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Effect of mechanical treatment on the reactivity of ammonium perchlorate

SEETHARAMA C. DEEVI*
Departments of Metallurgy and Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India

Thermal reactivities of ammonium perchlorate (AP) pressed at 1500 kg cm^{-2} for various dwell times ranging from 0 to 45 min have been investigated. Reactivity of AP is observed to (a) increase with increase of dwell time up to 15 min and (b) decrease for the compacts obtained at higher dwell times. X-ray diffraction profiles of the compacts indicated a broadening up to 15 min dwell time and a narrowing thereafter. The increase in the reactivity has been attributed to the increase in the number of gross imperfections and plastic deformation of particles. The decrease in the reactivity is explained in terms of recrystallization after plastic deformation. Local heating is shown to exist during compaction though its macroscopic effect is insignificant during compaction of AP.

1. Introduction

During the last two decades, the decomposition of a wide range of solids has been studied and the rate of reaction has been shown to depend on various pre-treatments such as grinding, X-ray-, γ-ray-, and uv-irradiation. Recently, it has been shown that thermal and chemical decomposition could be altered with an applied electric field [1, 2]. Pre-treatments, in general, increase the number of nuclei (due to an increase in the number of gross imperfections, which include point defects and dislocations) resulting in either a decrease or elimination of induction period for solid state decompositions [3–6]. Theories of dislocations suggest that straining of a crystal beyond its elastic limit causes plastic flow to occur involving multiplication of dislocations and formation of slip bands. A severe strain can be imposed on a crystal with mechanical treatments such as grinding and compaction. Bridgman [7] studied the plastic deformation of nearly 300 inorganic solids with 20 mg of powders by confining them with hydrostatic pressures as high as 50 000 kg cm^{-2}. He observed an irreversible change in the chemical reactivity of the solids. Larsen and Drickamer [8] observed that plastic deformation (induced at pressures ranging from 3000 to 50 000 kg cm^{-2}) converts potassium hexacyanoferrate (III) to potassium hexacyanoferrate (II). Boldyrev and Avvakumov [9] predicted a lowering in the reactivity after a maximum has been reached as a consequence of recrystallization. Since such a lowering of the reactivity has not been reported so far, this paper addresses the thermal reactivity of a severely strained solid and the associated physical changes prior to plastic deformation and during the stages of recrystallization.

Ammonium perchlorate (AP), $NH_4^+ClO_4^-$, has been chosen for this experimental investigation since it has been a representative candidate for various solid state decompositions and is a technologically important material for solid rocket propellant formulations. In the present work, application of pressure on AP is shown to induce a strain on a the crystal lattice, and eventually, plastic deformation. It is shown that understanding the nature of solid state processes taking place on compaction is vital to tune or alter the thermal behaviour of solids, in general, and AP pellets in particular. The study also focuses on the importance of local hot spots in the compaction of thermally sensitive solids such as AP and KP (potassium perchlorate, $KClO_4$).

2. Experimental procedure

Crystalline AP used in the present work was analytical grade material from Veb Laborchemie, Apolda, Germany. The crystals (ground and sieved) were $< 37\,\mu$m in diameter with an average particle size of 11 μm. Pellets were prepared using a hydraulic press and a 5 cm-diameter die with 20 g of powder, at 1500 kg cm^{-2} pressure for dwell times ranging from 0 to 45 min. To avoid non-homogeneity in the density of samples due to axial pressing, the diameter to thickness ratio was kept very high, and varied from 10 : 1 to 12 : 1 in the dwell time range 0 to 45 min. Compacts were weighed to detect any decomposition of AP, and surprisingly no decomposition was observed even when the compact was pelletized at 45 min. Pellets pressed for 15 min or longer were translucent in appearance. Densities of the compacts were determined from the weight and dimensions of the pellet and the reported "percentage theoretical maximum density" (Table I) is an average of four or five separately pressed pellets.

Hardness measurements of the pellets were made using a Vickers microhardness tester. Indentations for microhardness were made with a 100 g load and

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[*] Present address: Department of Mechanical Engineering, University of California, Davis, California 95616, USA.

