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In-situ electron microscopy study of the reactivity of molybdenum disulphide in various gaseous environments

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The interaction of single crystal molybdenum disulphide with various gases has been followed dynamically using *in situ* scanning transmission electron microscopy. It is found that in the presence of oxygen attack takes place preferentially at edges and point defects on the basal plane. It appears that the reaction proceeds by two pathways, conversion to MoO_2 predominates at low temperatures (690 K) and formation of MoO_3 becoming significant at higher temperatures (800 K), with intermediate metastable oxides playing some role. Reduction of molybdenum disulphide in hydrogen is a relatively sluggish reaction and attack occurs exclusively at the edge regions of crystals resulting in the formation of metallic molybdenum as major product with a minor amount of Mo_2S_3.

1. Introduction

Over the years we have used controlled atmosphere electron microscopy to study the influence of many additives on the gasification of graphite in various gaseous environments [1]. In addition to providing qualitative information on morphological detail, the technique has yielded quantitative estimates of kinetic parameters from rates of motion and has proved invaluable in the deduction of the factors controlling the mode by which a catalyst operates in graphite gasification processes. We have chosen to extend this type of investigation to cover the behaviour of other layered materials, and here we report on the interaction of molybdenum disulphide with various gases. In subsequent papers we shall deal with the catalytic influence of certain metals on these same reactions.

In contrast to graphite, far fewer microscopy studies have been made on molybdenum disulphide. Bahl *et al.* [2] have used the gold decoration technique in conjunction with transmission electron microscopy to examine various features of the cleaved surfaces of molybdenite and to study the topographical effects produced in these specimens following reaction in oxygen. According to these workers, the surface steps produced by cleavage of molybdenum disulphide all run along the $\langle 11\bar{2}0 \rangle$ directions. Furthermore, they found that the sides of etch pits created in the basal plane during oxidation were also oriented parallel to $\langle 11\bar{2}0 \rangle$ directions. Mild oxidation was shown to produce triangular pits of one monolayer depth, whereas intensive oxidation resulted in the creation of hexagonal pits which were believed to originate by the merging of successive triangular depressions. A rough correlation was found to exist between the pit size and the height of the cleavage step associated with it; at 873 K the ratio of the width to the depth of the oxidation pit was claimed to be about 10.

In a more recent study, Chianelli and coworkers [3] used a combination of optical microscopy and scanning Auger spectroscopy to study the reaction of molybdenum disulphide and oxygen. They confirmed the findings of Bahl *et al.* [2] that the edge planes of molybdenum disulphide were particularly reactive towards oxygen. They further demonstrated that if low levels of cobalt were introduced onto these crystals, then during reaction the metal would tend to segregate at the molybdenum disulphide edge sites.

This latter aspect was examined in some detail by Sørensen *et al.* [4] who used both high resolution and analytical electron microscopy to elucidate the structure of the catalytically active Co–Mo–S phase, and establish the nature of the cobalt phase by the use of Mössbauer emission spectroscopy.

Tauster and coworkers [5] used dynamic chemisorption procedures to demonstrate that a linear relationship existed between the ability of molybdenum disulphide to chemisorb oxygen and its catalytic activity for hydrodesulphurization (HDS) of dibenzothiophene. They claimed that since the edge sites of single crystal molybdenum disulphide were oxidized more easily than the basal plane that the amount of oxygen chemisorbed by molybdenum disulphide was a measure of the edge to basal plane ratio and further suggested that the HDS activity of the molybdenum disulphide catalyst was related to the number of edge sites.

Low energy helium scattering was used by Davis and Carver [6] to investigate oxygen chemisorption on single crystal molybdenum disulphide basal plane

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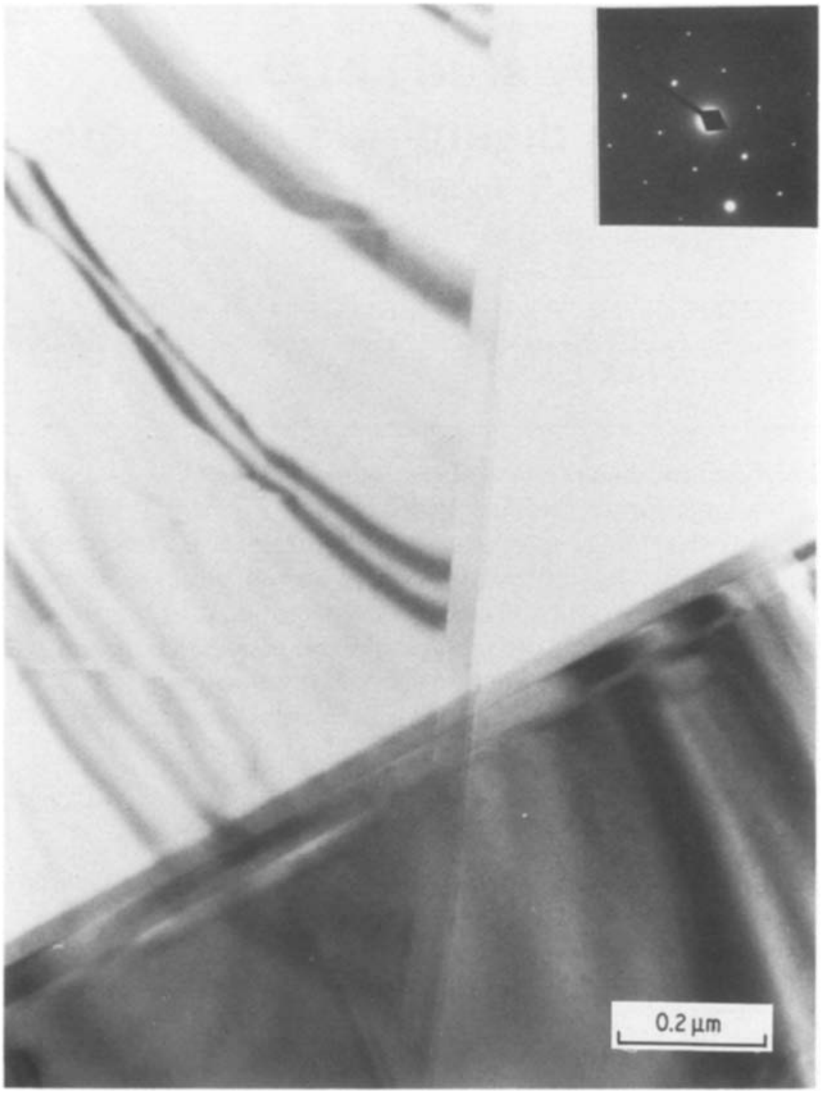


Figure 1 Transmission micrograph of a molybdenum disulphide specimen in the presence of 4.1×10^2 Pa oxygen at 475 K. Inset shows the electron diffraction of the sample under these conditions.

surfaces which had been sputtered in order to create a large defect site concentration. From this study they were able to establish that in addition to edge site vacancies, defects in the basal plane also displayed high reactivity for oxygen chemisorption. Farias and coworkers [7] performed similar experiments and reached the same conclusions.

In the present work we have been able to directly observe such features as the recession of edges, the creation and expansion of pits in the basal plane, and the structural changes which accompany the reaction of molybdenum disulphide as it is heated in various gas atmospheres. In addition, it has been possible to carry out detailed quantitative kinetic analysis from the recordings of some of these dynamics events, and to perform *in situ* analysis of chemical changes which occurred.

