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BLISTERING OF MOLYBDENUM UNDER HELIUM ION BOMBARDMENT

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BLISTERING OF MOLYBDENUM UNDER HELIUM ION BOMBARDMENT

by

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ABSTRACT

Polished molybdenum targets have been bombarded with helium ions of energy from 7 to 80 keV in ultra-high vacuum. During bombardment the release of gas was continuously monitored and after bombardment the targets were examined in a scanning electron microscope.

Blister formation was observed to occur after a critical dose of $\sim 5 \times 10^{17}$ ions/cm^2, and the appearance of blisters coincides with gas release from the surface. The average size of the blisters increases with energy but not with ion dose. In addition to room temperature observations, blisters have also been examined following high temperature bombardment of molybdenum, and room temperature bombardments of W, Pt, Ni, Cu and Zr targets.

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C O N T E N T S

1. INTRODUCTION

Radiation blistering of materials due to high energy, α, proton and deuteron bombardment has been known for some time[1,2,3,4]. Initial work on bubble formation[5,6] all indicated that temperatures sufficiently high to allow vacancy migration were required before bubbles (hence blisters) could be observed. However, Nelson[7], has observed bubbles in copper following 60 keV He^+ irradiation at a temperature of only 20 ^oC. In addition, recent work on blister formation in palladium[8] showed 5 μ diameter blisters after 300 keV He^+ bombardments at 93 K. However, observations of these blisters were made at room temperature and the thermal release spectra of helium from palladium indicated mobility at temperatures as low as - 160 ^oC.

Blisters have also been observed in erbium and erbium deuteride thin films following 160 keV He^+ ion irradiation[9]. The size and density of blisters was found to depend on the post implantation annealing temperature. At 400 ^oC, a critical dose (3 x 10^{17} atoms/cm^2) was required before blistering occurred.

In the present work blister formation on molybdenum is examined, both at temperatures near ambient (< 50 ^oC) and at elevated temperatures, (up to 1500 ^oC) during ion bombardment. Examination was by means of the Surrey University scanning electron microscope, (S.E.M.) from which blister diameters could be recorded both as a function of total ion dose, and incident ion energy. The He gas thermal release spectra has also been obtained following bombardment at 50 ^oC.

2. EXPERIMENT

Molybdenum samples 2 cm x 0.5 cm x 0.1 cm were cut from 99.96% purity sheet. Prior to bombardment these were mechanically polished using finally a ¼ μ diamond abrasive and then annealed at 2000 K for 5 minutes. Each sample was examined for scratches on the optical microscope with magnification 1500 x.

Bombardments were carried out in the U.H.V. light ion accelerator used previously for the study of gas release from surfaces[10]. The vacuum system was modified for use with helium by adding two mercury diffusion pumps. A background gas pressure of 1×10^{-9} torr in the target chamber was obtained after baking. The beam was electrostatically scanned which results in a more uniform ion dose over the bombarded area and hence better resolution in the helium release curves measured as a function of dose.

A turntable allowed up to six targets to be positioned in the beam during an experiment. Each one could be heated from the back face by electron bombardment, up to temperatures in excess of 2000 K. Platinum, platinum-rhodium thermo-couples were used for temperature measurement. The helium re-emission both during and after bombardment, was measured using the quadrupole mass spectrometer as in previous work[11], Care was taken not to disturb the bombarded areas prior to observation on the Stereoscan electron microscope, with magnifications of 1000-20,000 x.

3. RESULTS AND DISCUSSION

3.1 Gas Release During Bombardment

The helium partial pressure, beam current and target temperature are monitored continuously during bombardment. With the highest ion dose rate (2×10^{15} ions/cm^2/sec), the target temperature rises by ∿ 50 K. Figure 1 shows the helium re-emission as a function of ion dose during bombardment with 36 keV He^+ ions. The curve exhibits features similar to those observed when nickel is bombarded by deuterons at low temperatures[12] namely a constant (< 10%) re-emission of the beam, followed by a sharp break point and a rapid rise in the release rate towards 100% re-emission.