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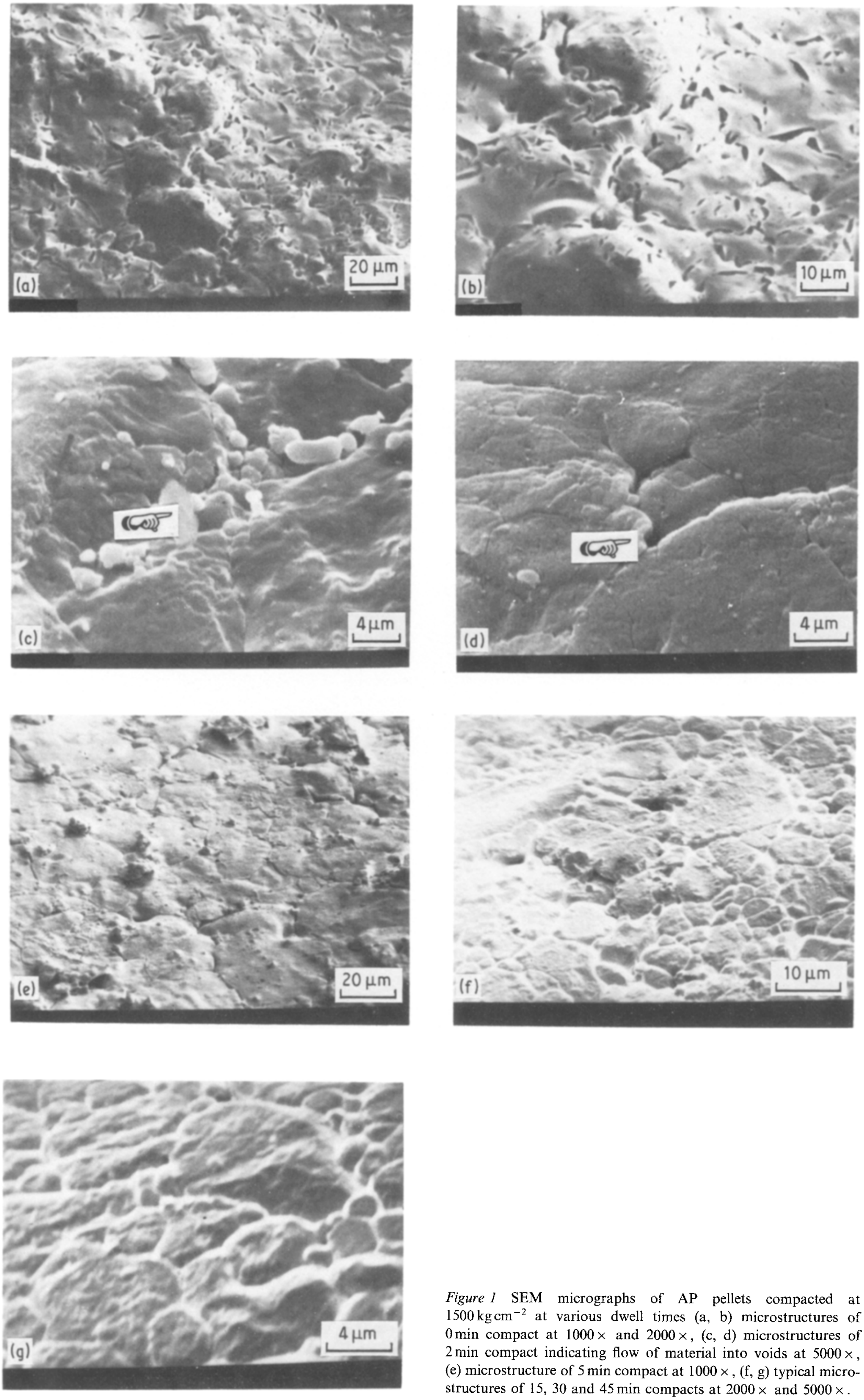


Figure 1 SEM micrographs of AP pellets compacted at 1500 kg cm^{-2} at various dwell times (a, b) microstructures of 0 min compact at 1000 × and 2000 ×, (c, d) microstructures of 2 min compact indicating flow of material into voids at 5000 ×, (e) microstructure of 5 min compact at 1000 ×, (f, g) typical microstructures of 15, 30 and 45 min compacts at 2000 × and 5000 ×.