2. Experimental procedure

The experiments described in this paper were carried out in the controlled atmosphere scanning transmission electron microscope [8]. This technique enables one to continuously observe reactions between gases and solids at a resolution of greater than 1 nm and also perform chemical analysis of the solid as it is undergoing reaction.

Transmission specimens (< 50 nm thickness) of molybdenum disulphide were prepared from natural molybdenite (originating from Froland, Norway) by the same cleaving procedure as that used for obtaining thin sections of graphite [9]. These specimens were picked up from a clean water surface on stainless steel microscope grids and mounted into a Gatan heating stage. Finally, the whole assembly was inserted into the modified specimen chamber of a JEOL 200 CX TEM/STEM electron microscope in such a manner that the specimen was positioned between two gas restricting apertures, which had been pre-aligned to fall on the electron optical axis.

The reactant gases used in this work, oxygen and hydrogen had stated minimum purities of 99.99% (Scientific Gas Products, Inc.) and were used without further purification.

3. Results

3.1. Molybdenum disulphide–oxygen

Fig. 1 is a micrograph of a typical molybdenum disulphide specimen prior to reaction showing the relatively featureless appearance of the basal plane and the smooth profile of the edge regions. The presence of Moiré fringes across the specimen surface is indicative of a certain degree of strain in the crystal. Included as an inset on this micrograph is the electron

TABLE I Electron diffraction analysis of the basal plane regions of molybdenum disulphide during reaction in oxygen at 300 K

Calculated d-spacings (nm)	d-spacings for MoS_2 (nm)
0.271	0.271
0.158	0.158
0.155	
0.136	0.136
0.101	0.102

diffraction pattern of the material for which the corresponding analytical data is presented in Table I.

When specimens were heated in 4.1×10^2 Pa oxygen, an extremely complex, but reproducible, pattern of behaviour was observed. In an attempt to clarify the situation, we have documented the various chemical and structural changes under the headings of temperatures where they occurred.

3.1.1. 580–600 K

The first signs of attack were seen over this temperature range. The original smooth edges and steps started to acquire a rippled profile and darker globular material developed along these features. At the same time, the initial "clean" state of the basal plane changed to a mottled appearance. This condition can be seen in Fig. 2, a photograph taken from the video replay.

3.1.2. 630 K

When specimens were held at this temperature, then over a period of 0.25 h the material which was present at edges slowly transformed into faceted crystallites and needles. However, once formed, these structures did not appear to grow. During this time, no further change in the condition of the basal plane was apparent.

3.1.3. 675–690 K

On raising the temperature the faceted crystallites and needles which had formed at the edges of the molybdenite became progressively rounded and eventually transformed back into globular shapes. Also, over this temperature range recession of the edges was observed, and this behaviour coincided with an increase in the size of the existing globules and the formation of more of these particles, which were found to exhibit strong wetting characteristics with the substrate edges.

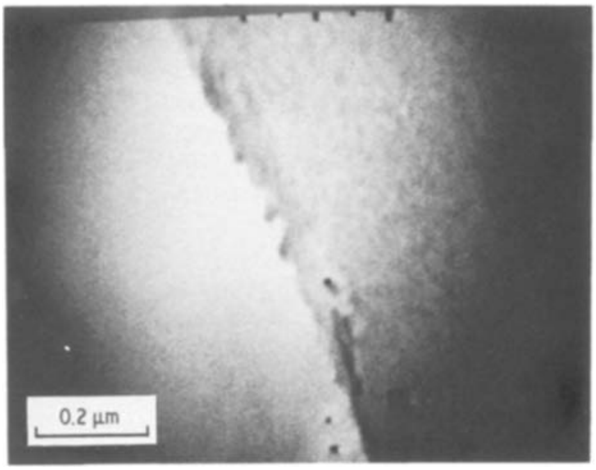


Figure 2 Attack of the edge regions of a molybdenum disulphide crystal in 4.1×10^2 Pa oxygen at 600 K.

TABLE II Electron diffraction analysis of the edge regions of molybdenum disulphide during reaction in oxygen at 700 K

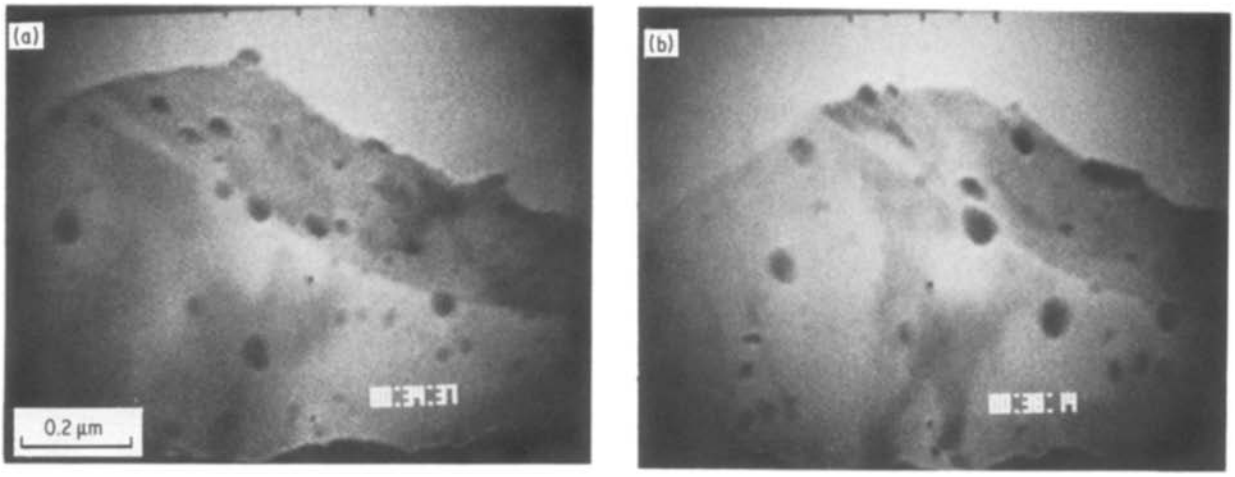
Calculated d-spacings (nm)	d-spacings (nm)		
	MoS_2	S	MoO_2
0.271	0.271		
0.182			0.182
0.173			0.172
0.159	0.158		
0.156		0.156	
0.151		0.151	
0.136	0.136		0.135
0.103	0.103		
0.101	0.102		

A survey of the basal plane regions showed that particles with similar characteristics, up to 20 nm in size, were being generated in a uniform fashion all over the specimen. At 690 K these particles became mobile, and as a result of collisions and coalescence with neighbouring particles, the average size reached 50 nm. It was significant that when the particles came into contact with edges they tended to stick and as a consequence lost their mobility, indicating that the interaction with edges was considerably stronger than that with the basal plane. Throughout this period of the reaction fresh particles were being generated at the expense of the molybdenum disulphide substrate, which tended to become progressively thinner. It was significant to find that during this time Moiré fringes remained static, indicating that the action was taking place layer by layer rather than by a macroscale change in the molybdenum disulphide crystal. Many of the features described above can be seen in the sequence of stills taken from the television monitor, Fig. 3, which show the changes in appearance of the same area of a specimen as it is heated from 670 to 710 K over a 10 min period. Selected area electron diffraction analysis under these conditions showed the formation of a new phase, MoO_2, in addition to unreacted molybdenum disulphide (Fig. 4a and Table II).

