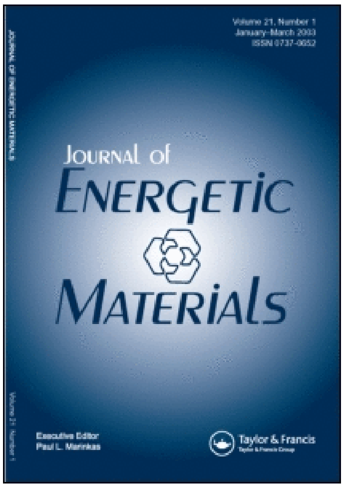

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STUDY OF THE THERMAL INITIATION OF AMMONIUM DINITRAMIDE (ADN) CRYSTALS AND PRILLS

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The thermal initiation by electron beam heating (and calibrated hot stage), of single crystals and prills of ADN, has been filmed / recorded in an Environmental Scanning Electron Microscope, from the formation of microscopic "reaction sites" (0.01 μm in diameter) to full crystal consumption. The transformations of the ADN prills and crystals were compared and recorded in real time at various magnifications (x10,000-100) and under different atmospheres (pure nitrogen and nitrogen/water vapour mixtures). The initiation characteristics of the prills and crystals were found to differ and are related to the microstructural characteristics produced by different prill manufacturing techniques namely, the "prilling tower" technique (Thiokol) and the "melt-stir" technique (CSD).

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INTRODUCTION

Ammonium dintramide (ADN) is a candidate potential oxidizer for use in propellant formulations. It was recently discovered in the U.S.A. by J. C. Bottaro et al.[1]. However it appears to have been used in the former Soviet Union (FSU) for more than two decades. The molecular structure of ADN ($H_4N_4O_4$), shown in Figure 1, consists of an ammonium cation and dinitramide anion. ADN may thus combine the desirable properties of lower sensitivity of ammonium salts together with the nitramine high performance characteristics[2]. In addition ADN is halogen-free and does not produce the toxic HCl acidic plume which AP combustion generates, an acid known to be detrimental to the earth's ozone layer[3]. ADN has thus been considered as a replacement oxidizer of AP in propellant formulations to achieve both the elimination of hydrogen chloride from the combustion products and to obtain an increase in energy output[3].

$$NH_4^+N(NO_2)_2^-$$

FIGURE 1

MOLECULAR STRUCTURE OF AMMONIUM DINITRAMIDE (ADN)

However, as is the role of energetic crystalline components of propellant formulations, only particles with low crystal aspect ratios, preferentially approaching a nearly round shape, allow their full potential to be used as well as considerably easing the propellant manufacturing processes, namely the formulation mixing and increasing the energy output control. ADN typically crystallizes with a needle-shaped or platelet-like morphology having very high aspect ratios ranging from 10-100:1 an undesirable shape for use in propellant formulations. A mass crystallization technology capable of converting flat, elongated needles into roundish spherical particles is thus very valuable for the manufacture of ADN and/or other candidate energetic material prills for use in propellant formulations[3].

Prilling is the formation of a rounded, granular solid by allowing molten droplets to be cooled by a fluid medium. Two main ADN prilling technologies have been developed. The "prilling tower", developed at Thiokol[4], reminiscent of the AN prilling technology, which allows the molten droplets of ADN to fall by gravity into a tower of flowing inert cold gas. The "melt-stir" technique developed at different laboratories namely, CSD[5], NAWC China Lake[6] and FOA/Bofors[7], cools the molten droplets of ADN by stirring them in a carrier liquid or oil immiscible with the molten ADN[6]. Further modifications are made to the base-line ADN by addition of thermal stabilizers and anti-caking agents[4,5,6].

The prilled ADN was tested by the various manufacturers or laboratories in small-scale safety sensitivity tests[4,5,6,8]. It was reported[4] that the modifications made to base-line ADN in the form of prilling appeared to have produced an ADN with dramatically improved small-scale safety properties. However there was no clear consensus amongst the sensitivity data reported by different sources[8]. This was investigated further, firstly by studying the initiation of single crystals and prills in an Environmental Scanning Electron Microscope (ESEM) in great detail to compare the behavior of the single crystals and prills made by the different manufacturing processes, effect of environment etc. The apparent discrepancy between the sensitivity data was found to arise from the fact that prills made by different manufacturing processes were being compared. The microstructure of the prills is in fact different and reflects the manufacturing techniques used and thus affects the observed sensitivity data. A detail of the analyzed prill microstructure is given in another publication[9], herewith the Environmental Scanning Electron Microscopy studies will be described.

