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Review
Mechanically initiated chemical reactions in solids

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The mechanical initiation of chemical reactions is of technological importance in such processes as cutting, drilling, grinding, crushing and lubrication which are often facilitated by chemical compound formation at the worked interface. The mechanisms whereby mechanical energy can be utilized in these reactions is reviewed with especial emphasis on the distinction between brittle and ductile, crystalline and amorphous materials. The practical examples mentioned above are discussed as well as the mechanical initiation of very fast reactions in solids.

1. Introduction

The possibility that chemical reactions in solids can be initiated by mechanical deformation seems to have been considered in the last century although at that time little was known about the equivalence of different forms of energy and whether these were convertible one to the other. The first systematic work which demonstrated that like heat, light and electricity, mechanical energy is also effective in inducing chemical decomposition was reported by Carey-Lea [1] who showed that shearing action was more effective than simple hydrostatic pressure [2, 3] and also that the halogens produced by the grinding of silver halides were able to react with moisture to produce the corresponding acid. The efficacy of mechanical shearing in bringing about chemical reaction was later demonstrated more conclusively by Parker [4, 5] who set out to show that in a number of double decomposition reactions between simple salts, the possible influences of reaction in the vapour phase, electrical effects due to grinding and reaction in the solution formed from water of crystallization, were not responsible for promoting chemical reaction. He further concluded that local heating facilitated the reaction which possibility had been ruled out by Carey-Lea on the grounds that the temperature rise could not be large enough to bring about decomposition in such thermally stable materials as the silver halides.

Since this early work, interest in this area has been spasmodic, particularly in western countries where little seems to have been done except in the one area of mechanically initiated explosive reactions in solids, an interest stimulated by the last World War. The notable exceptions to this lie in the work of two schools, one in the Soviet Union whose results on the application of mechano-chemistry to such technological processes as leaching, decomposition and chemical synthesis, catalysis and mineral treatment processes has recently been summarized by Boldyrev and Avvakumov [6]. The second is the work of the East German group under the direction of Thiessen, whose work has also been reviewed [7].

With recent growing interest in the technological application of high strength and often brittle non-metallic materials and the necessity to be able to fabricate and shape components from these materials, interest in mechanochemistry in the west is evolving from the possibility that chemical effects at surfaces and interfaces of these "difficult" materials may be used to modify mechanical properties in such a way as to make them more easily worked. Mention may be made of the machining of brittle solids and the drilling of hard rock [172].

In this article, we discuss some of the possible mechanisms whereby chemical and mechanical effects may be interrelated. Particular attention is paid to the materials properties which may be important in the mechanical initiation of

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chemical reactions. We take the view that, at least in ductile solids, reactions are thermal in origin and in brittle materials molecular excitation leading to bond breaking is induced by violent shearing and, in some cases, fracture. A number of practical examples of mechanically induced reactions are considered although the list is by no means comprehensive, reflecting the author's particular interests.

2. Mechanisms of mechanical initiation

2.1. Plastic deformation

2.1.1. Crystalline materials

Since the early work of Farren and Taylor [8] and Taylor and Quinney [9], it has been known that the energy of plastic deformation in metals is converted into heat with something like 95% efficiency, the remainder being stored in the lattice and associated with defects. It is this generation of heat which gives rise to an increase in temperature on cold working. However, it is common experience that, for modest amounts of deformation and at low strain-rates, the temperature rise is at most a few tens of degrees and unlikely to be high enough to initiate most chemical reactions. The possibility of localizing the energy at slip planes in the solid was considered by Stepanov [10] who tried to explain a large increase in electrical conductivity during the plastic deformation of sodium chloride as due to local melting. This is now thought to be unlikely (Nabarro, [11]) and Cottrell [12] has given quantitative arguments to show that a metal should not melt under these conditions.

The theory of heat generation by mobile dislocations has been given by Eshelby and Pratt [13] in terms of the temperature rise T produced by the movement of n dislocations at velocity V in a medium of thermal diffusivity K. Two cases were considered: one in which the mean spacing of the dislocations, λ, is small compared with $\Lambda = 2K/V$ and the second in which $\lambda \gg \Lambda$. The final expressions are,

$$T \approx \frac{\boldsymbol{b}\sigma V}{2\pi K} n \ln \frac{n\Lambda}{\lambda} \qquad \lambda \ll \Lambda$$

and

$$T \approx \frac{\boldsymbol{b}\sigma V}{2\pi K} n \left(\frac{2\pi\Lambda}{\lambda}\right)^{\frac{1}{2}} \qquad \lambda \gg \Lambda$$

where $\boldsymbol{b}$ is the Burgers vector of the dislocation. From these expressions, estimates show that for moderate dislocation densities only modest temperature rises are produced (see also Freundenthal and Weiner [14]) and that for a significant rise in temperature to occur, slip must take place simultaneously on a number of parallel and closely spaced planes. This situation obtains, for example, in the high speed rolling of ductile metals such as aluminium where at present day rolling speeds, temperatures near the melting point of the metal are generated.

A second and perhaps more important way of generating locally high temperatures which may initiate chemical reaction, is by the rubbing of two solid surfaces one against the other. This was the situation existing in the experiments of Carey-Lea and Parker and is one in which small asperities or protrusions on one surface contact the other resulting in locally high rates of strain and the generation of a large temperature rise.

Observations on this temperature rise between metal surfaces were made by Shore [15] and Herbert [16] in connection with the machining of metals. This was followed by the detailed studies of Bowden and his co-workers [17-19] who showed that transient temperatures of several hundreds of degrees could be recorded between solids in frictional contact at high sliding speeds.

Although it now seems well established that temperatures high enough for the initiation of chemical reactions are generated by plastic deformation in crystalline solids, the mechanism whereby the strain energy is converted into heat is still obscure. Nicholas [20] considered four mechanisms by which the energy of moving dislocations may be utilized: (i) that the kinetic energy of fast moving dislocations is converted to heat when these come to rest, (ii) energy conversion is brought about by dislocation damping and the scattering of sound waves, (iii) by the creation and annihilation of dislocations during plastic deformation and (iv) the conversion to heat of the energy of annihilation of point defects generated by the motion of a dislocation through a forest of dislocations which cuts its glide plane. Of these four possibilities (iv) seems to be the most likely explanation, although no experimental work seems to have been carried out to test these possibilities.

2.1.2. Non-crystalline materials

The situation in the case of non-crystalline materials such as amorphous polymers is in many ways less complicated. Here a temperature rise can be produced by the mechanical excitation of molecules sliding past each other during viscous flow of the polymer. Observations of this effect were made by Marshall and Thompson [21] who reported that the temperature rise which occurred during the necking of terylene could be felt with the fingers. A 70 K rise was measured by Müller and Jäckel [22] in polyvinylchloride and as high as 200 K in nylon 6.6 at high draw rates (Badami *et al.* [23]).

The thermal energy dissipation rate is given by

$$\frac{dQ}{dt} = \mu \left(\frac{du}{dz}\right)^2$$

where μ is the coefficient of viscosity and (du/dz) is the shear gradient in the material. This has been applied to specific problems such as the extrusion and cold pressing of plastic materials by Prandtl [24] and Nadai [25] and to the extrusion of liquids from between impacting surfaces by Cherry [26] and by Eirich and Tabor [27]. The latter work demonstrated that viscous heating on high energy impact is able to account for temperature rises up to several thousands of degrees.

These considerations show that for materials which readily undergo plastic deformation, a possible and perhaps most likely mechanism of initiation of chemical reactions by mechanical means is purely thermal in origin. Many examples of mechanically initiated reactions for which this is an adequate explanation exist and some of these are considered later in this article (Sections 5.1 and 6.1).

2.2. Brittle materials

The mechanisms of heat generation by the movement of crystalline defects or viscous flow cannot be applied to brittle materials which because of their more limited possibilities for deformation are liable to fracture rather than plastically deform on the application of a stress. Although, with the possible exception of diamond (Seal [28], Gane and Cox [29]), few materials are ideally brittle even at low temperature and some plastic deformation with the generation of heat is possible. How effectively this takes place in crystalline materials will depend upon the ease with which dislocations can be generated and made to move in the material and for quasi-brittle materials this will depend upon the rate of strain produced by the deformation. A well known example of this effect is exhibited by the amorphous organic solid pitch which under the force of gravity flows as a highly viscous liquid but if struck by a sharp blow behaves like a glass.