3.1.4. 700–725 K

Examination of the basal plane regions showed that while the majority of particles retained their globular outline some of them underwent a rearrangement into thin faceted structures with a concomitant loss of mobility. Following this action the particles would then contract and assume their initial globular morphology leaving behind the imprint of a shallow pit, the dimensions of which were identical to that of the particle in its spread condition.

On continued heating the pits were observed to expand laterally and acquire a hexagonal shape and also become deeper, as judged by the contrast



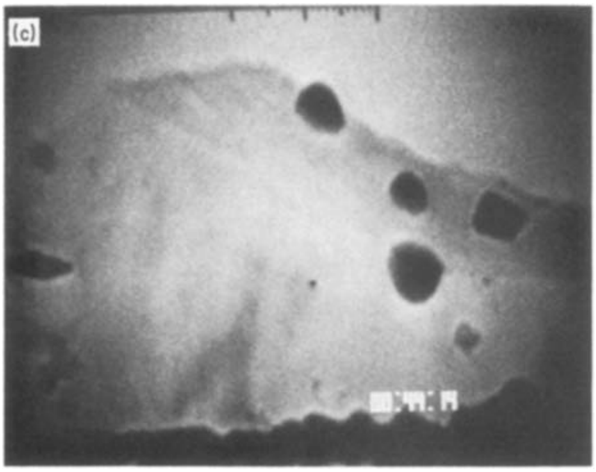


Figure 3 Sequence showing the formation and mobility of MoO_2 particles on molybdenum disulphide as the specimen is heated in oxygen from 670 to 710 K.

difference between the pit and the surrounding areas of less reactive substrate. In general, as the size of the pit increased so did that of the particle associated with it, suggesting that material was being transported from the substrate to the particle. From the sequence, Fig. 5, it is possible to follow the formation of a pit surrounding the particle marked "X".

The shapes of particles associated with pits varied and appeared to be controlled, to some degree, by the following situations, depicted schematically in Fig 6a to c. In (a) the particle was faceted only at the points of contact with the sides of the pit and appeared to be quite globular at "unattached regions". The particle underwent a constant change of shape as the pit expanded causing the particle to break and make points of contact with the receding edges. In case (b), the particle completely lost contact with the sides of the pit and reverted back to its energetically preferred shape of a globule. Finally, case (c) was a less common observation where a particle had apparently lost contact with the sides of the pit but still retained a thin hexagonal shaped form and remained motionless in this state. It is possible that this condition arose from the development of a secondary pit from a vacancy in lower layer of the molybdenum disulphide structure.

Fig. 7 is a micrograph taken after the reaction and shows the details of a pit which has been developed from a defect which penetrated through the crystal. During cooling to room temperature the particle which was associated with this pit has fragmented into many smaller entities.

Continuous observation of the reaction showed that particles which lost contact with the sides of a pit and subsequently assumed a globular form became mobile and frequently developed sufficient momentum to escape from the confines of the shallower pits. In contrast, particles which were mobile on the defect-observed to fall into vacant or partially occupied pits, and in some instances, underwent a rapid transformation in shape from a globule to a thin hexagonal platelet, which covered the whole area of the pit.

Examination of the characteristics of many pits showed that no consistent relationship existed between the width and the depth. However, it was evident that the sides of the pits were aligned in a preferred orientation with respect to molybdenum disulphide crystallographic structure and that they expanded in a uniform manner as the reaction proceeded.

Over this temperature range particles which had adhered to edges and steps started to spread along these regions and proceeded to facilitate the removal of the substrate material. This action was similar in many respects to catalytic edge recession exhibited by a number of metal oxides on the graphite–oxygen reaction [1]. Edge recession also occurred at a significantly slower rate, at regions which were initially devoid of large particles, and in these cases, a residual lacy network of small particles tended to collect at the receding edges as the reaction proceeded.

3.1.5. 750–800 K

As the temperature was raised the rates of both edge recession and pit expansion increased. It was also apparent that some of the smaller particles (2.5 nm in size) on the basal plane were in the form of triangular and hexagonal arrays suggesting that they were decorating the edges of monolayer pits, which would not otherwise be visible in the transmission image.

Also, at this time, the large globular particles

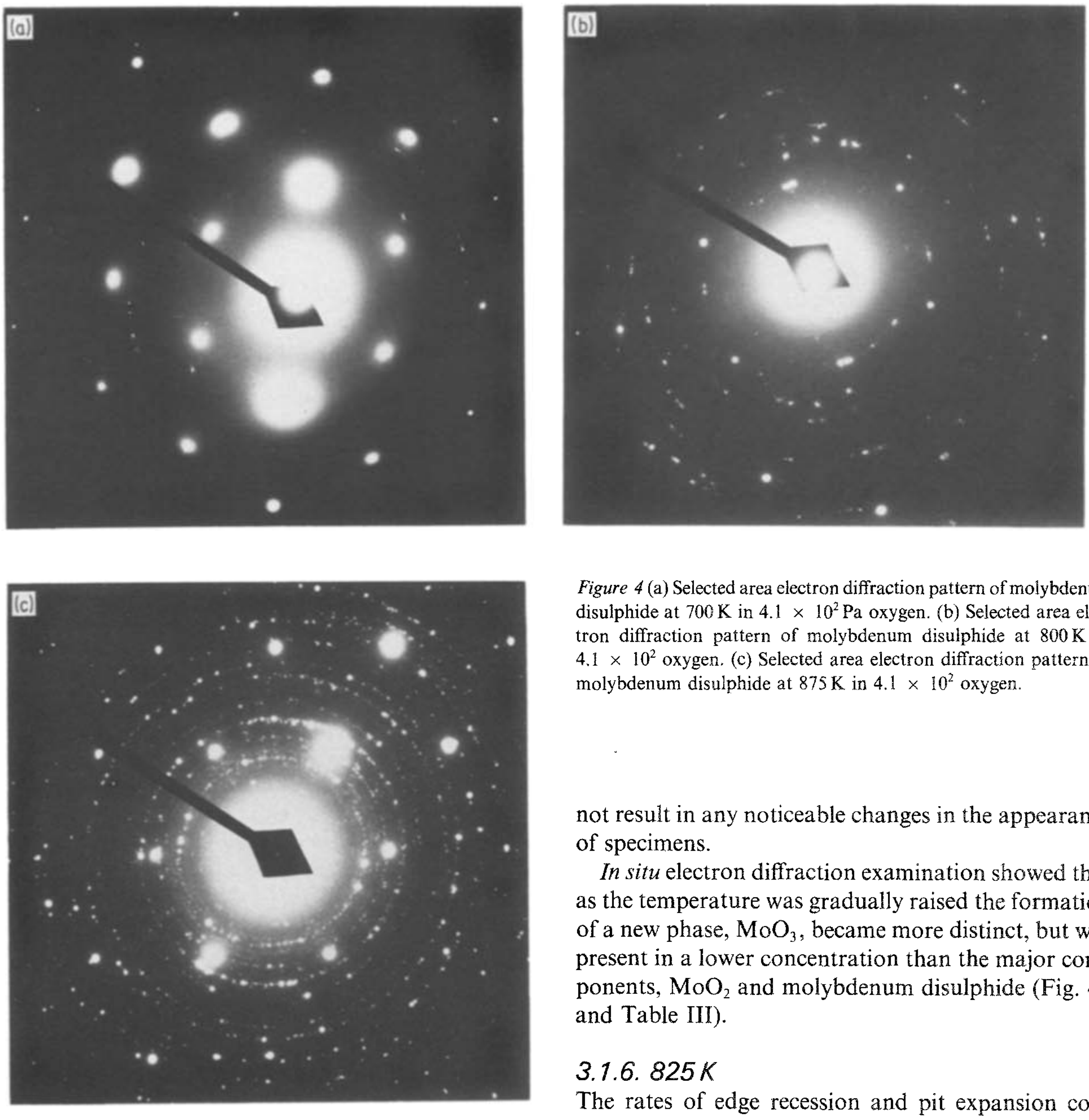


Figure 4 (a) Selected area electron diffraction pattern of molybdenum disulphide at 700 K in 4.1 × 10^2 Pa oxygen. (b) Selected area electron diffraction pattern of molybdenum disulphide at 800 K in 4.1 × 10^2 oxygen. (c) Selected area electron diffraction pattern of molybdenum disulphide at 875 K in 4.1 × 10^2 oxygen.