EXPERIMENTAL

The ADN crystals and prills used in the studies were obtained from three separate sources, namely Indian Head NSWC, Thiokol and CSD. Crystals from Indian Head NSWC had the characteristic crystal platelet morphology whereas the samples from Thiokol and CSD had been prilled or spherodized from melt. Electron micrographs of typical NSWC crystals and Thiokol, CSD prills can be seen respectively in Figures 3, 6 and 7.

The thermal initiation by electron beam heating (and calibrated hot stage), of single crystals and prills of ADN, has been filmed / recorded in an Environmental Scanning Electron Microscope, from the formation of microscopic "reaction sites" (0.01 μm in diameter) to full crystal consumption. The transformations were recorded with a Philips Electroscan Environmental Scanning Electron Microscope Model E3. The crystals and prills were placed on a carbon tape applied to the surface of an aluminium stub. The samples were initiated thermally by heating with the microscope electron beam and/or calibrated "hot stage". The electron beam voltage was kept at 10 kV with a filament emission current of about 90 μA and vacuum chamber pressure of 2.4 Torr. All transformations were recorded in real time on a video-camera connected to the microscope. The microscope environment can be varied by the introduction of different "atmospheres". Thus various percentages of water vapour were introduced in the microscope "atmosphere/environment" to observe the effect on the ADN initiation. ADN is particularly sensitive to a humid environment since it is a hygroscopic material.

The electron beam in the scanning electron microscope can cause considerable heating in a sample, especially at higher electron beam energy densities. The electron beam can thus be used to simultaneously locally heat a sample and view the transformations. The transfer of energy created by the collision between the primary beam of electrons and the sample atoms is known to cause a number of phenomena[10]. Heat is generated, back-scattered and secondary electrons emitted (produce the sample image), cathodoluminescence forms and x-rays (characteristic and continuum) are produced. With the electron beam focussed down to micron spots, a considerable amount of electrical energy is concentrated in a small sample volume, approaching 8 x 10^7 W cm^{-2}. This energy causes a rise in temperature, which if the specimen has a low thermal conductivity, may be considerable. Even for the case of very short and high intensity electron pulses, initiation of energetic materials has been determined to take place by a thermal mechanism[11].

The temperature rise by the electron beam can be estimated from the following equation derived by Castaing[12] in 1951 where the temperature rise ΔT (°C) is from an electron beam of diameter d (μm) impinging on a sample of thermal conductivity k (W cm^{-1} K^{-1})

$$\Delta T = 4.8(Ei/kd)$$

where E is the incident energy of the electron beam (in keV) of current i (µA). From the above, the estimated temperature rise produced in the crystals by the electron beam is several hundreds °C or more depending on the electron beam energy density or beam radius. The depth of the electron beam penetration produced in a scanning electron microscope is depicted in Figure 2.