2.2.1. The mechanical behaviour of nearly brittle materials

One approach to the problem of ductile-brittle (d-b) behaviour is through the d-b transition temperature. This makes use of the ideas of fracture mechanics to predict from the temperature dependence of the macroscopic strain-rate, the temperature at which the material is no longer able to deform plastically and so must fracture in a brittle fashion.

Starting from the Griffith criterion for fracture in an ideally brittle solid (Griffith [30]) and introducing the modification of Mott [31] which restricts the velocity of the crack V_c to some fraction of the velocity of sound V_0, it can be shown that

$$V_c = AV_0 \left(1 - \frac{E_s}{E_{el}}\right)^{\frac{1}{2}}$$

where $A \sim 0.3$ in a wide variety of materials. This equation predicts that no crack is possible if the elastic strain energy E_{el} is less than the energy of the new surfaces formed E_s. If the material is capable of undergoing plastic deformation at the crack tip then

$$V_c = AV_0 \left[1 - \frac{E_{pl}}{E_{el}}\right]^{\frac{1}{2}}$$

which assumes that the energy dissipated in plastic deformation and which gives rise to the temperature increase, E_{pl} is much greater than E_s. This is very often the case for most practical materials. The d-b transition is deduced by expressing E_{pl} in terms of the stress and strain in the material and from the temperature dependence of the strain-rate. Thus

$$dE_{pl} = \sigma d\epsilon \, .$$

The strain rate usually takes the form

$$d\epsilon = B\sigma \exp\left[-\frac{Z}{kT}\right] dt$$

where B is a constant and Z is the activation energy for the deformation process, whence

$$dE_{pl} = B\sigma^2 \exp\left[-\frac{Z}{kT}\right] dt \, .$$

Expressing the stress distribution around the crack tip in a suitable form (see Mott [31] for a particularly simple example), allows E_{pl} to be calculated and hence the temperature at which $E_{pl} = E_{el}$ the latter being given by the Griffith theory (Griffith [30]). In practice neither the stress distribution nor the strain-rate dependence on temperature are known for most materials. However, this approach has been used successfully by Gilman [32] to calculate the d-b transition temperature in zinc. In addition Johnston *et al.* [33] have measured the transition temperatures of a number of ionic materials and as an example of the effect of strain rate they indicate that the d-b transition in MgO is raised from room temperature to about 2300 K for an increase of strain-rate from 10^{-5} to 40 sec^{-1}. In comparison the effect in metals is small because of their greater ability to deform by slip in several crystallographic directions. For example, in body centred cubic tungsten (which compared with face centred cubic metals, is brittle) an increase in strain-rate of $\sim 10^5$ raises the d-b temperature by only 250 K (Magnussen and Baldwin [34]).

A more basic approach to the problem has been made by Kelly *et al.* [35] who, assuming a Lennard-Jones type potential between ions in a crystalline lattice, have computed the conditions for failure in a ductile or brittle fashion. They show that when the maximum tensile strength σ_m of the crystal is comparable with the maximum shear strength τ_m, then the material fails in a brittle fashion. The condition for ductile behaviour is that $(\sigma_m/\tau_m) > 10$. However, these computations assume that the lattice is at 0 K and the problem of extrapolating the elastic properties of the material to more realistic working temperatures is severe.

Finally mention may be made of detailed studies on the effect of fracture velocity and temperature on the mobility of dislocations in iron–3% Si and in a number of alkali halides (Tetelman [36], Schmidt [37]). In the former, several dislocation mechanisms were examined from the point of view of energy dissipation at the tip of a moving crack and it was concluded that it is the density of dislocation sources leading to multiple cross glide on planes adjacent to the fracture plane which is the most important factor in determining the ductility of the crystal. In the latter study, the stress distribution around the tip of a moving crack was computed as a function of velocity and the effect of this on the range of dislocation movements into the bulk of the solid away from the fracture surface was studied by very careful etching and gold decoration techniques. It was found that the extent of the deformed zone decreased with increasing crack velocity indicating that the faster the material is stressed, the more brittle its behaviour. This of course bears out the results of common experience.

Notwithstanding these theoretical predictions and experimental observations, several examples are to be found in the literature which suggest that brittle materials at high rates of strain are capable of reacting chemically implying that the reaction is promoted thermally. The early grinding experiments of Carey Lea are a good example of this and later Parker concluded that intense local heating at points of contact between crystals may have resulted in fusion and subsequent chemical reaction of the compounds. Similar observations have since been made by Pawljutschenko and Gilewitsch [38], and Smekal [39] has reported the formation of a eutectic mixture between a silicate glass and aluminium oxide by scratching one with the other. Probably the most spectacular observation is that of Naeser and Scholtz [40] who report the explosion of iron and molybdenum oxides and of calcium carbonate on rolling. More recently Fox and Soria-Ruiz [41] have made direct measurements of the amount of decomposition produced by propagating high velocity cracks in single crystals of a number of inorganic materials including calcium, magnesium and lead carbonates and the azides of sodium and lead. The amounts of decomposition per unit area were in all cases rather small necessitating the use of sensitive ultra high vacuum techniques combined with mass spectrometry. In each case fracture resulted in decomposition, the carbonates evolving carbon dioxide and the azides, nitrogen gas and by relating the amounts of gas evolved to the temperature dependence of decomposition rates (measured independently) an effective crack tip temperature could be deduced. The significant feature of these results is that this temperature was found to be inversely proportional to the hardness of the material, i.e. the more brittle the material, the less elastic energy is dissipated in plastic flow leaving more available for bond breaking and decomposition.

The exact mechanisms by which these processes occur have not been studied in any detail. It is possible that locally high pressures generated by attrition in the grinding experiments, leads to plastic flow and subsequent heating of the material. It is well established by the experiments of Bridgman [42, 43] that many materials if subjected to high enough pressure flow plastically and indeed the slip systems in calcite have been studied by observing the flow of this material under high hydrostatic pressure (Turner *et al.* [44]). The possibility that lowering of the melting temperature leads to reaction in the liquid phase, seems unlikely.

The mechanism of decomposition in the fracture experiments is even more obscure. It is likely that the passage of the crack results simply in the tearing apart of chemical bonds and if the decomposition reaction is endothermic, the extent of reaction is limited by the amount of available energy released on fracture. However, for exothermic reactions there is a possibility that the release of thermal energy by decomposition leads to self propagation of the chemical reaction and the application of this idea to very fast reactions in solids is discussed later, (Section 6.2).

3. The influence of dislocations on reactivity

Here we introduce a brief diversion to consider the effect of dislocations on solid reactivity since it is well known that the mechanical deformation in crystalline solids is always accompanied by the movement of dislocations and often the production of new ones.

That the reactivity of a solid in the vicinity of dislocations is changed, is now undisputed. For instance, the enhanced dissolution rate around the points of emergent dislocations at the surface of crystalline solids, has long been used as a method of revealing the presence of and estimating the density of dislocations (Regel *et al.* [45] Johnston [46]). It is still not yet clear why dislocations should affect chemical reactivity unless purely stereochemical effects are important, for it is difficult to understand how the stored elastic strain energy around the core of a dislocation could be utilized chemically.

Probably the first experimental observation of a change in reactivity caused by the introduction of defects in crystalline solids was that of Faraday [47] who noticed that certain hydrated salts, dehydrated spontaneously when scratched with a pin. Since then numerous reports have appeared on the correlation of dislocation generation and bulk and surface reactivity (Tompkins [48]). Much of this work suffers from the drawback that insufficient attention has been paid to the search for a direct one to one correlation between change in reactivity and dislocation density. For example it is usually not sufficient to observe that a change in reactivity occurs when the solid is subjected to some treatment which is assumed to change the concentration of defects, unless it can be shown that no other accompanying change can explain the observed effect.

Thomas and his co-workers have recently studied a series of reactions in solids in which the movement of dislocations in certain slip planes can be related with (usually) enhanced reactivity (Thomas [49]). The most extensive study has been made on the thermal decomposition of calcite for which the dislocation configurations have been well worked out (Turner *et al.* [44], Klassen-Neklyudova [50]). A great deal is also known about those slip systems which can be related to the thermal decomposition reaction (Thomas and Renshaw [51]) and in particular the decomposition kinetics of these particular systems (Fox and Soria-Ruiz [52]). The latter study revealed that the four simplest slip systems in calcite can be activated at different temperatures and so it was possible to relate the decomposition kinetics in different temperature ranges to each type of dislocation system. The correlation is tentative due to the difficulty of separating the effect of interfering slip systems as the dislocations anneal at the higher temperatures. Attempts to activate each system by compressing the crystal uniaxially were unsuccessful because of the difficulty of preventing accidental cracking.