present on the basal plane started to exhibit some fascinating transformations. Large needle-shaped structures were produced from the globules by what appeared to be an extrusion process. In general the needles were parallel-sided and ranged in length from 1 to 2 μm and were up to 100 nm in width. The size of a particular needle was directly related to the size of the globule from which it was derived. These structures were relatively thin since various features of the underlying substrate were clearly visible through them. The ends of the needle tended to be faceted, being either hexagonal or square in shape. In all cases, the needles appeared to lie flat on the substrate surface and be aligned in definite orientations with respect to each other. This aspect can be seen from Fig. 8, a micrograph of a specimen which had been heated to 825 K and then cooled to room temperature. A further feature which is apparent from Fig. 8 is that a given globule can be growth centre for a number of needles. Cooling from the reaction temperature of 825 K did not result in any noticeable changes in the appearance of specimens.

In situ electron diffraction examination showed that as the temperature was gradually raised the formation of a new phase, MoO_3, became more distinct, but was present in a lower concentration than the major components, MoO_2 and molybdenum disulphide (Fig. 4b and Table III).

3.1.6. 825 K

The rates of edge recession and pit expansion continued to increase, and from a detailed quantitative kinetic analysis of many sequences we have been able to derive an apparent activation energy of 166.0 ± 16 kJ mol^{-1} from the data presented in Fig. 9, which was obtained from both edge recession and pit expansion processes.

At this temperature the globule–needle combination structures continued to show some amazing changes, an example of which can be seen in the sequence of stills, Figs 10a to d. In frames (a) and (b), we see the initiation of the growth of a needle from a globule which is adhering to the side of a pit. In frame (c), the globule loses contact with the pit side and slides along the needle appearing to "dissolve" it, and at the same time a second needle is ejected in the opposite direction. Finally, in frame (d), the globule flips back to near its initial location and the original needle is observed to increase in length at the same rate as the second needle contracts. In this sequence the arrows indicate the direction of growth of needles. A survey of many areas of the surface showed that simultaneous growth and contraction of needle structures was occurring on many of the globules, indicating that the phenomenon was not an isolated event.

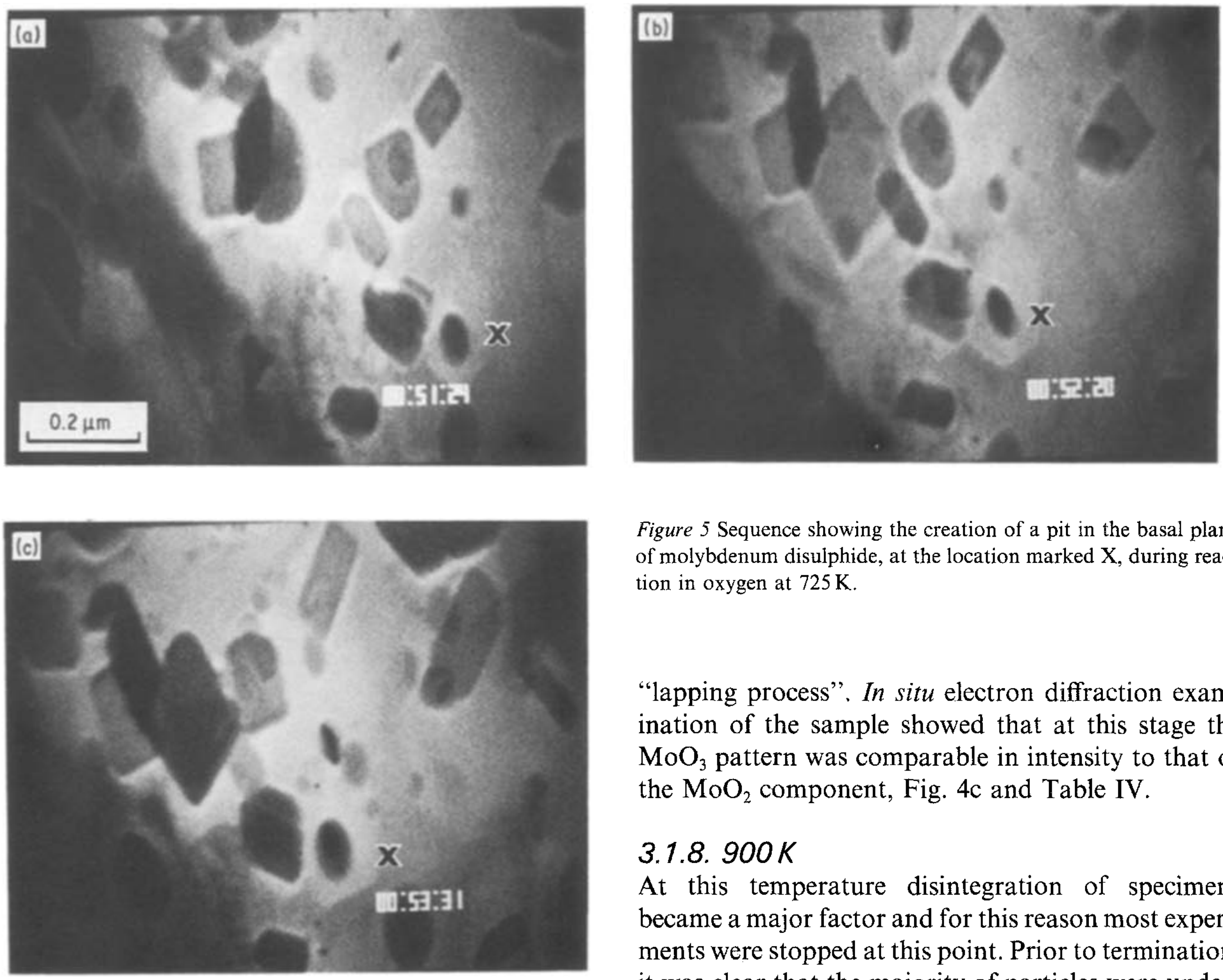


Figure 5 Sequence showing the creation of a pit in the basal plane of molybdenum disulphide, at the location marked X, during reaction in oxygen at 725 K.