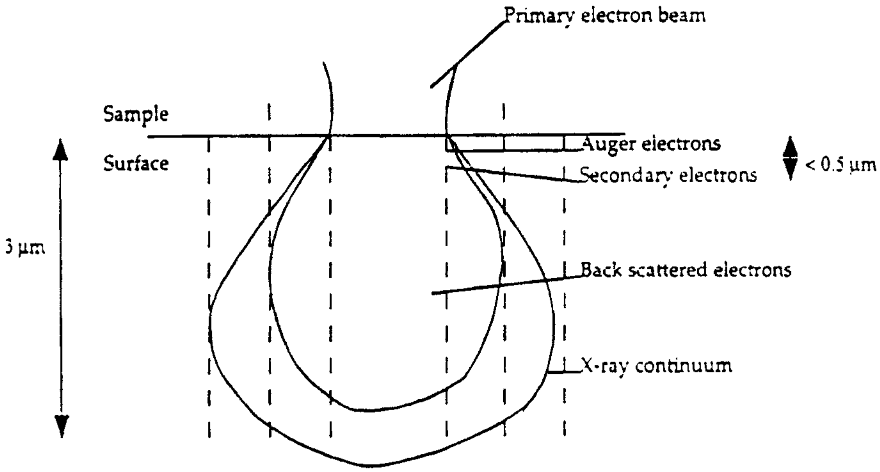

FIGURE 2

DEPTH OF SAMPLE ELECTRON BEAM PENETRATION IN SCANNING ELECTRON MICROSCOPE

RESULTS

The initiation of single crystals and prills of ADN (ammonium dinitramide) has been recorded/followed from the formation of microscopic "reaction sites" to full crystal consumption by filming in an Environmental Scanning Electron Microscope (ESEM) in real time under different atmospheres. The crystals and prills were initiated thermally by means of electron beam heating (and calibrated "hot-stage"). A summary of the observations follows.

Figure 3 is an electron micrograph of the NSWC Indian Head, ADN crystals showing the characteristic platelet morphology. Figure 4 depicts the crystal transformations, recorded in real time, of the heating of single crystals of ADN with an electron beam in the ESEM. The first video-clip shows the formation of microscopic "reaction sites", which appear at relatively low magnifications (low electron beam intensity), on the ADN crystal surfaces. The smallest "reaction sites" are about 0.01 μm in diameter. As the reaction progresses, the sites enlarge and increase in surface density. Focussing onto a small area of the crystal surface, the "reaction sites" are seen to expand and coalesce to form a porous residue material which eventually decomposes, leaving a hole to mark the spot or location of the electron beam heating. This is shown in the second video-clip. As

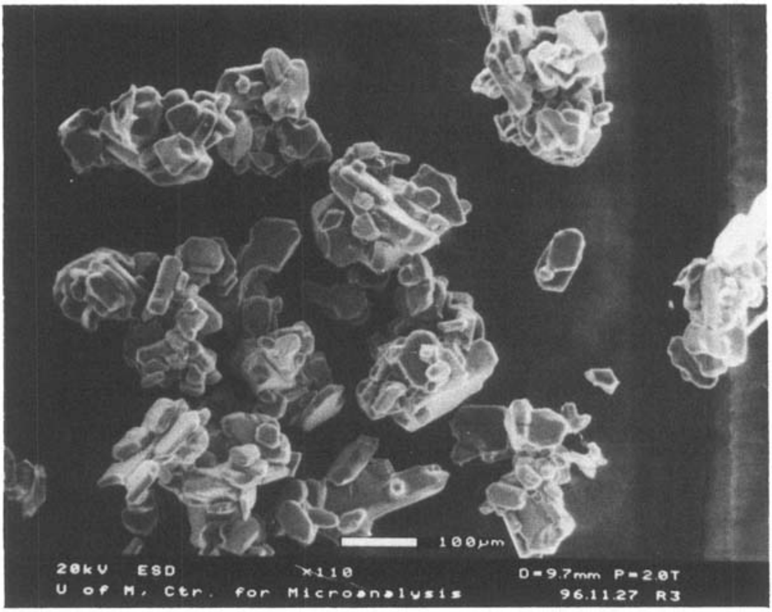

FIGURE 3

ESEM MICROGRAPH OF ADN CRYSTALS

the "reaction sites" expand, the shape of the sites becomes more distinguishable. The sites appear to have a crystallographic nature where the shape follows that of the crystal habit on which they are formed. An example micrograph is shown in Figure 5. The results are in agreement with the literature[13,14] where earlier observations of "nucleation sites" or more recently termed "reaction sites" have been reported, with crystallographic structure. The term "nucleation" arose from the fact that it was believed that "reaction sites" were formed by "nucleation" around a dislocation.

