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Spectroscopy of Reacted Surfaces [and Discussion]

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Spectroscopy of reacted surfaces

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Explosives were driven to the brink of ignition by shock or impact. The microscopic sites of early reaction in the damaged materials were investigated by scanning electron microscopy for their physical structure and by X-ray photoelectron spectroscopy for their chemistry. Morphological defects of micrometre or smaller size were observable on the surfaces and edges of the crystals. Near these defects chemically altered debris from the explosive was found. These contained reaction products which are more sensitive than the original explosive or have suffered exothermic reaction. The combination of morphological defects, sensitized products and exothermic energy would qualify these sites as hot spots where reaction could restart, at a lower stimulus. This provides us with an explanation for the sensitization of roughly handled explosives and gives us some insight into the early steps of the ignition process.

1. Introduction

When explosives are roughly handled they are known to get sensitized. The concept of 'hot spots' to explain sensitization of explosives and to explain the early stages of initiation was proposed by Bowden & Yoffe (1952). Bowden (1958) also suggested that the early reaction starts in micrometre or sub-micrometre size sites, and the growth to explosion 'is frequently a precarious process'. On the basis of his comment it can be argued that if an explosive is recovered from the edge of ignition, there should be many remnants of hot spots in various stages of development. This paper deals with the study of these remnants and is meant to provide information about the nature of hot spots and their role in the ignition of the explosive. Previously, attention has been given to the hot spots as morphological defects only and since they can qualify as points of high free energy, it was believed that action can easily start in them by a subsequent stimulus. Our results show that chemistry is also involved. Besides being major defects in the lattice, the hot spots contain degraded explosive, testifying to the existence of chemical reaction. Some of these products are more sensitive than the original material, so that in subsequent action the hot spots act as sensitization centres. Some of the other products are from the exothermic decomposition of the explosive. The existence of the two kinds of products forms the basis for the continuation of the disruptive process, once it is started. For ignition, the generation of sensitive products would ensure easy growth, whereas the exothermic steps provide the energy needed to sustain the process. In this paper some of the results reported earlier will be summarized. New results on the study of explosives subjected to shock or impact will be reported. Single crystal studies of ammonium perchlorate (AP) have been very educative. Also results obtained from exposing explosives to high-energy electrons or protons below the level of ignition

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will be mentioned. In this case the effects are essentially caused via heat, but some of the findings are relevant to hot spots.

Most of the present work is based on analysis of recovered samples with the surface specific X-ray photoelectron spectroscopic (XPS) technique. Since the hot spots appear more on the surface, there is an advantage of at least three orders of magnitude in using this technique compared with bulk techniques (Sharma & Beard 1990). XPS probes only about 5 nm of the material, consequently XPS picks up the surface alterations, whereas the signals from the underlying relatively unreacted sample is suppressed. XPS studies have been complemented by chemical ionization mass spectrometry, and liquid chromatography as needed.

Explosives studied were subjected to various stimuli such as impact between heat sensitive films (Coffey & Jacobs 1981), underwater aquarium shock (Liddiard 1965), high-rate shear with an explosive actuator (Boyle *et al*. 1988), and exposure to electrons and protons of energy ranging from 40 MeV to 300 MeV (Stolovy *et al*. 1987, 1989). Most of the work was concentrated on 1,3,5-tramino-2,4,6-trinitrobenzene (TATB), trinitrotoluene (TNT), cyclotrimethylene trinitramine (RDX), cyclotetramethylene tetranitramine (HMX) and AP.

2. Experimental

For most of the explosives, the XPS measurements were carried out with a Kratos ES 300 instrument. The study of shocked single crystal AP was carried out on a Physical Electronics 5400 photoelectron spectrometer described by Beard (1990). In this instrument, the spectra were obtained by monochromatic Al Kα_1 radiation yielding better resolving power and reduced radiation damage from the exciting X-rays. Despite the improved instrumental conditions, the XPS runs were always kept short and control samples were run to avoid the complication arising from radiation damage in the instrument. A Finnigan 4000 GC/MS EI-CI mass spectrometer was used with methane plasma in the chemical ionization mode for mass analysis of the residue from shock and impact experiments. This approach had the advantage of yielding molecular information about the reaction products without further decomposition in the instrument. In the case of electron damage, pulsed beams with energy deposition ranging from 1–200 cal g^{-1}† were used. Proton irradiation was carried at a pulse rate producing a heating rate of 1–2 cal g^{-1} s^{-1}. The samples were unconfined. After recovery of the irradiated samples, they were investigated with optical microscopy and the techniques described above.