3.1.7. 850–875 K

As the temperature was gradually raised to 875 K, there was an appreciable increase in the rate of reaction, and this was displayed in various forms. Pits were frequently found to have penetrated through the substrate structure. In some regions edge erosion was accompanied by the formation of a residue consisting of a lacy network of fine particles. In other regions where large particles (up to 1 μm in size) were present at edges the reaction appeared to be catalysed. An example of this kind of behaviour is presented in the series of stills, Figs 11a to f. The fluid nature of the particle is evident from its ability to undergo spreading at the interface with the substrate, and following this action it proceeds to increase in size by consuming material from the molybdenum disulphide by a "lapping process". *In situ* electron diffraction examination of the sample showed that at this stage the MoO_3 pattern was comparable in intensity to that of the MoO_2 component, Fig. 4c and Table IV.

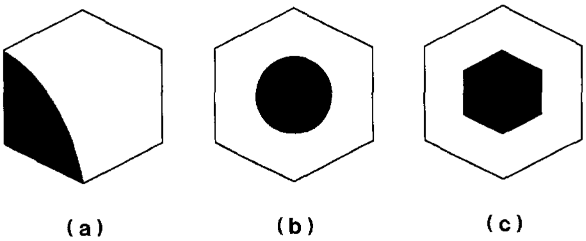


Figure 6 Schematic representation of variations in morphology of particles associated with pitting action.

3.1.8. 900 K

At this temperature disintegration of specimens became a major factor and for this reason most experiments were stopped at this point. Prior to termination, it was clear that the majority of particles were undergoing a decrease in size as a result of volatilization of material. Fig. 12 is a micrograph of specimen which has been cooled to room temperature after oxidation at 900 K. During cooling the globular particles have undergone a transformation to form well-defined crystallographic shapes and there are a profusion of very small particles present over the entire specimen. A measure of the severity of the treatment of molybdenum disulphide in oxygen can be obtained from a comparison of the appearance of the specimen in this micrograph with that of a specimen before reaction, Fig. 1.

In a separate series of experiments particles of MoO_2 were introduced onto the molybdenum disulphide substrate and this combination was heated in 4.1×10^2 Pa oxygen. On raising the temperature to 660 K the original rugged outline of the MoO_2 particles tended to become smooth, and at the same time, changes in the appearance of the molybdenum disulphide edge regions were observed. At 710 K, globular particles which had been formed on the molybdenum disulphide basal plane at lower temperatures had grown to such size that it was difficult to distinguish them from the original MoO_2, since all the particles exhibited identical characteristics.

3.2. Molybdenum disulphide–hydrogen

When molybdenum disulphide samples were heated in 6.8×10 Pa hydrogen, the observed pattern of behaviour was relatively simple compared to that seen in oxygen. Although some slight changes in the texture of the basal plane were seen at 640 K, the edge regions

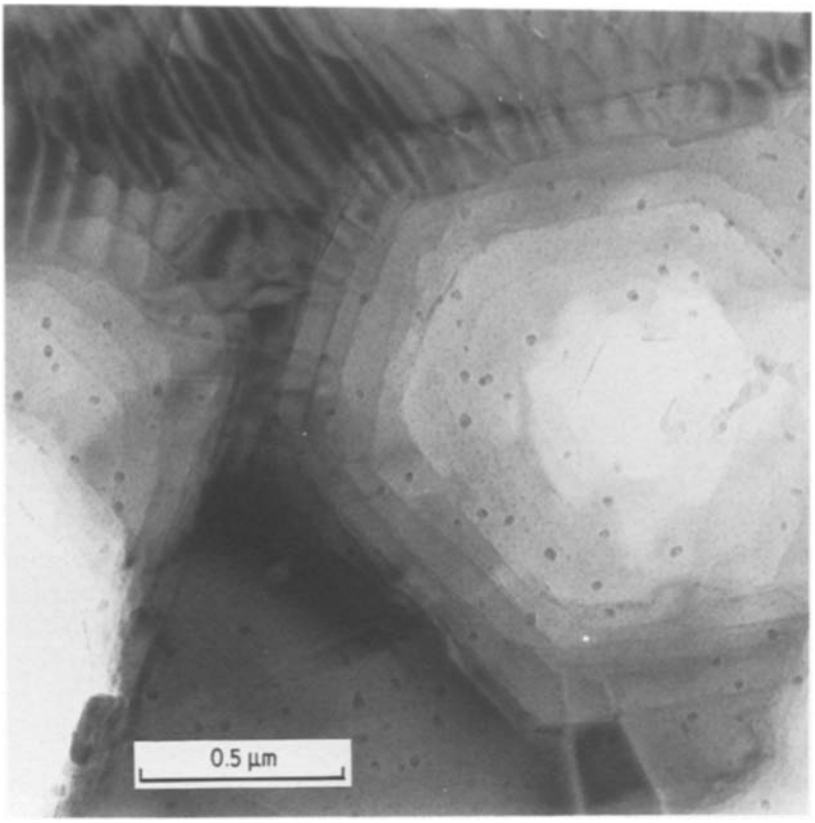


Figure 7 Transmission micrograph of a typical pit produced in the basal plane of molybdenum disulphide following treatment in oxygen at 875 K.

remained very clean and smooth until the temperature was increased to 950 K. After holding at this temperature for about 5 min, it was apparent that the edges were undergoing very slow recession but still maintained their uniform profile, i.e., at this stage the recession was not accompanied by the formation of other structures such as crystallites. A survey of the basal plane regions showed that the uniform texture observed at lower temperatures had gradually transformed into an array of particles, 25 to 150 nm in size. In contrast to the behaviour in oxygen, these particles showed no tendency to move on the surface. Furthermore, no difference in texture was seen in regions of the surface adjacent to edges indicating that the likelihood that hydrogen was diffusing into the layered structure under these conditions was small. We have shown that when this phenomenon occurs, it is easily detected in the transmission image as a "staining effect" along the edge regions [10].

On continued heating up to 1000 K, the rate of reaction increased appreciably; edges developed a feathery outline and the basal plane started to undergo complete reorganization with holes being created at various points on the surface. It was difficult

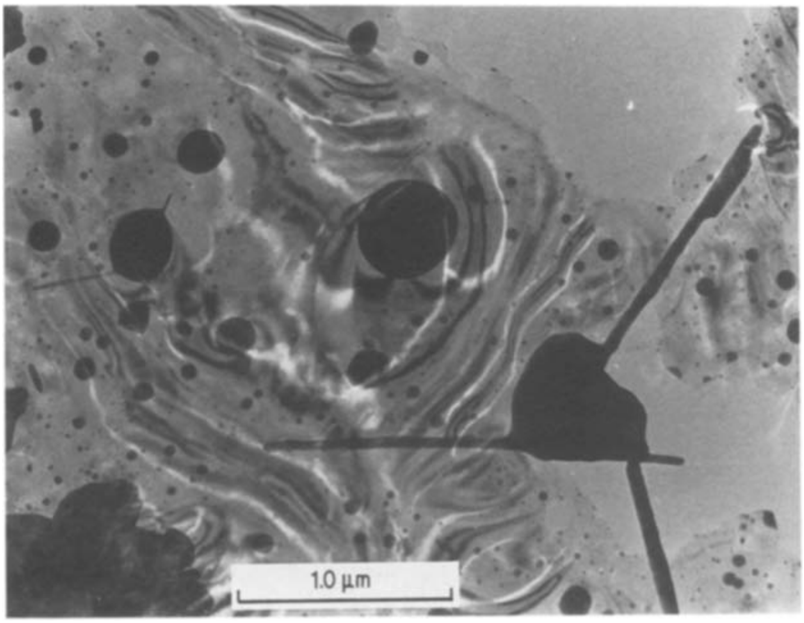


Figure 8 Transmission micrograph showing the needle structures which formed during the interaction of molybdenum disulphide with oxygen at 825 K.