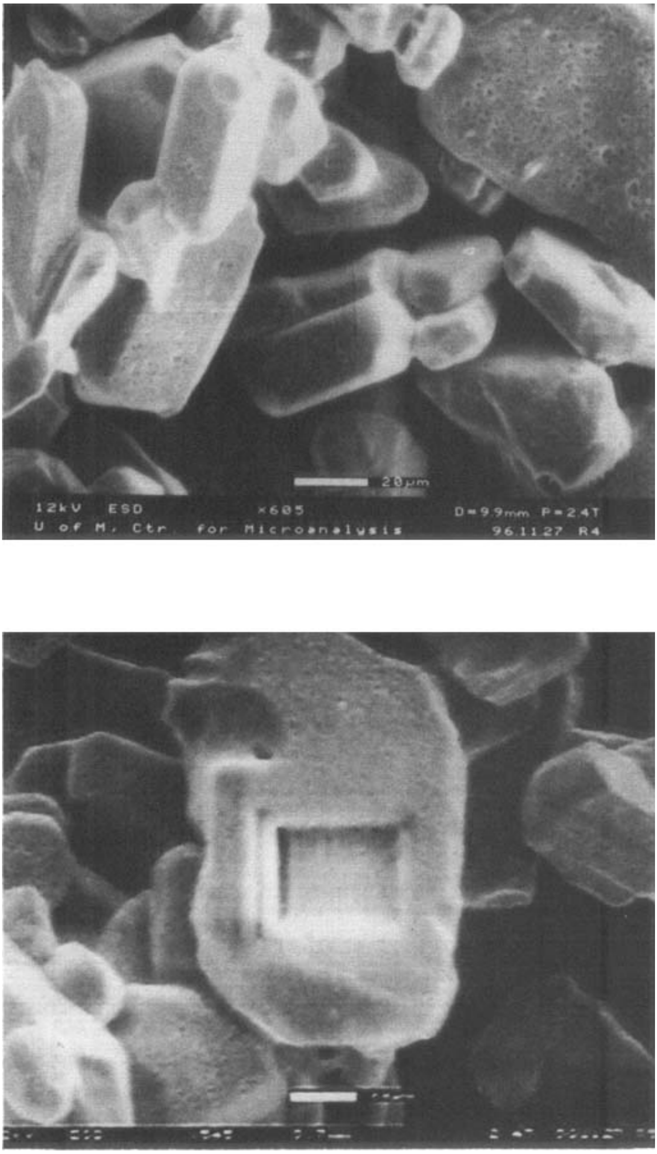

FIGURE 4

ADN SINGLE CRYSTAL TRANSFORMATIONS ON HEATING IN ESEM

As the reaction progresses the size of the sites increases at a rate depending on the atmosphere or environment. With water vapour added to the nitrogen "atmosphere", the ADN reactions become far more dramatic, where the rate of "reaction site" formation, expansion and propagation is increased considerably. Figure 5 is an example micrograph of a reacted ADN crystal in moisture. The crystallographic nature of the "reaction sites" can be clearly seen in the micrograph.