TABLE I Variation of physical properties and thermal reactivity with dwell time

Dwell time	% TMD	Microhardness ($\mathrm{kg\,mm^{-2}}$)	$t_{1/2}$ at 310° C (min)	Pure diffraction profile width (arbitrary units)
0	92.5	very low	50	0.024
2	95.4	16.9	39	0.027
5	96.9	28	28	0.030
15	98.5	30.5	15	0.058
30	99.1	31.4	24	0.042
45	99.3	31.8		

diagonals for the impressions were measured using a calibrated ocular at a magnification of 487×. The measurements were made at room temperature and the duration of the indentation was kept at 10 sec. The hardness values were calculated using the relation $H_v = 1.8544pd^{-2}$, where H_v is the Vickers hardness number, P is the indentor load in kg and d is the diagonal length of the impression in mm. Several indentations were made on each face of the compact and the reported value (Table I) was an average obtained from several impressions by measuring both the diagonals.

X-ray diffraction patterns of the compacts were taken using $\mathrm{Cu}K_\alpha$ radiation ($\lambda = 0.15405\,\mathrm{nm}$) at 30 kV and 2ϕ mA. The slit system used was 1°–0.2 mm–1°. The diffraction peak profiles were recorded at a chart speed of $4\,\mathrm{cm\,min^{-1}}$ by step-scanning at 2ϕ, $0.25°\,\mathrm{min^{-1}}$ and taking the number of counts for 4 sec. For X-ray diffraction purposes, the 5–cm diameter compact was cut into two pieces and one entire piece was used for obtaining the diffractogram. Compacts were examined on both sides for any crystallographic transformation from orthorhombic to cubic structure. The X-ray study revealed that the compact had retained its orthorhombic structure and the d-values of various reflections on both sides of the compact (and within the two pieces) were identical. Line broadening calculations were carried out on the (2 1 1) reflection, since the (2 1 1) reflection has a reasonably good I/I_0. The breadths were corrected for instrumental broadening and the pure diffraction breadths were utilized to calculate the crystallite sizes.

Differential thermal analysis (DTA) of the samples was carried out in air at a heating rate of $10°\,\mathrm{C\,min^{-1}}$. Platinum cups were used as sample holders and the sample was 52.5 mg in each case. Powdered alumina (ignited) was used as a reference standard. The uncertainty in the peak temperature was ± 1° C. Surface structural studies of gold coated samples were carried out using a Cambridge-150 model Scanning Electron Microscope (SEM).

3. Results

Pellets pressed at $1500\,\mathrm{kg\,cm^{-2}}$ show an increase in the percentage of theoretical maximum density (% TMD) and a decrease in the porosity with increase of dwell time (Table I).

Microstructures of compacts with 0 min dwell time indicate the presence of slit shaped voids without much grain boundary development (Figs 1a and b). Increasing the dwell time to 2 min causes breakage of particles and reduction of pores due to the material transfer to the voids. Such a material transfer leading to collapse of voids can be seen clearly in Figs 1c and d. Grain boundary development with further increase of dwell time can be seen in the microstructure of 5 min dwell time compact (Fig. 1e). Compacts pressed in the range 15 to 45 min dwell times exhibit grain boundaries with no detectable porosity seen under SEM. Typical microstructures are shown in Figs 1f and g. Fig. 1g obtained at a magnification of 5000× does not show any evidence of porosity agreeing with the density values reported in Table I. The compacts obtained at 15 min dwell time and beyond appeared oily and translucent. The hardness value reaches its maximum around 15 min and only a marginal increase is seen for compacts with higher dwell times.

Fig. 2 shows the DTA curves of AP with increase of dwell time. A significant shift in the second exotherm towards lower temperatures and an increase in the exothermicity of the first exotherm are noted for samples pelletized with dwell times in the range 0 to 15 min. Interestingly for the 30 min dwell time compact, a reverse trend from that of the 15 min compact is noticed. Such a trend is observed in the dynamic as well as in the isothermal thermogravimetric experiments. The initial and final temperatures of decomposition of AP in the dynamic thermogravimetric curves are also sensitized (decreased to lower temperatures) with increase in dwell time from 0 to 15 min and a reversal is noticed again for the 30 min compact. Isothermal experiments conducted at 354° C indicate that the time required for 50% decomposition decreased from 0 to 15 min and increased thereafter (see $t_{1/2}$ values in Table I).