TABLE III Electron diffraction analysis of basal plane region of molybdenum disulphide during reaction in oxygen at 800 K

Calculated *d*-spacings (nm)	*d*-spacings (nm)					
	MoS_2	MoO_2	MoO_3	$MoO_{2.8}$	Mo_4O_{11}	Mo_9O_{26}
0.354				0.359		0.358
0.271	0.271					
0.244		0.244			0.244	
0.222					0.222	
0.184		0.184				
0.173			0.173		0.173	
0.158	0.158					
0.141	0.140		0.140			
0.135	0.136	0.135				
0.134		0.134				
0.118	0.118					

to determine whether these holes were associated with any particular defect sites on the surface since they possessed no distinguishing features, as was seen in the case of the hexagonal pits formed in the presence of oxygen.

In most experiments the maximum temperature was limited to 1055 K, and at this stage the surface structure consisted of an interconnected arrangement of non-spherical islands, which resembled the typical appearance of a specimen which has undergone spinodal decomposition.

In a complementary series of experiments the change in the chemical nature of the specimen was followed as a function of increasing temperature by performing *in situ* electron diffraction examinations. A selection of the patterns obtained during this procedure and their corresponding analyses are presented in Fig. 13 and Table V. In addition to the major product, metallic molybdenum, some molybdenum trisulphide, was also found. The advantages of being able to perform this type of examination is evidenced from the fact that chemical analysis indicated that reduction of molybdenum disulphide to the metallic state commenced at 860 K, about 275 K below the temperature where the first signs of physical changes were observed in the transmission image.

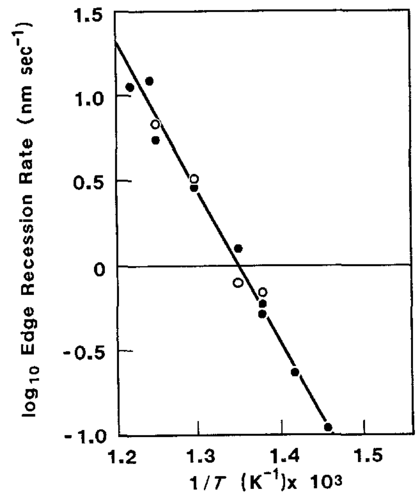


Figure 9 Arrhenius plot of (●) edge recession, and (○) pit expansion rates from molybdenum disulphide specimens undergoing reaction with oxygen.

4. Discussion

The results of this investigation provide evidence that oxidation of molybdenum disulphide occurs by attack at edges and point defects on the basal plane and confirm the claims made by previous workers [2, 3].

TABLE IV Electron diffraction analysis of edge region of molybdenum disulphide during reaction in oxygen at 875 K

Calculated *d*-spacings (nm)	*d*-spacings (nm)			
	MoS_2	MoO_2	MoO_3	Mo_4O_{11}
0.304			0.304	
0.271	0.271			
0.215			0.215	0.215
0.182			0.182	
0.169		0.170	0.169	
0.159	0.159		0.159	0.158
0.152		0.152		0.153
0.135	0.136	0.135		
0.132	0.131			
0.127	0.128		0.127	
0.121	0.121		0.121	
0.100	0.100			

TABLE V Electron diffraction analysis of the basal plane regions of molybdenum during reaction in hydrogen at 1040 K

Calculated *d*-spacings (nm)	*d*-spacings (nm)		
	MoS_2	Mo_2S_3	Mo
0.271	0.271		
0.264	0.263		
0.223			0.223
0.211		0.210	
0.201		0.203	
0.192		0.192	
0.175	0.176		
0.170		0.171	
0.157	0.158		0.157
0.152	0.153		
0.135	0.136		
0.129			0.129
0.125	0.125		
0.121	0.121		
0.118	0.118		
0.111			0.111
0.099			0.099
0.091			0.091
0.084			0.084

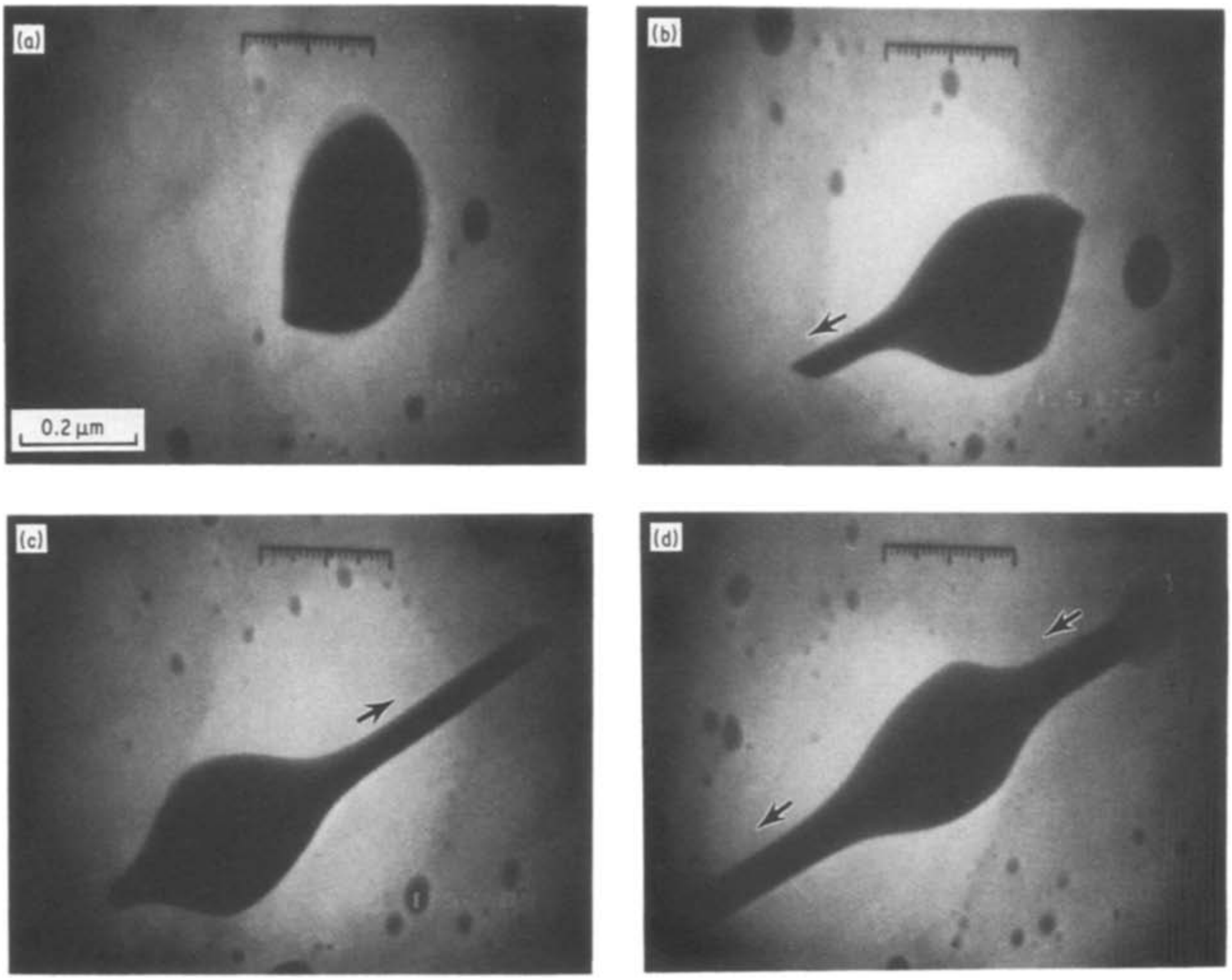


Figure 10 Sequence showing the development of needle-like structures from a globule at 825 K in oxygen. The arrows indicate the direction of growth of the needles.