3. Results

TATB. As reported earlier (Sharma *et al*. 1987), impacted samples of TATB showed the presence of furoxan and furazan products. Most effect was observed in the region of maximum shear. The central part of the sample, where compression dominates, showed no evidence of reaction. Decomposition as high as 50% was measured by XPS at the radial edge of the impacted sample, where heating of the viewgraph films due to exothermic chemical reaction could often be observed.

Compared with TATB, furoxan is far more sensitive, its drop height is like that of TNT. The furazan products are not as sensitive, as evident from Kamlet's oxygen balance relation and Storm *et al*.'s (1990) listing. A furazan molecule is produced by

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† 1 cal = 4.184 J.

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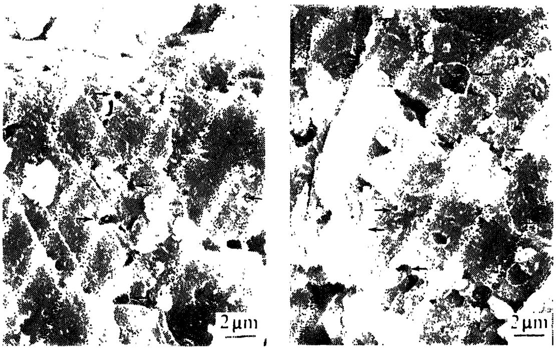

Figure 1. Effect of underwater shock on TATB (1.6–1.8 GPa, 1–2 μs), showing hot spot remnants and deposits of reaction products around them.

the release of a water molecule from a TATB. Consequently the production of furazan is an exothermic step, capable of yielding approximately 60 kcal mol^{-1} of energy, which coincides with the activation energy of TATB. The formation of the furoxan and furazan products, one more sensitive and the other from an exothermic step, fulfils the requirements needed to sustain the reaction. When the energy of impact was increased by adding sand to the sample, the surface showed a larger amount of the products than TATB. This indicates that the generation of the furoxan and furazan products is not confined to the very initial stage only.

Since a TATB molecule has three sets of nitro and amino functional groups there is a possibility of multiple furoxan or furazan rings being formed. Mass spectra representing double derivative of furazan have been observed in our studies. Thus the disruptive process of TATB can proceed in stages, oscillating between sensitive and insensitive phases. According to Storm *et al.* (1990) this feature contributes to TATB being the most insensitive of explosives. When samples of DATB, and picramide were impacted their products also consisted of furoxan and furazan derivatives.

The effect of under water shock on TATB has been found to be similar to that of impact. Evidence of hot spot formation in the form of ragged holes, like those of Swiss cheese, was seen on the surfaces and edge of the flat crystallites (figure 1). In the vicinity of these ragged holes fine deposits of extraneous material was observed. These deposits were composed of furoxan and furazan products. Extraction of the furoxan and furazan products was accomplished, without effecting the TATB, which is not soluble. Electron beam decomposition of TATB showed conversion into these products to an extent of 2–10 % for energy deposition in the range of 10^7–10^8 R. There is a similarity in the scanning electron microscope (SEM) pictures of beam damaged and under water shocked TATB, which arises perhaps from the similarity of products. Thus it appears that the chemical alteration of TATB is a prominent process seen both in the early stages as well as in later stages of ignition. Between the furoxan and furazan, the former seems to reach limiting value but the furazan increases with the severity of the stimulus.

TNT. As reported earlier (Sharma 1990), TNT impacted between sheets of heat sensitive films showed as high as 20 % decomposition into products identified by XPS to be anthranil, benzaldoxime and nitrile. As with TATB, the benzalodoxime would be the sensitizing product, facilitating the reaction during ignition and making the impacted TNT more sensitive after the impact. Anthranil formation, by the

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Figure 2

Figure 3

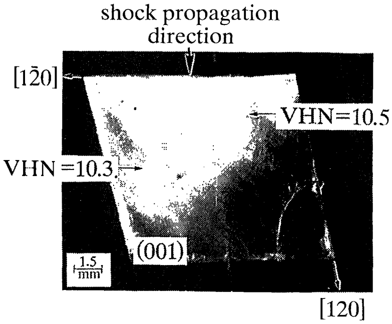

Figure 2. Photograph of seven pellets (5 mm diameter) of HMX after proton irradiation, showing melting, flowing, partial decomposition and trapping of gas bubbles during resolidification into more sensitive delta phase.

