. VI Int. Cong. for Electron Microscopy*, p. 291, Maruzen, Tokyo 1966.
16. F. P. Bowden, P. G. Fox, and J. Soria-Ruiz, *Nature (London)* **220**, 5169; 778 (1968).
17. P. G. Fox and J. Soria-Ruiz, *Proc. Roy. Soc. (London), Ser A* **314**, 429 (1970).
18. M. M. Chaudhri and J. E. Field, *5th Int. Sym. on Detonation, Pasadena, Calif.*, U.S. Office Naval Research, ACR-184, p. 301 (1970).