The enhanced reactivities with increase of dwell time is accompanied by line broadening coupled with a shift to higher 2ϕ values in the X-ray diffraction lines. Increase of dwell time from 0 to 15 min increases the breadth of diffraction lines followed by narrowing of the lines for the 30 min compact. Table I represents typical pure diffraction profile widths for the (2 1 1) reflection of AP compacts with an increase in dwell time. Generally, the increase in the pure diffraction breadth is attributed to an increase in the defect concentration and a decrease in the crystallite size [10–12]. Crystallite size variation (from the (2 1 1) reflection) indicates a minimum at a 15 min dwell time (Fig. 3). At 15 min dwell time, the crystallite size, peak temperature of the second exotherm and $t_{1/2}$ indicate low values as compared to the 5 and 30 min sample (Fig. 3).

To examine the thermal decomposition nuclei generated in AP pellets, 200 mg pellets were heated at 310° C causing partial decomposition of AP not exceeding 40% at any dwell time. The volume of the partially decomposed sample almost doubled due to the release of product gases, and the porous residue contained adsorbed gases. An examination of the sample under SEM indicates that the sample is quite porous with several thermal decomposition nuclei (Fig. 4a). Such porosity agrees with the brief descriptions reported by earlier authors [13, 14]. Consistent with the decomposition behaviour of AP, the size and

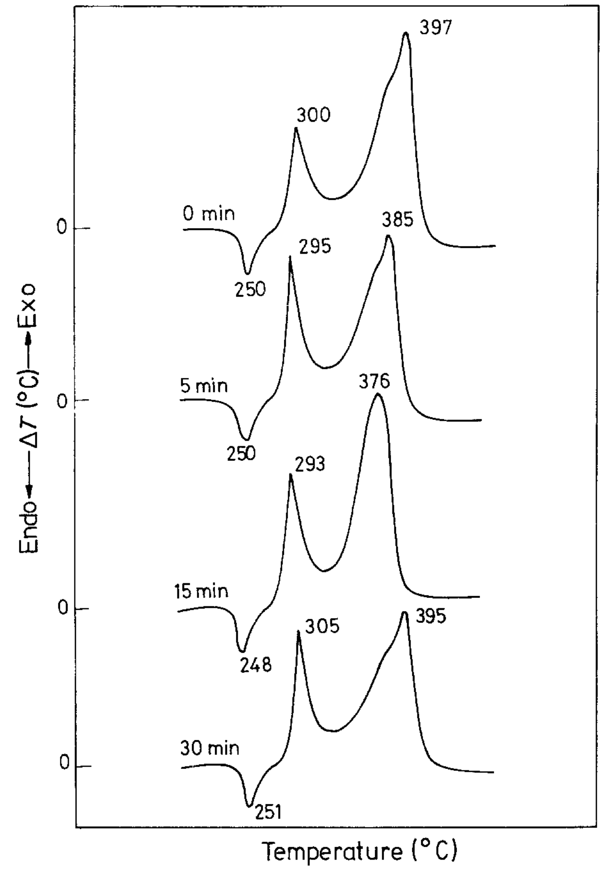


Figure 2 Differential thermal analysis curves of AP compacted at 1500 kg cm^{-2} at various dwell times. Heating rate = 10° C min^{-1}.

number of nuclei are smaller in the orthorhombic region (below 240° C). With increase of time and temperature, the size of decomposition nuclei increased and decomposition of material around the nuclei led to the appearance of voids. In Fig. 4a the arrow indicates a large crack due to the release of product gases. Thermal decomposition nuclei range from 6 to 80 μm and the number of smaller nuclei in the range 5 to 13 μm are twice the order of magnitude as compared to larger ones. Initially, the decomposition nuclei appear almost next to each other (Fig. 4a at sites indicated by the pointer). At a higher magnification (Fig. 4b), the surface exhibits a rectangular structure composed of layers of AP stacked next to each other. The layers indicate small nuclei and nuclei sometimes extend as tracks (notice at the sites indicated by pointers). Examination of the interior of the crack (by tilting the specimen stage of SEM) also displays a porous stacked structure as seen on the surface.