In the field of surface catalyzed reactivity the only study which has attempted to relate activity with the number and type of defects, appears to be that of Jaeger [53, 54] for the decomposition of formic acid on single crystals of silver. The results of this study suggest that the points of emergent dislocations are unimportant in influencing the reaction, but reaction takes place most readily in $\{111\}$ planes suggesting that it is stereochemical factors which have the greatest influence on chemical reactivity.

Finally, it may be noted that many phase changes including twinning and martensitic type transformations occur under the influence of high hydrostatic pressures and are often accompanied by shear stresses in the material. Many of these almost certainly take place by dislocation mechanisms the velocity of which may be accelerated by a local increase in temperature accompanying the application of the stress. Early observations include the conversion of γ-$Fe_2O_3.H_2O$ to α-Fe_2O_3 (Baudisch and Welo [55]) the γ to α transformations in Invar under tension (Nishiyama

[56]) the polymorphism of calcium carbide CaC_2 on grinding (Bredig [57]) and several phase transformations in elements and compounds under pressure, reported by Bridgman [42]. More recently, Burns and Bredig [58] have studied using X-ray methods, the transformation of calcite to aragonite which takes place on grinding (Fig. 1). Aragonite in the less stable of the two forms at ordinary temperatures and pressures and the effect of grinding is attributed to the possibility that because the critical shear stress in calcite is less than the fracture stress and vice versa for aragonite, the crystals of the latter will always break up before phase transformation can take place by shear thus precluding the transformation from aragonite to calcite which is indeed not observed. However, the reverse view has been taken by Dachille and Rustum Roy [59, 60] who argue that stresses leading to fracture accelerate phase transformations. These authors claim that shear stresses do not alter the equilibrium pressure of the transformation but affect the rate of the process. They conclude that shearing causes breaking of bonds and the possibility of storing strain energy, resulting in an acceleration of the kinetics of transformation. It appears, however, that continuous grinding leads to a dynamic equilibrium between the two forms of calcium carbonate which consists of about 30% of aragonite (Schrader and Hoffman [61]). This is hard to justify on the basis of the two previous non-equilibrium mechanisms unless heat generated in milling experiments of Schrader and Hoffman leads to a thermal reversion of aragonite to its more stable form. Many examples of non equilibrium (high temperature) forms are available in the literature (see for example Boldyrev and Avvakumov [6]).

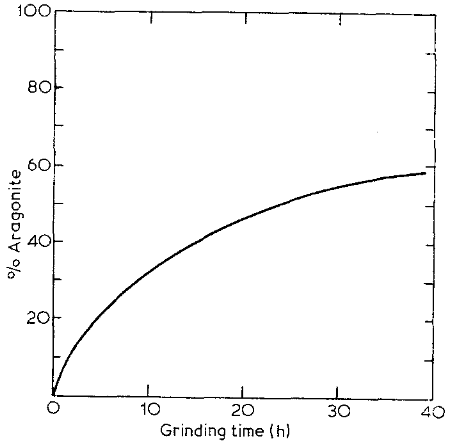

Figure 1 The effect of mortar grinding on the transformation of calcite to aragonite. The curve shows the increase in the proportion of aragonite with time.

The deduction that a high temperature must have been reached when a solid is subjected to mechanical deformation was made by Zener and Holloman [62] who showed that by impacting steel at a strain-rate $\sim 10^3$ sec^{-1}, a band of martensite could be observed adjacent to the punch. This implies that a high enough temperature had to be reached to stabilize the martensitic phase and this is then followed by rapid quenching. The authors estimate that the shear strain in the martensitic region must be in excess of 100 implying that a temperature of well in excess of 1300 K had been reached during deformation. These observations were later confirmed by Mannion and Stock [63, 64].

4. Electrical and optical effects associated with mechanically induced reactions

The separation of electrical charges by the expenditure of mechanical energy is a study dating back to antiquity and culminating in modern times in the static electricity generators used in the acceleration of nuclear particles. The study of the generation of static electricity and the formulation of reliable hypotheses to explain the phenomenon has been bedevilled by the enormous difficulty in obtaining reliably reproducible results. Much of the experimental work and the difficulties in interpretation have recently been reviewed by Harper [65].

The possibility that chemical reactions may be initiated in solids by charge separation can be considered in two parts (a) the generation of high voltages leading to electrostatic discharge and (b) the charging of the solid by the differential mobility of charged defects under the action of the stress. These two effects are almost certainly inter-related in many cases.

4.1. Effects associated with high voltages

The emission of light known as triboluminescence which occurs when solids are rubbed together as in grinding, has been known and reported in the literature for some time (Burke [66], Imhof [67]). The possibility that this was associated with an electrical discharge was investigated by Longchambon [68] who showed that bands associated with the ultraviolet spectrum of nitrogen were produced when cane sugar is ground in air. Similar effects were later observed in the triboluminescence of inorganic salts (Longchambon [69]). These observations were subsequently refined by Wick [70] who in a study of the carbohydrates, sucrose, maltose and lactose was able to conclude that it was the fracture of the crystals which produced the electrical discharge responsible for light emission. This conclusion was further strengthened by her observation that rapidly cooling the crystals in liquid air enhanced the light emission presumably due to fracture by thermal shock. In addition it was found that fluorescence could be induced in organic liquids surrounding the crystals and characteristic gaseous discharges were produced by cracking the crystals in different atmospheres. There was also some indication that although amorphous sugars phosphoresce they are not triboluminescent suggesting that the phenomenon of charge generation is due in some way to the crystallinity of the material.

There seems little doubt that high potentials resulting in electrical discharges are produced in the grinding process. Weyl [71] has shown that in the grinding of silica, atomic oxygen is produced from the oxygen in the atmosphere, to satisfy the stereochemical requirements of the SiO_4 tetrahedra, half of which on average have been depleted in oxygen by the fracturing process. (The suggestion is also made that the disease of silicosis common amongst people working in environments where silicate minerals are being crushed may be due to the toxic effect of this atomic oxygen.) Other reports of chemical reactions initiated in the presence of freshly ground silica have been given by Deuel and Gentile [72] and Benson and Castle [73]. Both refer to the formation of organic compounds although the mechanism of these reactions seems to be obscure. The latter authors do not favour free radical mechanisms since, for example, vinyl polymerization is shown to occur even in the presence of inhibitors. A surface charging mechanism is suggested in which charge separation occurs between adjacent SiO_4 tetrahedra although the great stability of the highly reactive silica surface when stored in an inert atmosphere (Walkers and Estle [74]) suggests that charge stabilization must occur through some form of defect mechanism.

More recently Mayer and Polly [75] have attempted to obtain quantitative information relating the emission of light in sucrose and several alkali halides to the mechanism of mechanical deformation in the crystal. In experiments in which a metal needle is allowed to impact the crystal surface, they found that the intensity of triboluminescence is directly proportional to the size of the load and also extremely dependent upon the ambient gas pressure rising rapidly to a maximum for all materials at a few hundred N m^{-2} pressure. However, unlike Wick, they conclude that discharges between charged fracture surfaces are not responsible for the luminescence. Instead they postulate that charging is due to the movement of jogs and kinks at dislocation lines. The duration of the light flashes was found to be $\sim 10^{-7}$ sec and this would seem to be of the wrong order of magnitude for an explanation based upon defect movements in the solid which are limited to a maximum of the speed of sound and hence a time scale $\sim 10^{-5}$ sec.