The ion dose at which the break point occurs changes slowly with both ion energy and target temperature. It also appears to be a function of the crystal face presented to the beam - samples annealed at 2000 K contain large grains with differing orientations. The break points ranged from 1-2 x 10^{17} for 7 keV ions, 4-6 x 10^{17} for 20 keV ions and 5-7 x 10^{17} ions/cm^2 for 36 keV ions. S.E.M. micrographs are shown in Fig.2 for the different doses. It is seen that the size distributions are very similar, large blisters being observed at doses just above the threshold. Samples examined just below the threshold as determined by the gas release curve show no sign of any blister formation even at the highest magnification used (25,000 x). The size distribution, obtained by measuring the size of blisters on the micrographs are shown in Fig.3. It is apparent that the distributions are approximately gaussian in shape and that the average size increases with energy. Micrographs of blisters at different energies are shown in Fig.4.

3.2 Mechanism of Blister Formation

The results of gas released versus dose indicate that initially a large fraction of the incident ions are trapped in the surface. The fact that they do not come out is consistent with the low observed rate of diffusion of helium in metals, and contrasts with the behaviour of hydrogen isotopes at room temperature[11]. The concentration of the gas in the surface must build-up during this time. Samples examined in a transmission electron microscope, (T.E.M.) show that very small bubbles with diameters in the range 20-40 Å are produced[13]. However, the size of these bubbles does not increase with dose, only the number density increases. The fact that blister formation at the surface occurs abruptly suggests that there is a critical concentration above which the metal lattice is ruptured. It is suggested that this is due to the mean distance between bubbles reducing to the point where they interact and there is then a sudden coalescence of bubbles within the range distribution of the incident ions. This coalescence would result in a pressure on the surface from a depth corresponding to the projected range of the incident ions in the metal. From the observed form of the blisters it is clear that there is plastic deformation at the surface with eventual fracture at the periphery of the blister. At the point of plastic deformation we have that

$$\pi r^2 P = 2\pi r\ RY \qquad \ldots (1)$$

or

$$r = \frac{2RY}{P} \qquad \ldots (2)$$

where r is the blister radius, R the projected range of ions in the solid, Y the yield strength of the material and P the gas pressure within the blister. Assuming that all the inplanted gas is collected in the coalescence process then the pressure will be given approximately by

$$P = D/2.7 \times 10^{19}\ \Delta R \text{ atmospheres} \qquad \ldots (3)$$

where D is the total ion dose per cm^2 and ΔR is the average height in cm of the void in the metal. It is assumed as a first approximation that ΔR will be equal to the range distribution of ions in the metal. The basis of the coalescence hypothesis is that the bubble density must reach a critical value before the blister can form. If a constant fraction of the incident ion flux goes into bubbles then the critical concentration C will be given approximately by the ion dose divided by the width of the range distribution or $C = D/\Delta R$. Thus

$$r = 5.4 \times 10^{19}\ RY/C \quad . \qquad \ldots (4)$$

By definition both C and Y are constant for a given material at any one temperature and hence we have that to a first approximation the blister radius is proportional to the range of the ions in the metal. Knowing $C \cdot \Delta R \simeq 5 \times 10^{17}$ ions cm^{-2} and $\Delta R \sim 1000$ Å we have $C \simeq 5 \times 10^{22}$ atoms . cm^{-3}. Thus taking the yield strength of molybdenum to be $\sim 5 \times 10^3$ atmospheres[14] we obtain:

$$\frac{r}{R} \sim 5 \qquad \ldots (5)$$

which is in quite good agreement with the relation between the radius and depth of the craters as observed in the S.E.M. micrographs. The yield modulus Y varies with temperature and material. Moreover it must also be a function of crystal orientation and be higher in single crystals than in polycrystalline material. The experiments carried out are essentially in single crystals since the size of the blisters are much smaller than the grain size in the molybdenum surfaces.