Figure 3. Photomicrograph of AP (001) surface after shocking at 2.44 GPa, pressure. Intense clouding of the crystal near the effected area is observable. This was associated with broadening of the XPS Cl 2p line, shown in figure 4, indicating change in the chlorine bonding, without change in its chemistry.

separation of a water molecule from TNT would be the energy donating exothermic step. TNT, subjected to high rate shear, also showed quite high (20 %) decomposition. The decomposition was very much confined to the surface.

RDX. This explosive along with HMX was difficult to investigate because it tends to leave very little solid residue after impact or shock. Impacted samples of RDX, as mentioned before (Sharma 1985), showed pronounced loss of the nitro peak compared with the amine peak. The growth of the nitroso and triazine peaks observed is much smaller than the loss of the nitro peak. It appears that most of the broken up NO_2 escapes out of the solid phase. This is confirmed by the fact that proton irradiated samples showed evidence of melting and of bubble formation in them. The formation of nitroso and triazine during thermal decomposition are confirmed by Behrens & Bulusu (1991). X-ray irradiated sample of RDX showed the additional presence of nitrite ester at low temperature, which along with nitroso and triazine products are lost during warming to room temperature (Beard 1990). In RDX, the nitrite ester can be recognized as the sensitizing component of the products.

HMX. The behaviour of HMX is very like that of RDX. HMX subjected to under water shock of 0.41 GPa showed 16 % loss of nitro functional groups and broadening of the amine peak due to products similar to those seen in RDX. SEM micrographs of impacted HMX showed consolidation of the material compared with the pressed pellets used in the experiments. This result would tend to support the idea that during the long duration of the underwater shock wave (a few microseconds) the HMX melted and resolidified. HMX, pyrolyzed from proton irradiation, also showed melting and resolidification into a mass full of bubbles (figure 2). It showed complete phase transition into the delta crystallographic form, which is known to be more sensitive (Cady & Smith 1961) than the common beta form.

AP. Unlike HMX or RDX, ammonium perchlorate showed profuse (60 %) decomposition products in the solid phase after impact. As reported earlier (Sharma *et al.* 1985), the dominating product was the hypochlorite, which is far more sensitive than AP. Small amounts of chloride and chlorate were also observed. A recent study,

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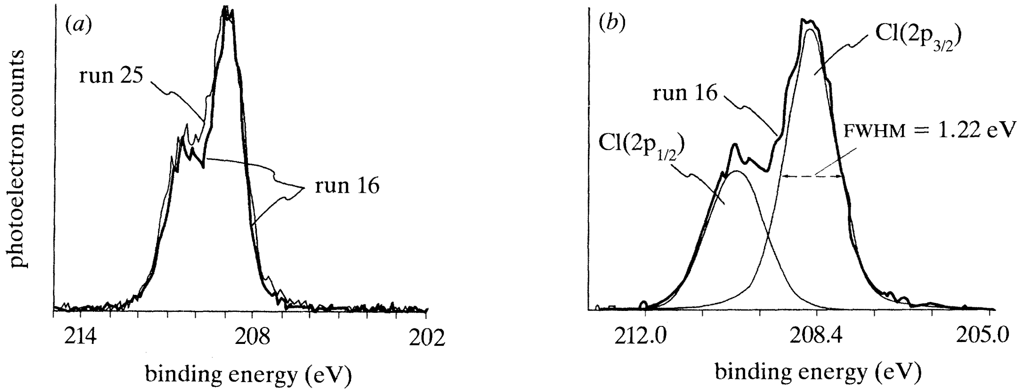

Figure 4. (*a*) Comparison of the narrowest Cl (2p) spectrum, run 16, (control) with spectrum from run 25 that shows a broadened Cl (2p) line due to shock but no shock induced chemistry. (*b*) Curve-fit results of run 16 Cl (2p) spectrum showing spin doublet components and illustrates definition of FWHM (full width half maximum).