Consistent with surface science studies, it was found that the perfect regions of the basal plane were relatively unreactive [7].

It is clear from the qualitative description presented above that there are a variety of dynamic events occurring during the reaction and at this time we do not have plausible explanations to account for the entire course of the reaction. It is, however, tempting to correlate the spreading and contracting behaviour of globular particles on the basal plane with a change in the nature of the substrate surface immediately surrounding a given particle. During reaction the state of the surface will oscillate from a condition where sulphur atoms are exposed to one where molybdenum atoms are exposed. Such a situation would be expected to produce significant changes in the interfacial energies

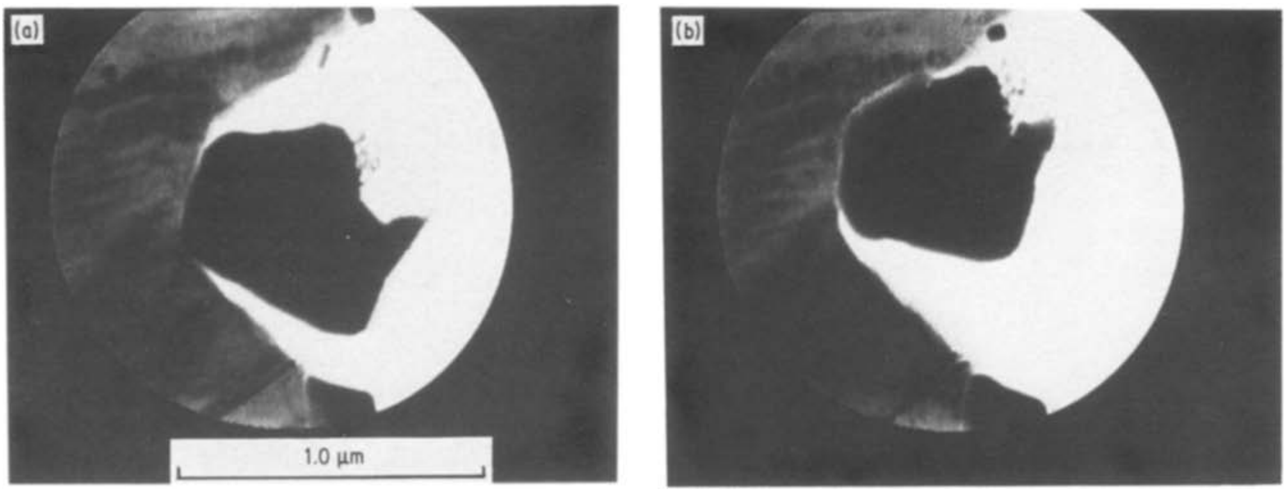


Figure 11 Sequence showing the catalyzed conversion of molybdenum disulphide to metal oxide particles at 875 K in oxygen.

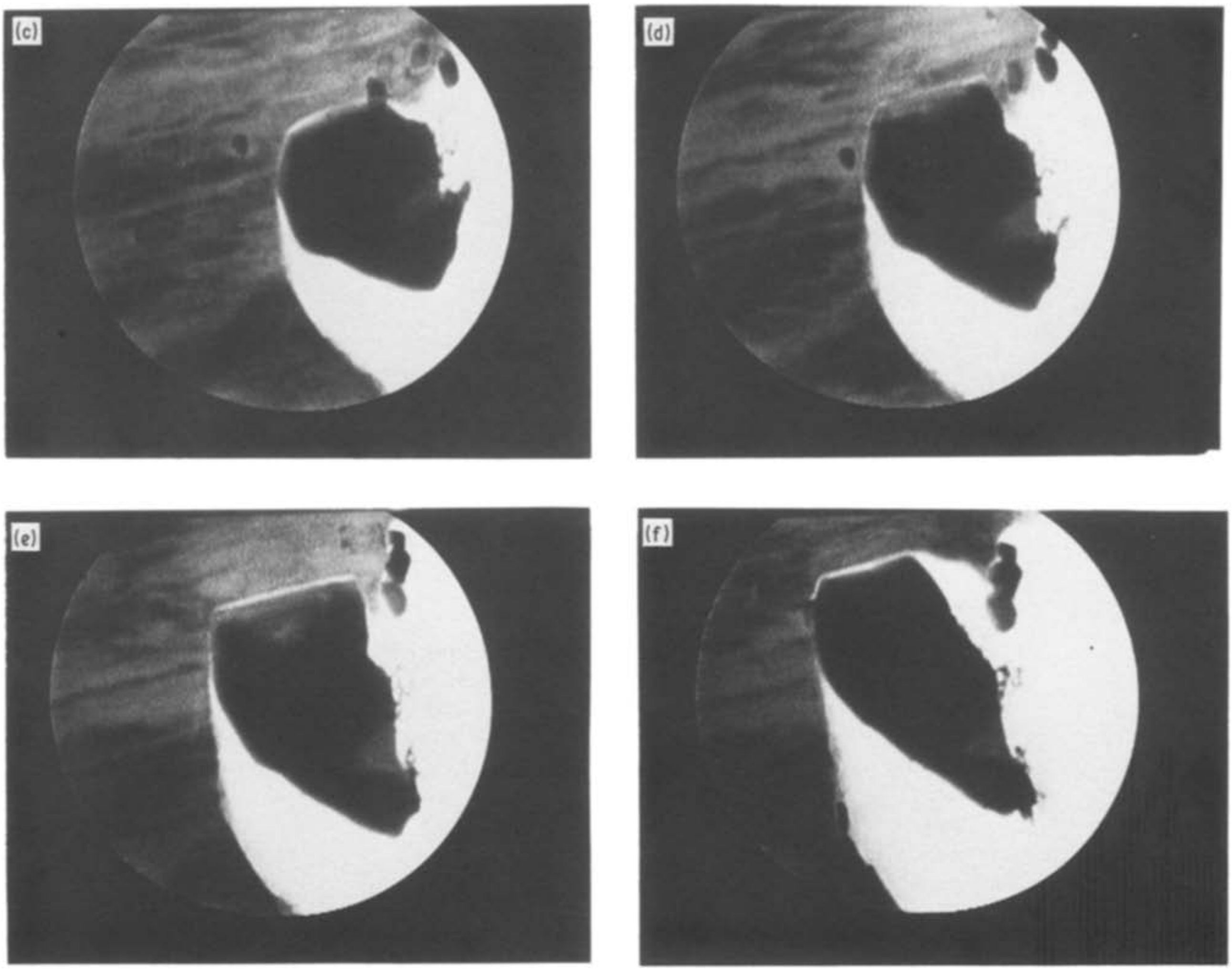


Figure 11 Continued.