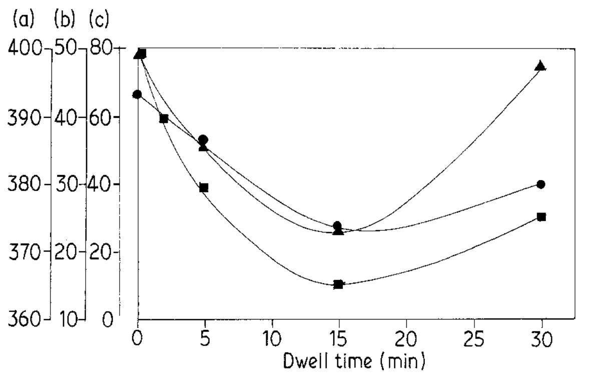


Figure 3 Representation of (a) (▲) peak temperature of the second exotherm, (b) (■) $t_{1/2}$ from Table I and (c) (●) relative crystallite size (D_{211}) of pellets with increase in dwell time. Note the minima observed in all the curves at 15 min dwell time.

The most striking differences apparent on comparison of Figs 1 and 4 are the loss of grains, grain boundaries of particles and the appearance of a layered structure. It is reasonable to expect that decomposition followed by recrystallization on quenching may produce the layered structure indicated in Figs 4b and c. Quenching rates were approximately 2×10^3 ° C min^{-1}. The lack of a hot stage microscope prevented the author from examining the nuclei during the incipient and growth stages of decomposition. It should be pointed out that an earlier paper [14] indicates a similar structure on the m-face of a single crystal of AP upon decomposition around 400° C. An examination of the surface structures of several quenched samples indicate that the features displayed in Fig. 4 are characteristic of partially decomposed AP pellets. It can be argued that defect concentration controls the nucleation centres for decomposition which in turn manifests itself in terms of the reactivity of the solid. Therefore, an estimation of the nucleation spots was carried out by irradiating a constant area of the pellet with an electron beam in a controlled manner by increasing the voltage from 4 to 20 kV for 30 sec and counting the number of nucleation centres generated upon electron irradiation. The experiment was carried out in a Cambridge Stereoscan SEM and is similar in nature to the well known work by Sawkill [15]. The results indicate that the number of nuclei generated on irradiation increase with increase in dwell time from 0 to 15 min. For the 15 min compact, the number decreased but the statistical sizing indicated that the dimensions of 80% of the spots are larger by a factor of six compared to those observed for the 5 min compact. It is concluded from the number and dimensions of the nucleation spots that an increase of dwell time from 0 to 15 min results in an exceedingly high nucleation and growth rate. For the 30 min compact a reversal from that of the 15 min compact is observed again, i.e. the number of nucleation spots is comparable to that of the 0 min compact, except that the dimensions increased slightly.

4. Discussion

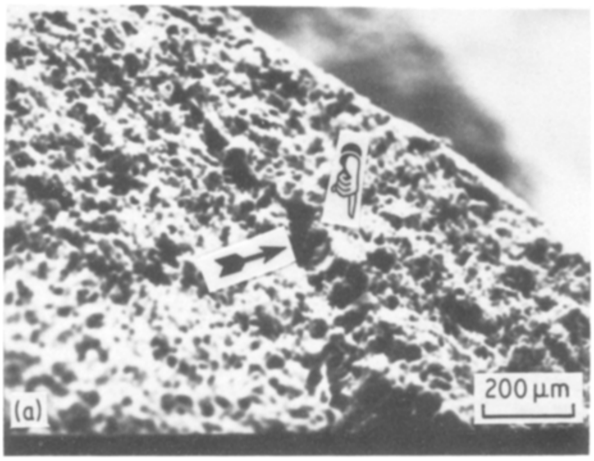
The results indicate that mechanical treatment induces changes in the reactivity. The changes in reactivity could be explained as due to the effects of lattice imperfections created on compaction. Though the relative importance of various kinds of imperfections is difficult to predict, discussion would be followed with the word "dislocations" since presence and role of dislocations in AP is well established [16–18]. The following is an attempt to explain the experimental observations based on the present understanding of thermal decomposition of solids and mechanical treatment on the reactivity of solids.