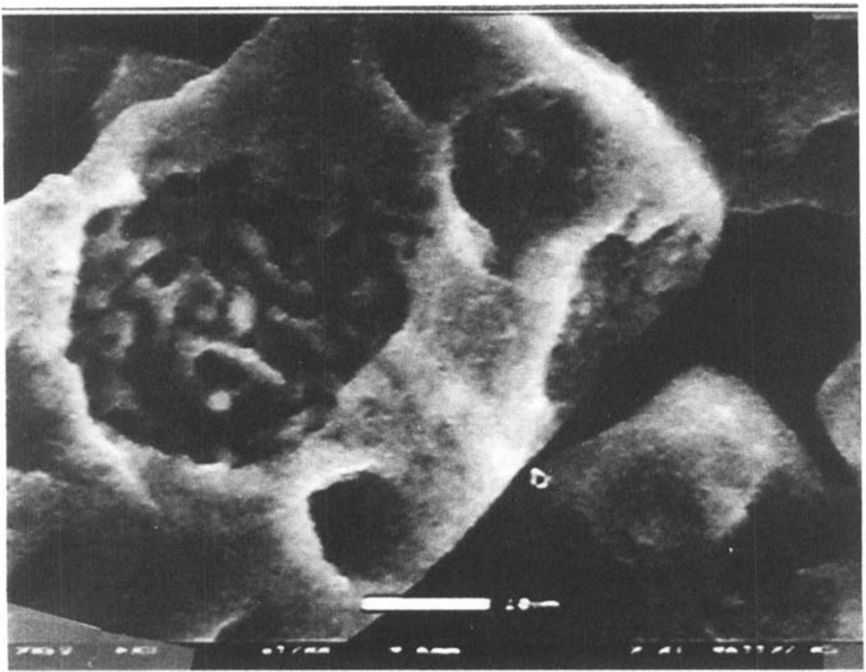

FIGURE 5

ADN CRYSTAL DECOMPOSED IN ESEM WITH "WET" ATMOSPHERE

Figure 6 shows the transformations obtained on heating the prills, manufactured by Thiokol using the "prilling tower technique", with the electron beam. The first video-clip shows the surface of an ADN prill which has undergone initiation. The initiation of the prills differs from that of the crystals. Thus, the "reaction sites" are not homogeneously distributed on the surface of the prill as was the case for the crystals. White particles emerge from the prill surface prior to initiation. The particles appeared white in the ESEM due to electron charging. Silica particles, would charge up in the electron microscope and since a prill surface settling of silica has been confirmed by chemical analysis, as described in another paper[9], the particlès are indeed believed to consist of silica. A surface settling of silica particles on the prill may act to quench the formation of "reaction sites" as evidenced by the recorded transformations which showed that once the surface layer was consumed, the reaction progressed very rapidly into the bulk of the prill. The second video-clip shows the propagation of the reaction into the prill. The internal "porous" residue appears to have a crystallographic structure. About six times higher electron beam energy density was necessary for the initiation and full decomposition of the Thiokol prills as compared to the single crystals. This provides support for the fact that the Thiokol prills have improved initiation properties with respect to the