(Beard *et al.* 1992) with XPS on single crystal AP has revealed new facts. In this work a high purity single crystal of AP was given an indent with a (Vickers) hardness indenter having a pyramidal diamond tip and then was subjected to shock loading of 2.44 GPa from the direction of the dent. The crystal survived the shock but became cloudy (figure 3) apparently due to the formation of dislocations and defects, in a non-uniform manner. The fogging was most intense near the indent but decreased deeper into the crystal. The recovered crystal was cleaved at different distances from the indentation and XPS analysis was carried out. Two things were shown by XPS. Close to the indentation, the Cl (2p) spectrum showed evidence of chlorate formation but no hypochlorite. A maximum of 9.5% chlorate (Cl (+5)), a partial decomposition product was detected. The chlorate decreased as a function of distance from the indentation. Another effect seen was that the Cl 2p line of the perchlorate showed broadening (figure 4) without shift. The width of the Cl $2p_{3/2}$ was 1.70 eV near the indentation and it progressively decreased to the value of undamaged AP, 1.22 eV, at a distance of approximately 1 cm. This broadening appears to be an important finding. It indicates that some change in the bonding of the perchlorate ion is taking place but the change is subtle and it has not yet led to a chemical reaction or change in the oxidation state of the chlorine. Grunthaner *et al.* (1979) have suggested that the electronic redistribution resulting from bond angle displacement in the damaged area can cause small displacement leading to such a broadening. Quantum mechanical calculations by J. Ritchie (personal communication) suggest that the broadening observed can come from bond shortening, lengthening and bond angle variations. Beard *et al.* (1992) have associated this broadening to dislocation formation and have estimated the number of dislocations on this basis. It appears that a dislocation density of 10^7 cm^{-2} is generated at the surface of the crystal, close to the indentation. An indented control crystal, not subjected to shock compression, did not show evidence of XPS line broadening or chlorate formation. The above cited results have encouraged us to the idea of using atomic force microscopy to map out the defects. In pursuit of this, de Lozanne (1992) has taken successful pictures of AP at atomic resolution, but the stage of seeing hot spots has not yet been reached.

The phenomenon of line-broadening in shocked material was previously observed

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in TNT by Owens & Sharma (1980): the nitro peak broadened towards lower binding energy, in other words towards lower oxidation state. Very recently we have observed this in RDX crystals of differing preparation histories. The implications are being further investigated.

4. Discussion

The above results show that the hot spots have two aspects. They produce crystallographic and morphological defects and are found mostly on the surfaces or edges of crystallites. These sites or dislocation clusters provide the nucleus for the growth of reaction. The present work has shown the hot spots to be approximately micrometre or sub-micrometre in size, as predicted by Bowden (1952). It is not clear whether the size determined is limited by the instrument used. It would be helpful if SEM micrographs could be obtained at higher magnification. Alternately the technique of atomic force microscopy, which is capable of showing the atoms and their dispositions on the surface, should be brought to bear on the problem. It does not seem that crystal defects of any kind are likely to make the explosive more sensitive, it is important to narrow down and determine the critical types.

The other aspect of the present results is that the formation of hot spots is associated with changes in the local chemistry. XPS has shown that the nitro functional group is the first victim in explosives bearing nitro groups. The nitro nitrogen in all cases shows a decrease compared with other components of the molecule. Part of the nitro nitrogen appears in new peaks but most is lost, perhaps as gaseous products. This has been found to be so in TATB, TNT and more pronouncedly in HMX and RDX. In all cases the new peaks that show up are located at the low binding-energy side of the nitro peak, indicating that the nitrogen is transforming into a chemically more reduced state. This is also true with the oxidizer ammonium perchlorate, where the chlorine in all the new products is in a lower oxidation state. The formation of a major product with Cl^{+1} is noteworthy. The true identity of this compound is uncertain, however, it may be a hypochlorite or a chloramine.

The generation of more sensitive products by shock or impact gives a ready explanation of the sensitization of energetic materials from rough handling. Examples of pure chemical sensitization of explosives do exist. Mukundan *et al.* (1992) have shown such effect in TNT, TNB, etc., whereas Engelke *et al.* (1985) have observed so in nitromethane.

Since the chemical properties such as solubility, etc., of the new products in the impacted explosives are different than that of the original material, it is possible to think that a sensitized explosive can possibly be cured by the removal of the undesirable components.

During the study of chemical changes from electron or proton irradiation, attempts were made to check if the sensitization from the decomposed products could be demonstrated. Although sensitive reaction products were detected, the samples could never be ignited at a lower level of the stimulus during second irradiation. We do not have a ready explanation of this perplexing question. It can be speculated that during particle radiation the distribution of the decomposition is not exactly like that of hot spots. The size could be different. It would be of interest to find out what size of a reaction centre is critical for sustained ignition.