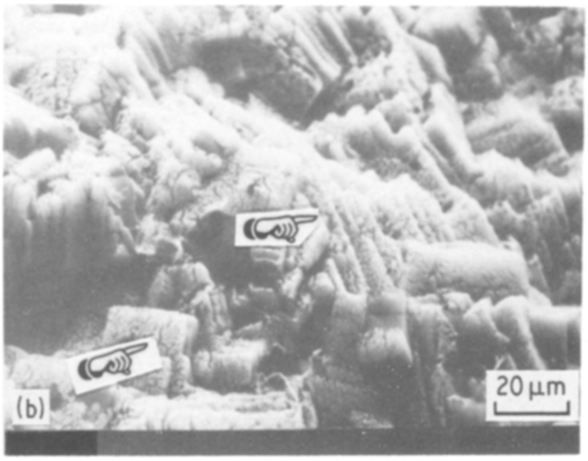
During the early stages of compaction, an increase in density results due to the mutual movement of particles and filling up of the voids between the particles. Such a stage can be recognized from the micrographs in Figs 1a to d. After the optimal packing is achieved, further increase in density with dwell time is achieved, first and foremost, from the deformation of particles leading to smaller crystallites. From the crystallite size data, it is reasonable to expect that such a process is occurring in the dwell time range 0 to 15 min. Microstructural observations and % TMD indicate that the density increase from 5 to 15 min is less significant as compared to the dramatic decrease in the crystallite size. Such deformation of particles induces the onset of plastic deformation, increasing the dislocation density due to the various types of defects generated as a result of increase of dwell time. Still further application of dwell time (after the plastic deformation) increases the contact area between the surfaces, causing ultimately an effective transport of material into the pores. This is akin to recrystallization and dislocation density should decrease accordingly.

Compacts of AP with 15, 30 and 45 min dwell times appeared "oily and translucent" indicating that a flow might have occurred. Cohen Nir [18] also indicated earlier that a "certain melting" of the solid phase occurred leading to the disappearance of voids. About fifty years ago, Bridgman [7] reported a smooth rotation in shearing experiments with AP powder implying that much resistance was not encountered for the plastic flow. Cohen Nir [18] and Bridgman's [7] observations and the present study strongly suggest that mechanical treatment brings about plastic flow in AP. Therefore the sequence of events leading to multiplication of defects followed by annihilation is a plausible explanation for the observed changes on compaction.

Broad diffraction lines are characteristic of cold worked particles and tend to sharpen during recovery. The shift of diffraction angles, 2ϕs, to higher values is indicative of stacking faults; however, doubling of reflections was not noticed. The microhardness of AP pellets clearly suggest that a large number of gross imperfections or dislocations are generated on compression in the initial stages of the curve i.e., 0 to 15 min and hence the observed increase in the reactivity from 0 to 15 min. As the dwell time is increased from 15 to 30 min, the increase in hardness as well as density is marginal. Added to this, the process of recrystallization renders the particles in these compacts relatively defect free and therefore the reactivity is reduced.

It is obvious from the results presented above that a one to one correlation can be made – increasing the dwell time alters the dislocation density. Increasing the dwell time (at a certain pressure) on polycrystalline AP can be visualized in terms of a prolonged cold working of single crystals (ionic or covalent or metallic). It is clear that the thermal decomposition behaviour is influenced by the dislocation density (created by the severe strain imposed on the crystals) and the observed effect is somewhat similar in magnitude to what was observed earlier with an electric field [2] and irradiation [1]. The present results strongly support and confirm the preferential activity observed at dislocations in various solid state decompositions [20–22]. The interesting features observed for the 30 min dwell time compact–higher decomposition temperature, lower percentage of decomposition at 354° C, and lower broadening of the X-ray diffraction profile, indicate that prolonged cold working or mechanical damage beyond a certain point lowers the dislocation density which is reflected in terms of lower reactivity.





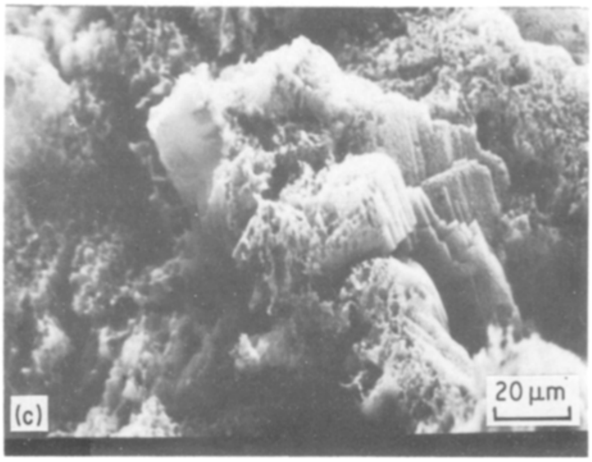


Figure 4 SEM micrographs of quenched AP compact after partially decomposing at 310° C. (a) Microstructure of 5 min compact at 100 ×. Arrow indicates crack due to sudden release of product gases. Pointer indicates small decomposition nuclei at the growth stage. (b) Microstructure of Fig. 4a at a higher magnification, 1000 ×. Note the layered structure as indicated by a pointer. (c) Microstructure of 30 min compact at 1000 ×.