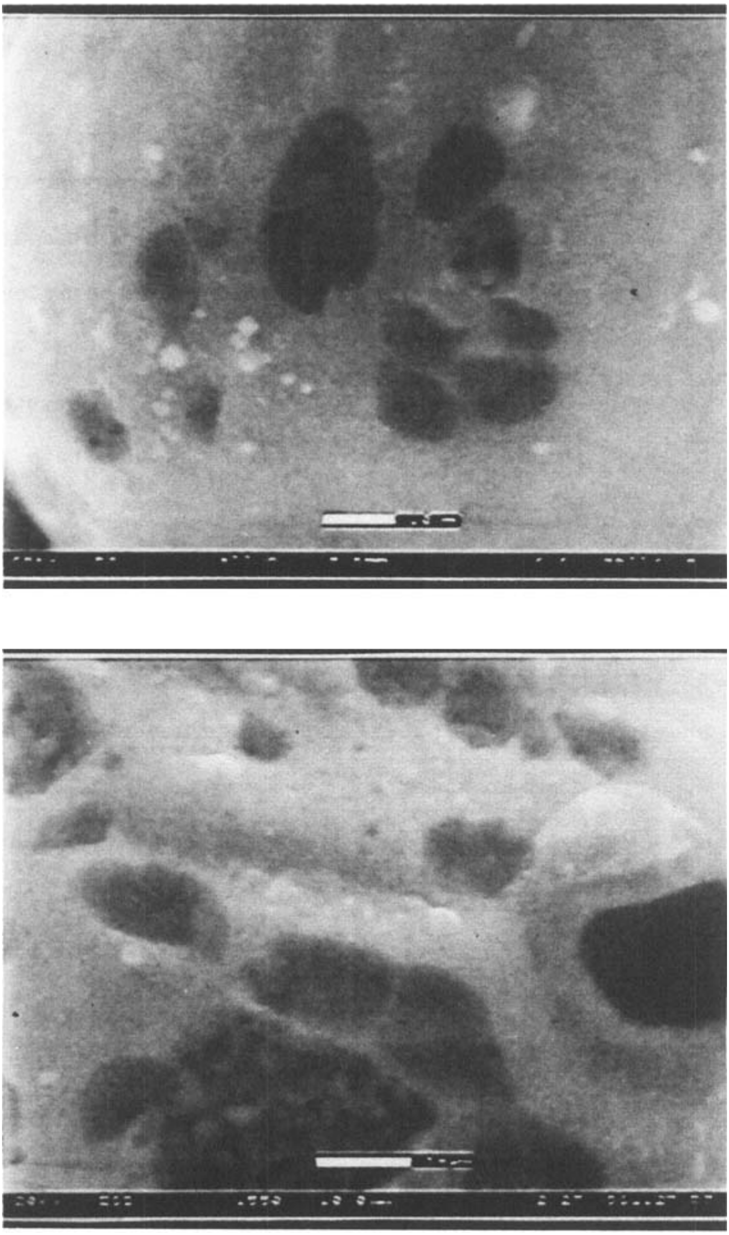

FIGURE 6

ADN PRILL TRANSFORMATIONS ON HEATING IN ESEM crystals. The improved properties appear to be related to the prill microstructure. Thus a surface settling of silica acts to quench the formation of "reaction sites". The silica is added during the course of the prilling manufacturing process in the "prilling tower" technique. Furthermore, as is described in more detail in another publication[9], these prills have been found to have a very smooth surface almost to the molecular level and are multi-crystalline on the surface and almost "single crystal" in bulk. All these microstructural characteristics contribute to the improved initiation properties.

As for the case of the single crystals addition of water in the atmosphere increases the rate of decomposition of the prills, but the effect is rather negligble as compared to the crystals. This is as expected since the silica surface layer would act to protect the prill from moisture.

The prills made by the "melt-stir" technique, initiate at similar electron beam energy densities as the single crystals. The "reaction sites" appear to be more homogenously distributed and clearly initiate at surface microstructural imperfections. Figure 7 shows a typical prill made by the "oil-immersion" technique. The prills have a rough surface structure, where crystallization is seen to occur along the cooling oil fluid stream-lines. Many smaller prills are fused onto the surface of the larger prills. Thus "reaction sites" are seen initially to form along surface imperfections such as the striation lines produced by crystallization along the cooling oil fluid streamlines. The CSD prills thus appear to show similar initiation properties as the single crystals. As described in detail in another publication[9], this batch of prills, in addition to possessing very rough surface structure was found to be multicrystalline in bulk as well as on the surface, forming numerous defect sites where "reaction sites" can form.

When heating the crystals and/or prills on a calibrated hot

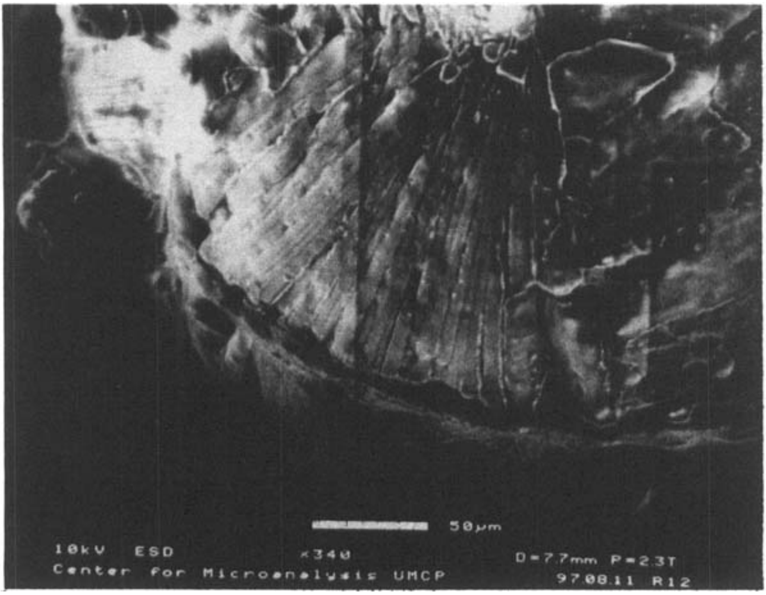

FIGURE 7

ESEM MICROGRAPH OF ADN CSD PRILL

stage in an ESEM, the filmed transformations are similar to those achieved by electron beam heating. Figure 8 is an example reacted prill surface heated on the "hot stage" in an ESEM. Again the porous residue or the shape of the "reaction sites" can be clearly seen to have a crystallographic nature.