It might be supposed that a very sensitive test of the hypothesis that electrostatic discharges are capable of initiating chemical reactions in solids may be made on materials which decompose exothermically and in which therefore the reaction, once started, can become self propagating. Recently, Taylor and Thomas [76] have proposed that the explanation for the occurrence of apparently spontaneous reactions in solutions of the explosive material lead azide, is due to the build up of electrostatic charge at the surface of crystals growing from solution. The discharges which occur on coallescence of these crystals were believed to be responsible for initiating the decomposition reaction. This hypothesis was tested by Fox *et al.* [77] who measured the charging of a parallel plate condenser formed between rafts of crystals of pentaerythritol growing on the surface of its supersaturated solution and a reference electrode situated a short distance away. It was found that erratic charge build up occurred as individual crystals formed on the surface the sign of which was reversed as coallescence of the crystals took place (Fig. 2). When the experiments were repeated with lead azide solutions broadly similar behaviour was recorded and in some cases rapid fluctuations in charge were followed by "spontaneous" explosion, (Fig. 3).

4.2. The origin of electrical charging effects

The earliest attempt to make quantitative observations on electrical charging in plastically

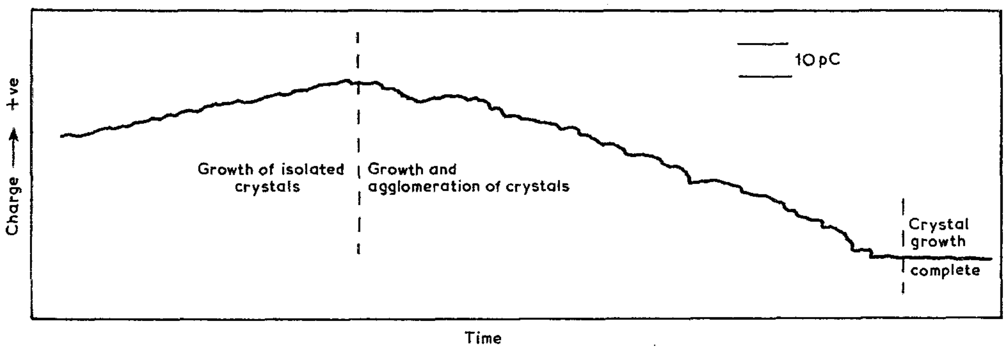

Figure 2 The fluctuations in electric charge on the surface of pentaerythritol crystals growing on the surface of their supersaturated solution in water.

deformed crystals seems to be that of Joffe and Zechnowitzer [78] who observed transient increases in current flowing through NaCl crystals when cracked to expose fresh surfaces. Shortly after Gyulai and Hartly [79] measured a large increase in the ionic conductivity of NaCl on plastic deformation and Stepanov [10] showed that a potential difference occurred across the faces of a crystal when mechanically deformed. The long history of such charging effects in ionic crystals has been reviewed by Pratt [80].

Predicting the sign of the charge is more difficult since this will depend upon the mechanism of formation and type and mobility of the defects giving rise to the effect (Nabarro [81]). However, since the energy of formation of positive and negative vacancies in ionic crystals is not the same, that for positive being lower than that for negative, (Mott and Littleton [82]), Seitz ([83]) has suggested that NaCl, for instance, should be positively charged and Bassani and Thomson [84] have calculated the energy of association between a dislocation in sodium chloride and a positive vacancy.

The theory of charge generation in plastically deformed ionic crystals has been given by Eshelby *et al.* [85] who likened the situation to that which exists in solutions of strong electrolytes except that in this case, the charged dislocation is surrounded by a Debye-Huckel type atmosphere of vacancies or point defects whose mobility depends upon the applied stress and the temperature. This theory was successful

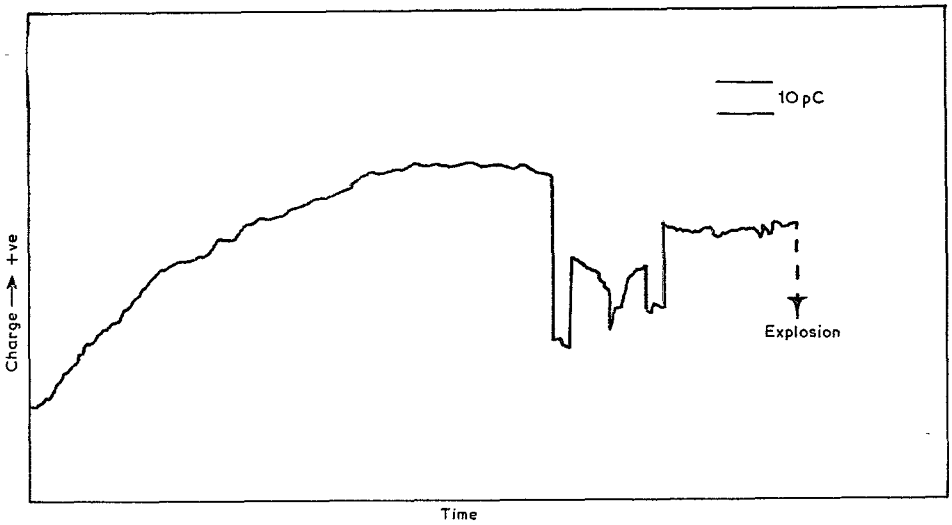

Figure 3 The charging of lead azide crystals growing from solution. The rapid fluctuations eventually lead to explosion.

in accounting for the anomalous temperature dependence of the yield stress of sodium chloride (Fig. 4) and the effect on the flow properties of the crystal of adding divalent cations.

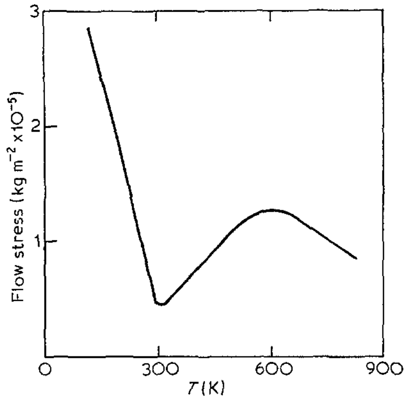

Figure 4 The anomalous temperature dependence of the flow stress of sodium chloride crystals showing the effect of the charge on immobile point defect clusters on dislocation mobility.

The sign of the electrical charge to be expected from a given set of deformation conditions seems to be still in some doubt. Vennik *et al.* [86] showed that dislocations are negatively charged while Caffyn and Goodfellow [87] measured positive charges between the faces and neutral axis of a sodium chloride crystal deformed in four-point bending. Whitworth [88] has suggested that edge dislocations in NaCl acquire a positive charge by sweeping up otherwise immobile positive vacancies.

That the sign of the observed effect depends upon the mechanism of deformation is probably best demonstrated by experiments carried out at high strain-rates under conditions of shock loading. Thus Wong *et al.* [89] have observed that electrical effects are produced in shocked crystals of NaCl and that the size and sign of the effect depends upon crystallographic direction as well as shock intensity. Moreover, there are two changes in sign occurring at ~ 10^6 and 10^7 N m^{-2} (Fig. 5). These authors attribute the variation in the sign of the effect to impurities and the size of the effect to the mobilities of dislocations relative to their Debye-Huckel cloud of compensating point defect charges according to the theory of Eshelby *et al.* [85].

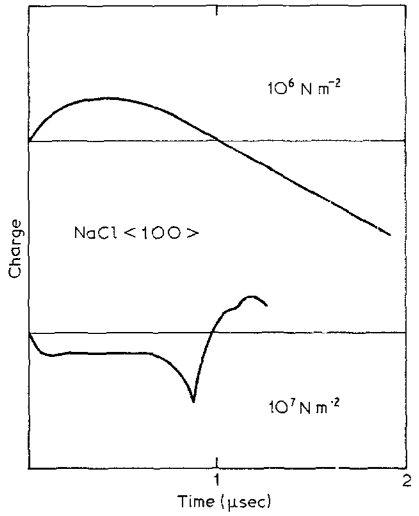

Figure 5 Charging effects in sodium chloride crystals subjected to shock waves of two different intensities.