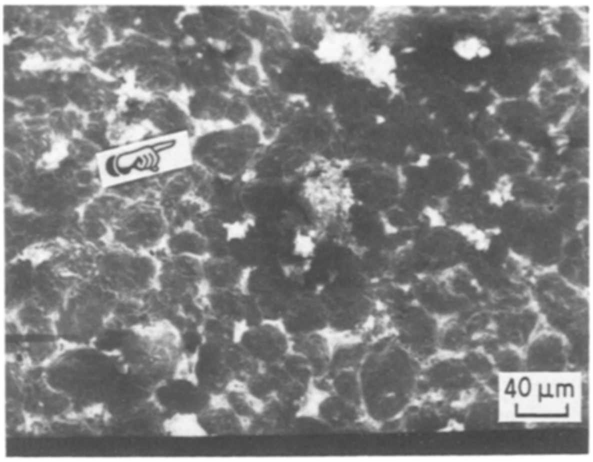


Figure 5 SEM micrograph of 50% AP–50% KP indicating melting at the grain boundaries. Compacted at 1500 kg cm^{-2} for 5 min.

The results are in qualitative agreement with the findings of previous workers. Ryabinin [23] also indicated that compounds subjected to high pressures decomposed at a higher rate, and the extent of decomposition was dependent on the particular compound. Larsen and Drickamer [8] reported that potassium dichromate subjected to high pressures decomposed at a much higher rate. As indicated by Boldyrev and Avvakumov [9], the reactivity of AP decreased due to recrystallization after a maximum has been achieved.

Local heating is an important factor to be considered in the compaction of materials, especially in the case of thermally sensitive materials. Decomposition of AP was not noticed at a pressure of 1500 kg cm^{-2} even at 45 min dwell time (see experimental section). It can be inferred that the average temperature of the compact due to local heating may not have risen sufficiently to decompose AP (AP is known to decompose even around 130° C, and a maximum of 30% decomposition occurs below 240° C, see [24]). Bridgman [7] studied the effect of hydrostatic pressure (up to 50 000 kg cm^{-2}) along with shear stress on various explosive compounds and concluded that mechanical stress alone could not initiate a reaction leading to detonation, implying that high temperatures were not generated. Larsen and Drickamer's [8] experiments on 10 mg of sample did not reveal any local heating effects. The important aspect of the present experiments is that 20 g of AP is used for compaction whereas previous researchers [7, 8] used only a few milligrams of sample. It was estimated that mechanical treatment could generate temperature pulses of the order of 10^3 to 10^5° C much higher than the average at grain boundaries for short periods of time such as 10^{-11} sec [25]. Dislocations could also generate temperature pulses but the rate at which dislocations dissipate their energy [26] makes local heating due to dislocations an unimportant factor. Therefore, it can be concluded that local heating generated due to mechanical treatment may not be sufficient enough to decompose samples. Local heating at grain boundaries could give rise to incipient melting, provided that the material exhibits melting prior to decomposition. To test this, potassium perchlorate, $KClO_4$, has been chosen since $KClO_4$ melts prior to decomposition leading to KCl [27]. $KClO_4$ has an orthorhombic crystal structure and the ionic sizes and valences of the NH_4^+ and K^+ ions are similar. It has been shown [28] that local melting does indeed occur when 10 g of NH_4ClO_4 is deliberately replaced with $KClO_4$ in the 20 g pellets. A second phase at the grain boundaries was observed due to the incipient melting caused by local hot spots. Fig. 5 shows a typical micrograph of a compact exhibiting melting at the grain boundaries due to local heating. Even in this case no weight loss was observed and the X-ray powder diffraction pattern of the pellet did not exhibit any reflections corresponding to KCl. This clearly indicates that local hot spots do not lead to macroscopic decompositions.

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