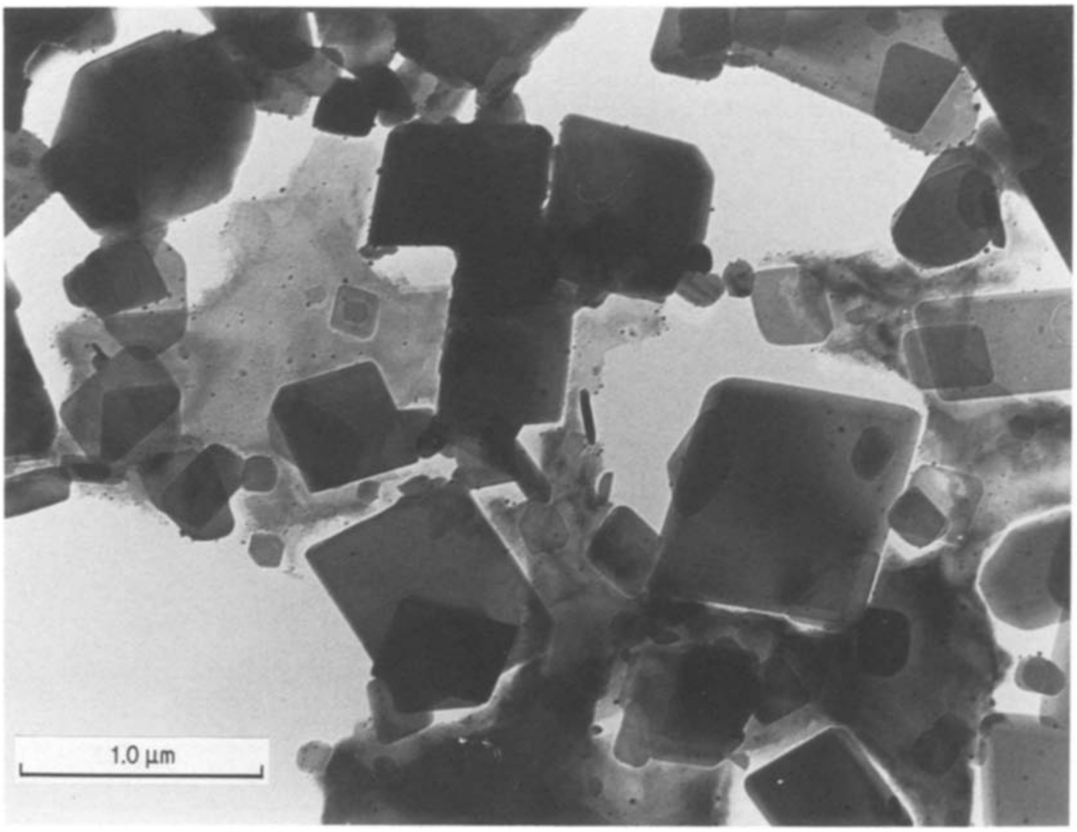


Figure 12 Transmission micrograph of a molybdenum disulphide specimen which has been treated in oxygen at 900 K.

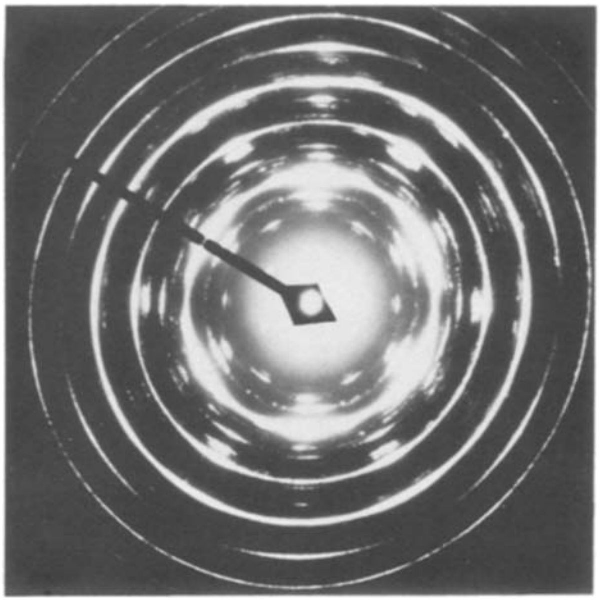


Figure 13 Selected area electron diffraction pattern of molybdenum disulphide at 1040 K in 6.8 × 10 Pa hydrogen.

prevailing at the particle/substrate interface and as a consequence induce transformations in the particle morphology.

Perhaps the most intriguing observation was the emergence of needle structures from the globular particles at temperatures of around 800 K, which are probably the result of formation of a metastable oxide. These structures appear to be quite similar to those found by Hashimoto and coworkers [11] from the thermal decomposition of ammonium molybdate at 775 K and identified as Mo_9O_{26} (β'-oxide).

The finding that at 900 K shrinkage of particles was observed is consistent with the fact that MoO_3 undergoes sublimation under these conditions [12].

The *in situ* selected area electron diffraction analysis shows that the oxidation of molybdenum disulphide by oxygen proceeds through two main stages. At temperatures below 800 K MoO_2 was the predominant phase produced, which suggests that under these conditions the oxidation proceeds via the following pathway:

$$MoS_2 + 3O_2 \rightarrow MoO_2 + 2SO_2 \qquad (1)$$

At temperatures in excess of 800 K the formation of MoO_3 becomes significant with intermediate metastable oxides playing some role. Although we cannot state with any certainty the particular mechanism whereby MoO_3 is formed, the finding that the Arrhenius plot, Fig. 11, does not exhibit any major deviations over the high temperature region would seem to indicate that Reaction 1 is the primary step and that MoO_3 is formed by the consecutive reaction

$$2MoO_2 + O_2 \rightarrow 2MoO_3 \qquad (2)$$

rather than by an alternative direct route such as proposed by other workers [13]

$$2MoS_2 + 7O_2 \rightarrow 2MoO_3 + 4SO_2 \qquad (3)$$

Based on these arguments, it is probable that the measured activation energy of $166.0\,kJ\,mol^{-1}$ is the value for the conversion of molybdenum disulphide to MoO_2.

A further aspect to emerge from the kinetic data is the finding that within experimental error at any given temperature the rates of edge recession and pit expansion are the same. This is an interesting observation since the characteristics of the edge and vacancy sites from which pits are developed are quite different. Edge sites consist of a S–Mo–S structure whereas basal plane vacancies expose metal sites in a triangular configuration. The present results appear to indicate that these different sites have comparable reactivity towards oxygen, and as a consequence, creation of defect sites in the basal plane may provide a means of enhancing catalytic activity of molybdenum disulphide [6, 7, 14].

Treatment of molybdenum disulphide in hydrogen was a relatively unreactive process compared to that in oxygen. Furthermore, since hexagonal shaped pits were not created in the basal plane, it appears that hydrogen discriminates in its chemisorption behaviour, attacking only the edge sites. This observation is consistent with the surface chemical studies of Farias and coworkers [7], which showed that hydrogen was not capable of removing sulphur atoms from the basal plane of a sulphide surface which contained a significant number of defect sites.

There is widespread agreement in the literature that hydrogen firstly dissociates on the exposed molybdenum edge atoms to form S–H groups [15–18]. In contrast, a disagreement exists as to whether hydrogen is absorbed within the molybdenum disulphide structure [18]. Recent NMR studies support the view that such a process does occur [19]. In this regard the current observations should be treated with caution as such a process may not induce the same structural changes which are found when hydrogen is absorbed in the graphite structure [10]. Furthermore, its effect may have been missed if hydrogen is desorbed from molybdenum sulphide at temperatures of about 425 K, and on heating to 775 K relaxation of the structure occurs.

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