Electrical charging is not confined to ionic crystals since similar effects have been observed in polymers under shock loading conditions at much higher pressures. Experiments on poly (methylmethacrylate) and polystyrene have been described by Hauver [90] down to 2.5×10^6 N m^2 and 5.0×10^6 N m^2 respectively and these are associated with characteristic relaxation times ~ 1 μsec (Fig. 6). The mechanism of charging remains obscure for these materials although a

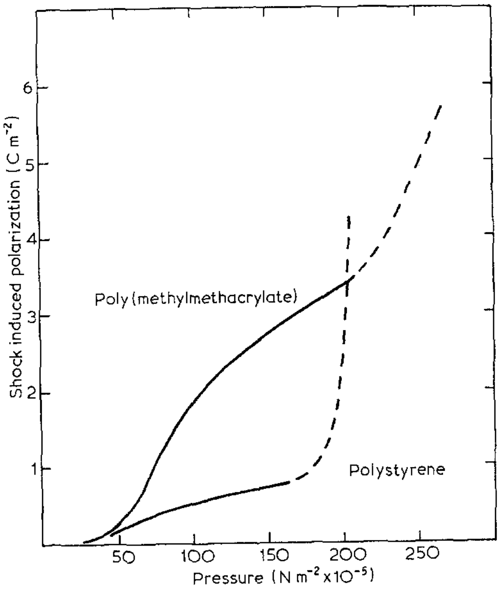

Figure 6 Shock induced polarization of polymers. Dotted portions represent phase transition at which polarization and dielectric constant are changing rapidly.

theory based on polarization effects which take place as the shock wave passes, has been given by Allison [91].

4.3. Exo-electron emission

Metallic surfaces when subjected to mechanical working such as abrasion or cutting show a weak emission of electrons which falls off with time. This seems to have been noticed first by Lewis and Burcham [92] during the preparation of Geiger counter tubes. Later an extensive study of the phenomenon was made by Kramer [93] who believing the effect to be associated with exothermic processes in the solid termed it exo-electron emission (sometimes known as the Kramer effect). Since these early studies, exo emission has been observed in a wide variety of materials [94] both metallic and non-metallic.

The mechanism for exo-electron emission is not well understood but the feature which seems common to most experiments so far reported is that it is associated with defect formation in the solid and may be augmented by radiation of suitable wavelength. Indeed since emission is observed at energies well below the photoelectric threshold, the presence of surface contaminant layers often involving adsorbed oxygen, has been suggested as a necessary prerequisite for the effect to occur. A mechanism which is essentially dependent upon defect formation is supported by the work of Bohun [95] who correlated emission with the presence of colour centres in the alkali halides (Fig. 7). This work was later refined by Kramer [96]. The parallel between exo-emission and luminescence phenomena lends support to the idea that impurity centres which provide energy levels between the valence and conduction bands in non-conductors are responsible for the emission of electrons. More recently Pimbley and Francis [97] have proposed that diffusion of vacancies produced by abrasion of aluminium surfaces is a possible mechanism in which the vacancy gives up its energy to an electron which under the further stimulus of irradiation is emitted from the surface. However, it is not yet clear whether a contaminant layer of non-conductor is necessary for exo-emission nor yet what is the role of surface illumination [98, 99]. Experiments of Gesell *et al.* [100] carried out under carefully controlled vacuum conditions suggest that exo-emission from freshly abraded magnesium surfaces exposed to oxygen or water vapour is due to the chemical interaction of these gases with the surface. It is suggested that the work function of the surface is lowered by adsorption to the point where electrons are ejected. The main difficulty in all this work remains that of deciding by what mechanism electrons are released from the surface.

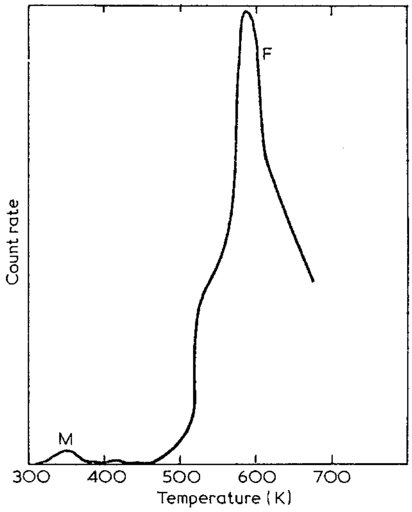

Figure 7 Exo-electron emission glow curve for additively coloured rock salt.

Thiessen and his co-workers [7] have been working on the experimental aspects of the degradation of mechanical energy produced by the impact of solids. They combine all the observed phenomena such as lattice distortion and break up, phase changes, triboluminescence, triboemission of electrons and chemical reactions in a scheme referred to as the Magma-Plasma deformation model (Fig. 8). In this they envisage that between the two colliding bodies exists a region of high disorder in which dislocations are produced and induced to move in the surface layers of the colliding solids. Between these two

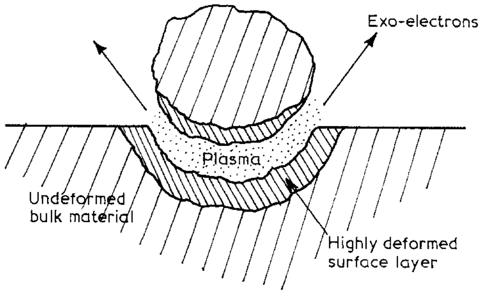

Figure 8 Schematic representation of the Magma-Plasma model of Thiessen.

highly deformed surface regions exists a plasma from which electrons are emitted and where triboluminescence occurs. Because of the state of excitation in this region it is assumed that chemical reactions can take place. The kinetic aspects of some of these are discussed in Section 5.1.

Exo-electrons are emitted with low energies; the possibility that they may be responsible for initiating chemical reactions by, for instance, free radical mechanisms would seem to be slight. However, several reports have appeared in the literature which associate chemical reaction and compound formation with the same conditions under which exo-emission is observed. For instance Grundberg has reported the formation of hydrogen peroxide in measurable amounts, from the interaction of oxygen and water in contact with freshly deformed metal surfaces and has suggested that the presence of peroxides in used lubricating oils may arise by the rubbing together of metal components from between which the lubricant has temporarily been squeezed. Also in the field of lubrication, Kramer has suggested that exo-electron emission may be responsible for the formation of metal soaps in surfaces immersed in surface active agents. In addition, Grohn and his co-workers [101] have suggested that the reaction of several aromatic chloro-compounds with metals in group V of the periodic table is due to mechanical stimulation of electrons from the metal and moreover that polymerization of methyl methacrylate and styrene by grinding with several different metals can be explained in the same way [102]. It should be pointed out, however, that control of experimental parameters in experiments such as these is difficult and usually not good enough to say unambiguously that any one mechanism is operative. For instance, most of the chemical reactions could have been thermally initiated by the rise in temperature produced on plastically deforming the rubbing surfaces. These reactions may have been further accelerated by catalytic effects. Grohn *et al.* [102] have observed that the efficacy of the polymerization reactions reported increases with decreasing work function of the metal.

5. Examples of mechanically initiated chemical reactions

In this section we discuss some practical examples of mechanically induced reactions. Those chosen by no means constitute an exhaustive list and apart from passing reference does not include the many well documented examples of polymer degradation which occurs for example during the fabrication of plastics materials. This has been reviewed by Barenboim [103, 104] and Simionescu and Oprea [105]. A variety of processes of technological importance particularly in mineral processing and extraction industries has recently been reviewed by Boldyrev and Avvakumov [6].

5.1. Chemical reactions at surfaces

A very comprehensive study of mechanically induced reactions has been made by Heinicke and his co-workers [106]. They have shown that under the action of mechanical forces compounds can be made to both form and decompose depending upon experimental conditions. The types of reactions include oxidation [107, 108], hydrogenation [109], decomposition [107], double decomposition [106] and catalytic reactions [106] as well as gaseous adsorption on solids [110]. A detailed study has been made of the effect of experimental parameters on the formation and decomposition of nickel carbonyl $Ni(CO)_4$ and it was shown that not only is the reaction sensitive to pressure and temperature as might be expected but also the reaction velocity and position of equilibrium is dependent upon the amount of mechanical work done on the system. This reaction is also particularly sensitive to the presence of hydrogen sulphide and other sulphur containing compounds and this is attributed to the intermediate formation of nickel sulphide, [111]. This sensitizing effect has been used by Heinicke and Harenz to study the lubricating action of molybdenum disulphide MoS_2 [112]. By contrast oxygen and oxy acid salts seem to inhibit the Ni/Co reaction [108] and this is attributed to the formation of protective layers of oxide on the surface of the nickel [113].