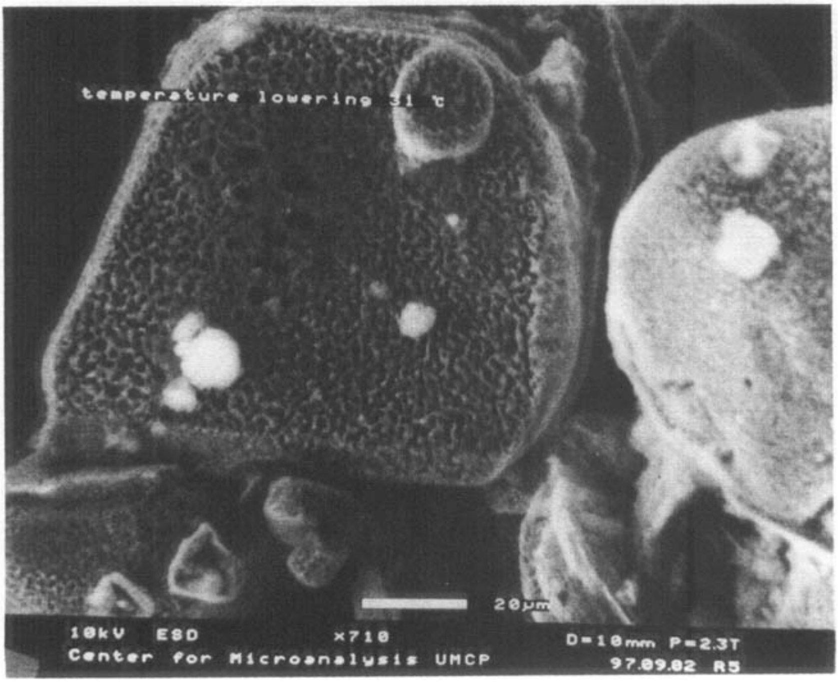

FIGURE 8

REACTED ADN PRILL SURFACE HEATED ON A "HOT-STAGE" IN AN ESEM

DISCUSSION

The recorded/filmed thermal initiation of prills made by different manufacturing processes and single crystals of ADN show marked differences which agree with the observed initiation properties of the single crystals and prills. The differences are related to the prill microstructure which reflect the manufacturing techniques used. Thus in summary the prills made by the "prilling tower" technique at Thiokol require higher electron beam energy density for initiation, the surface settling of silica is seen to quench the formation of "reaction sites" and the reactions then progress evenly into the prill. The prills made by the "oil-immersion" technique have numerous surface structural defects where "reaction sites" first form and then expand into the prill. How the manufacturing processes have affected the prill microstructure is described in detail in another paper[9]. Optimization of the various manufacturing processes may lead to different microstructural charateristics and hence initiation properties. The ADN purity and addition of thermal stabilizers may also affect the initiation properties. Thus ADN prills produced by the "prilling tower" technique contain a reported[4] 1% ammonium nitrate impurity produced during the melting process. About 0.25% urea[4] is added as thermal stabilizer to minimize the amount of decomposition. The percentage impurity in prills made by the "oil-immersion" technique should be similar (not reported) and that of the crystals is lower. The higher level of impurity in the prills may thus act to reduce the threshold energy density for initiation which is however counteracted by the observed microstructural characteristics of the prills and the presence of a thermal stabilizer.

The results have shown that initiation begins at microscopic sites, smaller than the critical "hot spot" size. Explosive initiation is in general thermal in origin where the mechanical or electrical energy is converted into heat in localized regions or "hot spots"[15,16,17]. The microscopic "reaction sites"[13,14] are numerous and form on the crystal/prill surfaces and edges. The size of the sites increases eventually reaching the "hot spot" size. All sites tend to coalesce and the material around the sites takes on a "porous" nature. The shape of the sites tends to follow that of the crystal habit on which they form. By comparison with single crystals of non-energetic materials which can also burn, it is seen that the formation of these microscopic "reaction sites" is typical or characteristic of energetic materials. From atomic force microscopy analysis of the surfaces, the structure of the "reaction sites" can better be resolved[18]. Such observations can provide further understanding in the microscopic mechanisms involved in initiation since the microscopic localization is evidence for the fact that the site begins at an atomic/molecular level where bond formation as well as rupture is important. The crystallographic shape of the "reaction sites" in fact is indicative of the fact that their formation depend on the precise position of the atoms in the crystal lattice relative to the surrounding atoms.

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