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Discussion

S. A. Kinloch (*RMCS*, *Shrivenham*, *U.K.*). TATB is known to decompose when subjected to electromagnetic radiation, for example, X-ray, γ-ray or ultraviolet). This decomposition is characterized by an obvious colour change of the yellow TATB to a green product. Is there any relation between the decomposition processes and products which you have described in the vicinity of hot spots in TATB and those of irradiation induced decomposition?

J. Sharma. We have tried to identify the green product on TATB from exposure to solar radiation, but have not succeeded in doing so. Ultraviolet and ionizing radiations do produce loss of nitro groups leading to furoxan and furazan products like those of hot spots, but they are yellow in colour. The green product may arise from mild photochromic reaction involving radical or secondary amine production as suggested by D. W. Firsich and M. P. Guse (*J. Energetic Mater.* **2**, 205–214 (1984)).

F. Volk (*Fraunhofer Institute*, *F.R.G.*). Were reaction products such as dinitrotoluene or aminonitrotoluene found when TNT was heated?

J. Sharma. For impacted TNT, only those products observed using XPS are reported. XPS results are based on the oxidation states of the nitrogen atom and do not distinguish between trinitro or dinitro derivatives. The products such as anthranil, benzaldoxime and nitrile, with lower oxidation states, are easily detected as new peaks. Ratio comparison with the carbon line might tell about dinitrotoluene, and aminonitrotoluene, but would be difficult. In the case of TATB, RDX or HMX, the amine nitrogen provides a comparison, so that the loss of nitro functional groups can be readily observed.

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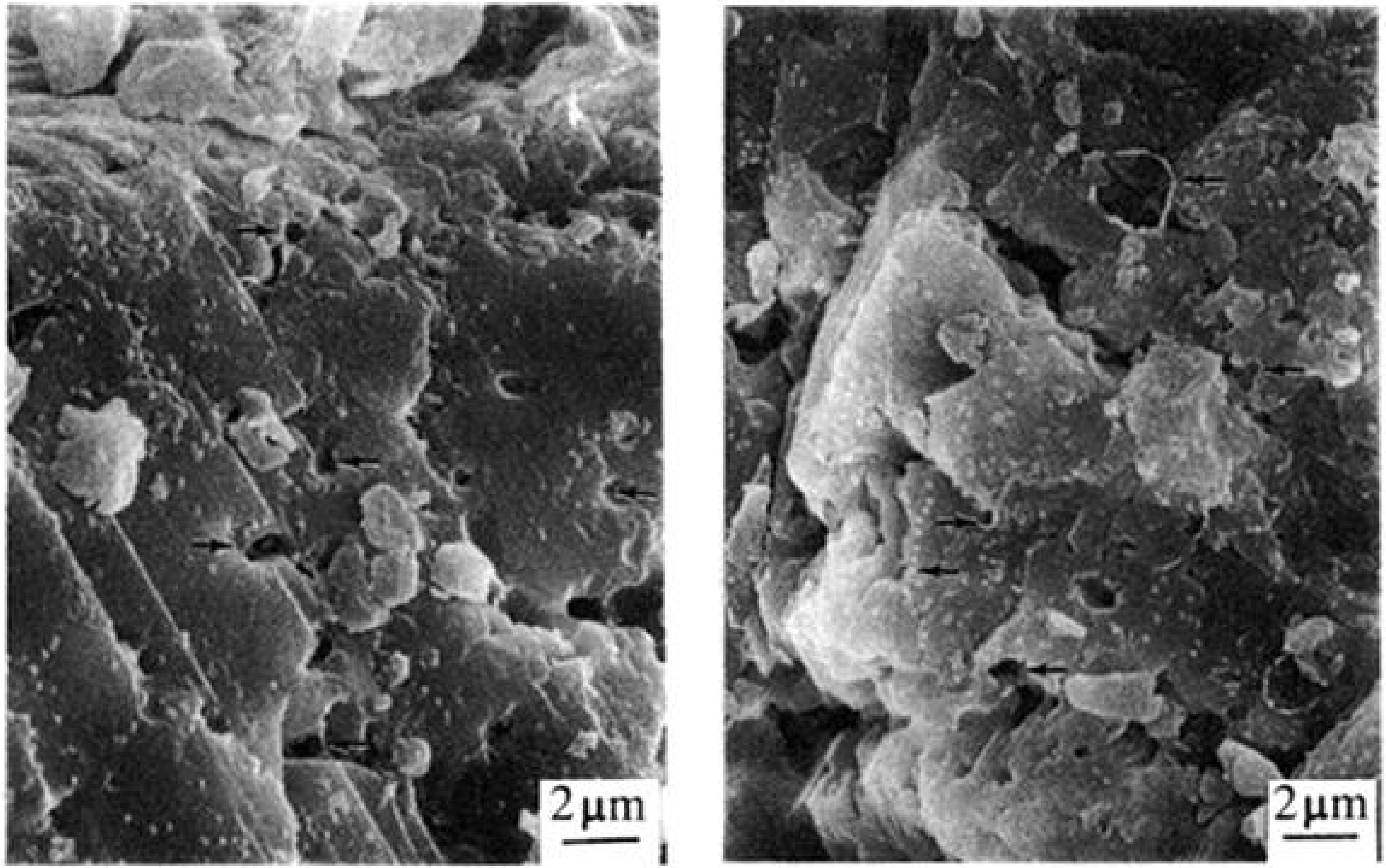