In assessing the value of this large body of experimental work by the German group it is necessary to bear in mind that these results were obtained by mechanical milling processes which involve bombarding the reactive surface with hard projectiles. A detailed description of the mechanical effects produced at the surface is thus impossible. It is reasonable to suppose that milling will produce plastic deformation and the generation of heat and the possibility of electron emission. In addition, brittle materials will fracture leading to chemical decomposition in a manner already discussed. In view of this very complex set of circumstances, it is not surprising than Heincke concludes that " . . . the standard equilibrium thermodynamics does not apply" (Heinicke [106] p. 108). Nevertheless using standard thermodynamic data, it is instructive to calculate the temperature necessary to initiate the mechanically induced chemical reactions and Heinicke has done this on the basis of the criterion that for reaction to take place the equilibrium constant should be at least unity. Some examples are given in Table I, [106]. This approach is similar to that used by Fox and Soria-Ruiz [41] in calculating the temperature generated at the tip of a fast moving crack in the fracture decomposition of some azides and carbonates. The assumption implicit in this approach is that the reaction mechanism in the mechanically induced reaction is the same as that for which the thermodynamic data was obtained. There is evidence to suggest that this may not be so [41] especially under the complex conditions which exist in the grinding and milling experiments.

A good example of such complex behaviour may be taken from the experiments by Heinicke *et al.* [114] for the formation of $Ni(CO)_4$. Thus it has been known for some time that mechanically worked nickel is a more effective catalyst than the well annealed metal [115]. However, if the activation energy for carbonyl formation is measured while the metal is being deformed, values are obtained which are different to those for experiments carried out on previously deformed metal; moreover, the former show a very complicated dependence upon temperature (Fig. 9). It is possible that the decreasing reaction rate with increasing temperature is due to contamination of the surface at which reaction occurs and that this contamination is removed only at higher temperatures when the rate again increases. Removal could take place by evaporation into the gas phase or by diffusion into the bulk of metal.

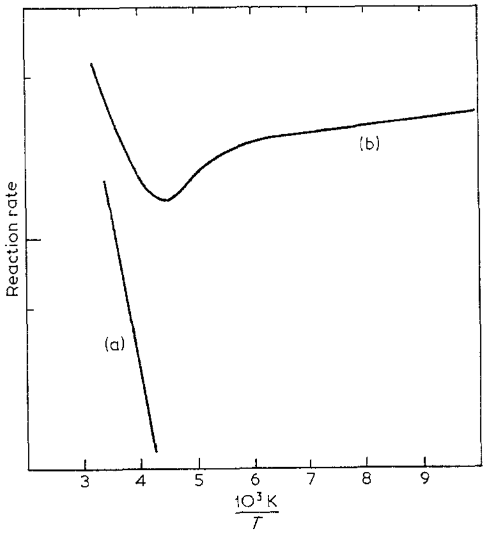

Figure 9 Temperature dependence of the mechanically activated formation of $Ni(CO)_4$: (a) previously deformed nickel; (b) nickel deformed during compound formation.

It has been suggested that tribochemical reactions should be considered in two parts (i) a truly chemical part which is temperature sensitive and (ii) a mechanical part whose rate does not depend upon temperature and which has a zero order rate constant. Evidence for the operation of a two part mechanism comes from experiments on the oxidation of nickel with carbon dioxide with the formation of NiO, $NiCO_3$ and Ni_3C [116] and from experiments on fretting corrosion in which, as with the formation of $Ni(CO)_4$, corrosion actually increases with decreasing ambient temperature [117].

There would seem to be little necessity for this division when it is borne in mind that many surface or catalytic reactions are zero order in the pressure range where there is a copious supply of reactants to the surface. Under these conditions, the rate becomes independent of the supply and also unless the temperature at the point on the surface where reaction occurs is known, localized

TABLE I

Reaction	*Kp* (298 K)*	*T* (K) for *Kp* = 1	*Kp* (expt)	Equivalent temperature (K)
$C_{graphite} + 2H_2 = CH_4$	10^{9}	930	10^{4}	532
$C + 2H_2O = CO_2 + 2H_2$	10^{-14}	980	10^{-4}	530
$Fe_3O_4 + 2C = 2CO_2 + 3Fe$	10^{-40}	940	10^{-8}	650
$2MgO + C = CO_2 + 2Mg$	10^{-131}	2550	10^{-5}	2100

**Kp* is the equilibrium constant for the reaction.

reactivity at hot spots may well appear to be independent of ambient temperature if the range of this latter is small and well below the temperature at which reaction is occurring.

5.2. Application to machining, grinding and polishing processes

5.2.1. *Machining*

This operation involves the expenditure of a large amount of mechanical energy to produce the required result. However, it is well known that it can be facilitated by the presence of substances whose action in many cases takes place through the formation of chemical compounds at the interface where material is being removed.

In the machining process, it is customary to use a cutting fluid to improve the cutting action of the tool and although no very clear picture of the role of this medium has emerged, it is generally believed to act as a lubricant between tool and work piece thus preventing adhesion of these two and thereby reducing wear of the former. This greatly affects the economics of the process. In high speed cutting, the fluid which may be oil or water based, may act as a coolant, dissipating the large amount of heat produced at the tool by rapid plastic deformation of the metal chip. Efficient cooling reduces thermally induced structural changes in the tool steel which may adversely affect its mechanical properties.

The mechanical engineering aspects of machining and cutting have been studied in some detail [118]. Less well understood is the part played by cutting fluids in improving machinability and for instance, their effect on surface finish. Why is it that certain substances notably those containing sulphur and the halogens are markedly more effective than others? To obtain answers to such questions is not easy and the situation is complicated by the fact that much of the information available applies to complex alloys for which little data exist on mechanical properties at very high rates of strain.

However, it now seems well established that the formation of a surface layer is an important factor and that the more strongly this layer is bound to the surface, the greater its efficacy. High temperatures generated in the machining operation facilitate compound formation at the surface and this has been noted in numerous reports in the literature [119-125]. Oxygen gas is particularly effective in this respect and this is attributed to the formation of a layer of oxide which subsequently prevents the two surfaces adhering [126-129]. At high cutting speeds the nature of the mechanically induced chemical reactions is less clear since at these speeds layer formation would need to be very rapid and presumably take place via the transport of molecules through the gas phase to the region of maximum mechanical deformation. Shaw [130] has attributed the effectiveness of organic chlorine containing compounds to the formation of organometallics which are in some way effective in reducing the shear stress of the metal although unless this takes place by the unlocking of dislocation tangles due to compound formation as envisaged by Rehbinder [131] and Barlow [132], it is difficult to propose a mechanism for the process. Shaw *et al.* [133] later discovered that carbon tetrachloride is more effective in compression than in tension and this led them to attribute the effectiveness of this material to the prevention of preformed microcracks reclosing due to filling by the liquid. This explanation, however, would apply to any fluid which wets the surface of the workpiece and does not take into account the rather specific effectiveness of chlorinated organic liquid and in particular carbon tetrachloride.

A second and very effective method of depositing a protective layer on the surface to be machined is by electrochemical means. Thus the elegant experiments of Barker and Young (see Bowden and Tabor, [128] p. 154) demonstrated that the coefficient of friction of platinum on itself was greatly reduced by electrochemically depositing a layer of either oxygen or hydrogen on the surface. The process can be controlled by adjusting both the potential at which deposition takes place and is sensitive to the pH of the solution used. The application of this technique has been reviewed by Waterhouse [134] and by Wilkinson and Warburton [135].

Heinike and Harenz [136] have recently attributed the stress corrosion cracking of Cr/Ni steel, brass and some aluminium alloys to the build up of negative potentials at regions associated with slip steps formed during plastic deformation. Cracks then develop due to the accumulation inside the metal of hydrogen formed by the electrochemical decomposition of the surrounding aqueous solution. The reaction of carbides with dissolved hydrogen in the metal is also thought to contribute to cracking through the production of gaseous hydrocarbons [137].

5.2.2. Grinding

The grinding process, also, is affected by the nature of the ambient atmosphere and compounds formation. Reports have appeared on the influence of H_2S [136, 138, 139], H_2O [117, 140, 141], H_2 [142], CO [136, 143], CO_2 [140, 143, 144] and low molecular weight hydrocarbons [145].

Frequent observations have been made on the mechanical degradation of organic polymers during grinding, rolling and milling. These are not reviewed in detail here; suffice it to say that recently a quantitative investigation has been made of these reactions by Zhurkov and his co-workers in relationship to the fracture mechanics of the materials. A combination of physical chemical techniques including electron spin resonance, infra-red spectroscopy and small-angle X-ray scattering has been used to follow the formation of free radicals within the bulk of the polymer in relationship to the break up of the material by the formation of sub-microcracks [146, 147].

5.2.3. Polishing

The mechanism of the mechanical polishing of metals probably involves a combination of the surface flow of asperities by plastic deformation and microcutting by the abrasive particles used in the polishing process. The broad outline of the principles involved in these two processes has been discussed by Bowden and Tabor [148] and by Samuels [149]. In plastic materials this is probably not aided by chemical transformations although temperature and strain induced phase changes may occur [149]. For brittle materials polishing by the smearing action of plastic deformation would seem to be excluded especially at the high rates of strain at which this process takes place. The question therefore arises as to whether polishing must inevitably take place by repeated microfracturing of the asperities responsible for surface roughness. Of special interest in this context is the polishing of diamond which although being the hardest known material has been very successfully polished for many centuries.

There is still some difference of opinion about whether diamond can be deformed plastically [29, 150] and the mechanism of deformation is complicated by the anomaly that the crystal shows "hard" and "soft" directions of polishing (despite its apparently isotropic structure) and this is mirrored in its frictional behaviour (Bowden and Tabor [148] Chapter 10). The mechanism of polishing is still not known, but Tabor has associated the wear mechanism with adhesion and the anisotropy of the frictional behaviour which in turn are affected by the presence of protective layers on the surface of the diamond. The generation of locally high temperatures by rubbing has also been postulated as a contributory factor in the polishing process by Seal [28], Bowden and Scott [151] and Bowden and Freitag [152] and this is evidenced by the appearance of a black powder around the polishing tool which is assumed to be graphite or amorphous carbon.

As already discussed, it is difficult to see how heat can be generated plastically when diamond is used to polish diamond at the high speeds involved in the operation. It seems more likely that the mechanism should be one in which smoothing of the surface takes place by the fracturing of asperities in a manner similar to that first described by Tolkowsky [153]. According to this mechanism, the elastic strain energy released on fracture is expected to contribute to the polishing process which should improve at higher speeds. Experimentally, a change in coefficient of friction with polishing (sliding) speed is found [152] and this is accompanied by a change in sound, incandescence of the polishing surface and accelerated wear.

It is common in practice to include in the polishing medium certain oxy-acid salts which are found to facilitate the smoothing process [154]. It is not known what part these play in diamond polishing but it may be that the grinding of these materials releases atomic oxygen in the same way as described for silica [71]. This very reactive species could then oxidize the diamond surface producing CO_2. This amounts to a delicate method of chemical polishing in which the polishing agent (atomic oxygen) is produced in situ by the fracture of crystals of the oxy salt and in close vicinity to the surface to be polished. There seems to have been no attempt at experimental verification of this hypothesis although the empirical addition of additives which may react chemically with the surface is well known in the art of polishing.

6. Very fast reactions in solids

6.1. Initiation by intense shock waves

Explosive reactions may be initiated in exothermic compounds by the passage of a shock wave and there seems to be general agreement that the reaction is started thermally. For shock waves with intensities p up to $\sim 10^7$ N m^{-2} (10^5 atm), the energy is partitioned in two modes; that required to compress the lattice against the repulsive intermolecular forces and so depends upon the elasticity of the material and that which excites molecular vibrations and which appears as heat. At low shock intensities the latter part is small. At very high intensities a third term may be added to the expression for the total energy of the solid to account for electronic excitations in which the electrons in the lattice behave as an energetic gas [155].

Thus

$$E = E_e + E_t + E_{\text{electron}}$$

where

$$E_e = \int_V^{V_0} p(V)\mathrm{d}V$$

$$E_t = 3Nk(T - T_0) + E_0$$

where T_0 is the ambient temperature and E_0 the lattice energy at that temperature, N is the number of atoms per unit weight and k Boltzmann's constant.

$$E_{\text{electron}} = \tfrac{1}{2}\beta_0 \left(\frac{V}{V_0}\right)^{\frac{1}{2}} T^2$$

where β_0 is proportional to the electron density in the solid and V_0 is its specific volume.

The evaluation of the temperature rise due to the passage of a shock wave in the solid requires some knowledge of the equation of state of the material. Thus neglecting the term E_{electron} which is only important at very high shock intensities (equivalent to the generation of temperature of 10 000 K or above), the equation of state can be written as,

$$p = p_e(V) + P_t(V, T)$$

and

$$E = E_e(V) + 3NkT$$

since

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$P_t = \Gamma(V)\frac{C_V T}{V} = \Gamma(V)\frac{E_t}{V}$$

where $\Gamma(V)$ is Gruneisen's coefficient for the solid and is equal to $(\gamma - 1)$ where $\gamma = C_p/C_V$. Thus

$$p = p_e(V) + \Gamma\frac{C_V T}{V}$$

and

$$\frac{p - p_e(V)}{p_{T_0}} = \left(\frac{T}{T_0}\right)^{\Gamma+1/\Gamma} = \left(\frac{V_0}{V}\right)^{\Gamma+1}$$

This may be represented on a p-V plot as shown in Fig. 10 in which the horizontally shaped portion represents the contribution to the total energy of the compressed lattice and that shaded vertically, the contribution from the thermal energy. When the shock wave is of sufficient intensity to initiate the chemical reaction and is itself sustained by the energy released in the reaction, the solid is said to detonate. The theory of detonation was first arrived at by Chapman [156] and independently by Jouguet [157-159]. The whole field of stable reactive shocks and the hydrodynamic theory of detonation has been reviewed by Eyring *et al.* [160] and Evans [161]. The results of these theories have been successfully applied to a variety of organic explosive materials in which at shock intensities $\sim 10^7$ N m^{-2} temperature rises of several hundreds of degrees are generated and the reaction takes place with explosive violence.

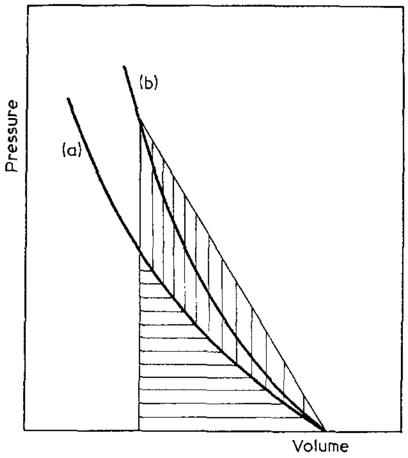

Figure 10 p-V diagram for shock compression of cold material. Curve (a) represents the effect of elastic deformation while curve (b) includes the effect of shock heating (represented by the portion shaded vertically).

While it seems possible to successfully treat solids as imperfect gases in predicting the temperatures generated at high shock intensities, this is not the case when dealing with weak shocks since the temperature rise calculated is not large enough to initiate the reaction. Nevertheless certain materials, e.g. some heavy metal azides and fulminates are known to be extremely sensitive to weak stimuli and some other explanation for their explosive behaviour would appear to be necessary.

6.2. Mechanical initiation by weak stimuli

Lead azide crystals can be made to explode when subjected to shocks $\sim 10^5$ N m^{-2}. Under these conditions the average temperature rise in the material is $\sim$10 K and certainly not high enough to start the explosive decomposition reaction. To overcome this apparent dilemma Bowden and Yoffe [162] have considered means whereby it is possible to localize the available energy in a volume sufficiently small for a high enough temperature to be reached. This idea is sometimes known as the hot spot theory.

Starting with the suggestion of Bernal [163] that friction between crystals may produce locally high temperature at the points of contact, experiments were carried out by two groups of workers [162, 164] to relate the amount of energy expended in friction and impact situations with the explosive sensitivity of the inorganic azides. The experimental evidence for frictional hot spots rests largely on observations made on the sliding contact of metal surfaces and follows the early work of Shore and Herbert already mentioned. These were later developed in an ingenious series of experiments (Bowden and Tabor [128] Chapter 2) in which temperature flashes of up to 1300 K and duration $\sim 10^{-4}$ sec were measured between dissimilar metal surfaces sliding together and acting as a thermocouple. For brittle materials this mechanism of hot spot formation which depends upon plastically deforming the material is not tenable. A solution to this apparent dilemma has recently been suggested by Fox [165] for materials like the inorganic azides, whereby the release of elastic strain energy at the tip of a fast moving crack in the material, is responsible for activating molecules in the region of the crack tip. This situation amounts to a hot spot moving through the solid at the speed of the crack and is limited to the maximum crack velocity, i.e. some fraction of the speed of sound in the solid. Mechanical activation of this type was first proposed by Taylor and Weale [166] who suggested that in compacts of granular high explosives, molecules could become activated by the attrition of individual crystals upon impact and that the dissipation of this activation energy could give rise to the fast reaction. Later Carl [167] suggested that the crystal lattice energy may be utilized.