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Figure 2

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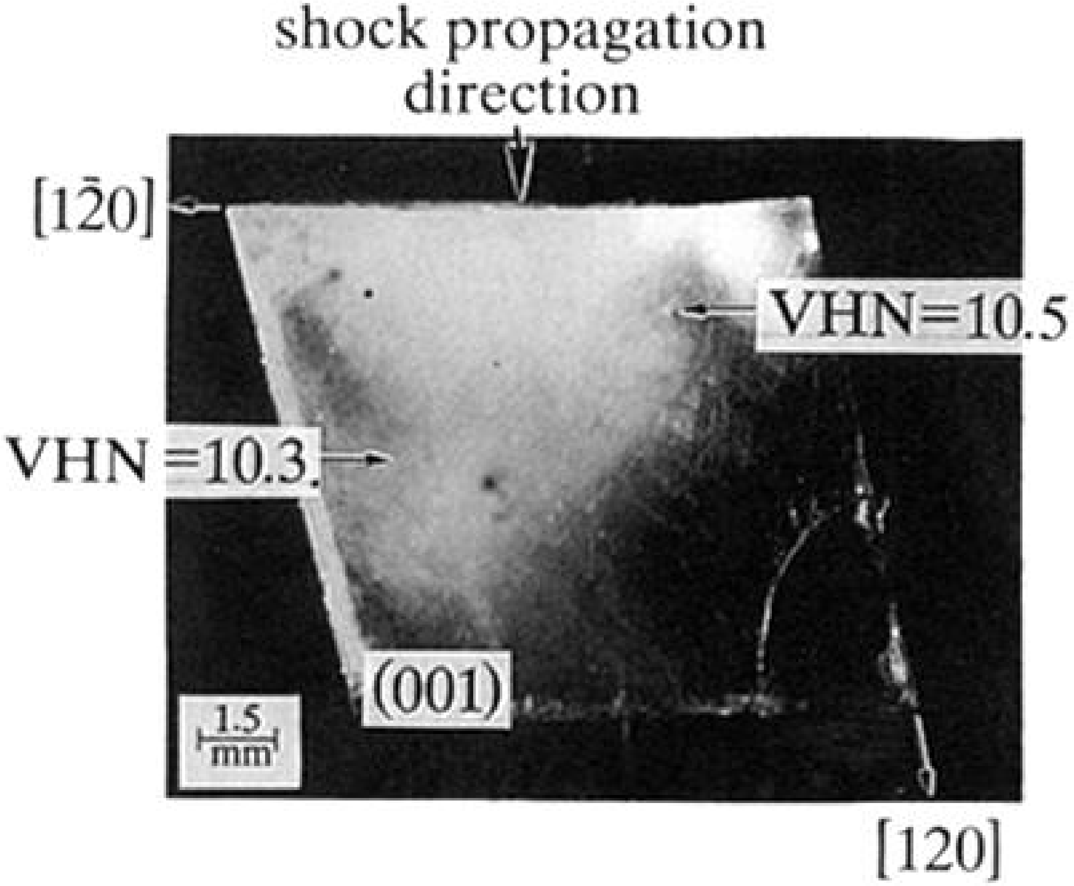

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