A quantitative test of the fracture method of initiation requires detailed knowledge of the mechanical properties of the materials particularly at high strain-rates and this is not readily available. From the point of view of the mechanics of the process, the most effective method of "siphoning" energy from the crack tip and hence reducing the temperature of the hot spot is by plastic flow. The greater the amount of energy dissipated in this way, the less will be available for activating molecules as the crack propagates. The necessary Griffith condition for a fast crack can then be written as

$$\frac{\mathrm{d}}{\mathrm{d}c}\{E_{\mathrm{el}} - [E_{\mathrm{s}} + E_{\mathrm{kin}} + (E_{\mathrm{pl}} + E_{\mathrm{chem}})]\} > 0$$

in which the terms in the square brackets represent the ways in which the released elastic strain energy E_{el} can be dissipated as the crack increases in length c. In this E_{s} represents the surface energy of the newly formed fracture surfaces and E_{kin} the kinetic energy of the rapidly parting fragments of specimen E_{pl} and E_{chem} are bracketed together to imply that only a fixed amount of energy is available for this sum which means that the fracture method of initiation will be most effective in brittle materials for which E_{pl} is small.

A preliminary attempt based upon this hypothesis [165] has been made to predict the sensitivity to impact of a group of three metal azides namely those of sodium, thallium and lead. These three materials show a wide variation in explosive sensitivity ranging from completely insensitive sodium azide to lead azide which explodes when lightly shocked. The criterion adopted was the ductile-brittle (d-b) transition temperature, the implication being that above the d-b temperature most of the elastic strain energy released on fracture will be dissipated in plastic flow at the crack tip, whereas below this temperature, most will be available for initiating the chemical reaction. The calculations show that on this basis although lead azide is predicted to be the most sensitive material, sodium and thallium azides should show equal sensitivities. This latter prediction is contrary to practical experience. Undoubtedly the main drawback in applying this method to the prediction of sensitivity is the great difficulty of obtaining mechanical property measurements at impact strain-rates, i.e. > 10 sec^{-1}. In the original publication [165] arguments are given which suggest that at high rates of strain the brittleness of these materials increases in the order Pb > Tl > Na which is the correct order of explosive sensitivities. However, more detailed experimental data are needed before this mechanism can be considered established.

In a parallel study attempts were made to measure the amount of decomposition which takes place during the fast fracture of crystals of several thermally unstable materials including both exothermic and endothermic compounds [41]. In this case decomposition is associated with a definite temperature rise which is predicted from independent measurements of the kinetics of decomposition relating the rate of reaction to the activation energy for decomposition. Thus

$$\text{rate} = \frac{\mathrm{d}N}{\mathrm{d}t} = A \exp\left[-\frac{E_{\text{decomp}}}{kT}\right]$$

where N is the number of molecules decomposed with an activation energy E_{decomp}. The problem of choosing the appropriate value of t, the time for which decomposition is occurring, depends upon the crack velocity which for maximum velocity cracks means that the crack tip traverses molecular dimensions in about the same time as is required for one bond vibration. This means that no true thermodynamic equilibrium is established and casts doubts on the validity of the above equation in such calculations. Nevertheless, values obtained for T are proportional to the brittleness of the materials as judged by indentation hardness (low strain-rate) measurements on the fracture face (Table II). This again implies that the less energy is used in plastic deformation, the more becomes available for the initiation of chemical reaction.

6.3. Chemical degradation in the fracture of amorphous polymers

The arguments of the last section assume brittle behaviour for the efficient initiation of chemical reactions during fracture and this is best achieved at high fracture velocities. However, these ideas have been extended to describe the mechanism of fracture in amorphous polymers which although brittle as judged from their stress/strain behaviour, fracture by an essentially ductile mechanism. In this process material known as craze develops ahead of the crack tip and it is the properties of this ductile material which control the mechanics of the fracture process. Little is known about either the structure or the way in which craze material is produced although Kambour [168, 169] in a series of optical and electron microscopic studies of craze in polycarbonates has shown that the material is like a sponge containing globular pores occupying about 50% of the total volume.

Recently, Fox and Fuller [170] have examined the possibility that the structure of the craze may result from the thermal decomposition of the polymer induced by the temperature rise generated by viscous heating in the rapidly deforming polymer ahead of the crack tip. Direct experimental measurements were made of the temperature rise around the crack tip during propagation (Fig. 11). The values are remarkably large being for instance 800 K in poly (methylmethacrylate) and 700 K in polystyrene. Calculations of the amounts of decomposition produced by these temperature increases show that, assuming all decomposition products are volatile [171], sufficient gas is produced to account for the sponge like structure of the craze. Support for this thermal mechanism of craze formation comes from the work of Regel and his co-workers [171] who have shown that

TABLE II

Material	Amount of fracture decomposition (molecules m^{-2})	Pre-exponential factor (molecules m^{-2} sec^{-1})	Activation energy for decomposition (kJ mol^{-1})	Hardness VHN (10 g load for 90 sec)	Crack tip temperature (K)
$CaCO_3$ (calcite)	2×10^{17}	1.2×10^{46}	382	160	1 250
$MgCO_3$ (magnesite)	1×10^{18}	2.3×10^{31}	176	460	15 000
$PbCO_3$ (cerasite)	7×10^{18}	4.8×10^{46}	239	—	850
NaN_3	1×10^{17}	3.0×10^{38}	193	10	1 000
β-$Pb(N_3)_2$	3×10^{19}	7.4×10^{30}	125	130	negative*

*Indicates that the reaction has become partially self sustaining because of the heat evolved on decomposition.

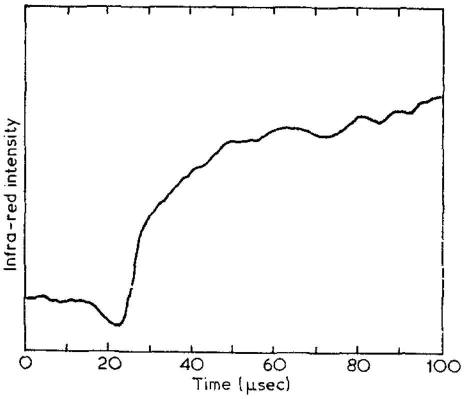

Figure 11 Infra-red radiation from the tip of a fast moving crack in poly(methylmethacrylate). The initial decrease is due to the thermoelastic cooling ahead of the crack where the material is in tension. The shape of the subsequent rising curve may be explained in detail in terms of the temperature rise at the crack tip and the rate of separation of the two halves of the specimen.

the molecular species which are produced by the fast fracture of poly (methacrylate) polystyrene and polypropylene are remarkably similar to those obtained by heating.

7. Conclusions

Although not new, the study of mechanically induced chemical reactions in solids has received sparse attention probably because the subject lies uncomfortably between chemistry and materials science. In this review we have examined a number of possible ways in which mechanical energy can initiate chemical reactions. In many cases this appears to take place through the generation of heat although examples exist in which electrical charging and direct bond excitation play an important part.

Emphasis has been laid on the importance of distinguishing between brittle and ductile behaviour and ultimately upon the dependence of these mechanical qualities on strain rate. Because of the necessity to make these distinctions it is not surprising that little data yet exists which can be used in describing the degradation of mechanical energy to other forms such as thermal electrical and optical which may be ultimately responsible for initiating chemical reactions.

Nevertheless, there are signs of a growing interest in this phenomenon largely because of the possibilities of using the effects in such technologically important processes as those already described and others not touched on here, such as the more efficient treatment of ores and minerals, the preparation of new compounds and phases by mechanical methods [6], friction and lubrication, stress corrosion cracking, fretting fatigue and liquid metal embrittlement.

On a more subtle level, the phenomenon may play an important part in the environmentally induced changes in mechanical properties of both metallic and ceramic materials (Rehbinder effect). Greater understanding in this area will lead to advances in the technology of maching operations including cutting and drilling [172].

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