The projected range R increases approximately linearly with energy E in the energy range investigated, and is given approximately by[15]

$$R = \frac{C_i(\mu)\,100\,A_2\,(z_1^{2/3} + z_2^{2/3})^{1/2}\,E}{z_1 z_2 \rho}\ \text{Å} \quad \text{for E in keV} \qquad \ldots (6)$$

where $c_i(\mu)$ is a function of the ratio of the mass of incident and target atoms, ρ is the target density in gms/cc and the other symbols have their usual meanings. Thus

$$R = 57.5\ E\ \text{Å} \quad . \qquad \ldots (7)$$

We would therefore expect that the blister radius should be proportional to energy. The experimental results shown in Fig.5 indicate this to be approximately correct.

Blisters have also been observed after helium irradiation in W, Pt, Zr, Ni and Cu. Some of these results are shown in Fig.6. The general character of the blisters is very similar to those observed in molybdenum, though only in tungsten are the blisters as clearly seen as in molybdenum. In metals other than W and Mo the number of burst blisters observed is very small, whereas for molybdenum it is $\sim$ 10%.

3.3 Effect of Temperature

Up to now we have discussed gas release and blister formation only near ambient temperatures. Experiments have also been carried out at higher temperatures and the thermal desorption spectra measured. Desorption spectra are shown in Fig.7 for molybdenum after irradiation at room temperature to a number of specified doses. Although the desorption peaks occur at much higher temperatures the general behaviour is again very similar to that previously observed for deuterium[12]. As the initial dose is increased a greater and greater fraction of the gas is desorbed from the low temperature peaks. It is well known that at very low doses (say < 10^{14} ions/cm^2) no helium is released from molybdenum or tungsten at temperatures below 2000 K following bombardments with ions $\gtrsim$ 5 keV. In the present range of doses the desorption peak at 1350 K is rapidly increasing with dose while the peak at 1700 K appears to decrease. Since it is reasonable to attribute the peak at 1700 K (0.59 T_m) to the self diffusion of lattice atoms, its decrease with increasing dose is consistent with the transfer of gas from substitutional sites to the small bubbles observed in the T.E.M. The peak at 1000 K is interesting in that there appears to be a threshold dose below which it is not observed. This dose of 5 x 10^{17} ions cm^{-2} coincides with that observed for the appearance of surface blisters and for the release of gas at room temperature (Fig.1). It is possible therefore that this peak is due to release of gas from blisters which have not actually ruptured before heating.

Micrographs of surfaces implanted at various temperatures are shown in Fig.8. These temperatures were chosen on the basis of the desorption spectra, 800 K is just below the first peak in the desorption spectra, 1100 K is between the first and second peak and 1600 K is above the second peak. The results obtained are not easy to explain. At 800 K the surface is flaking, at 1100 K it has formed into smooth blisters rather larger than at room temperature and at 1600 K it has an irregular appearance characterized by small pinholes. On the basis of equation 4 one would expect the blister radius to decrease, since the yield modulus decreases with increasing temperature. Many additional micrographs have been taken of samples which have been implanted at one temperature and then annealed at a higher temperature. The general conclusion from examining these is that the temperature of implantation is the most important factor in determining surface structure and the subsequent anneal modifies the surface only slightly. It is intended to present these results in more detail in another publication.

4. CONCLUSIONS

The present results confirm the previous evidence [2,3,8] that surface blistering of metals under irradiation results in the release of gas, and indicates that this is in fact the principal mechanism by which the implanted gas is released. The blisters occur after a well defined critical dose of ions has been implanted and this dose agrees quite well with an earlier estimate[16].

The size of the blisters increases with energy and a simple analysis indicates that this is explained by the increasing depth of implantation. Results are similar for a wide range of metals and the variation in the size from one metal to another is qualitatively in agreement with the variation in range. The appearance of the blisters in practice does not appear to be critically dependent on the properties of the metals although the simple model indicates that it should. Moreover the critical dose for blisters to appear is the same within 50% for all metals so far investigated.

The size distributions of the blisters examined are approximately gaussian within the statistics of the number of blisters counted. There appears to be no change in the mean size of the blisters with the incident ion dose. As the temperature of molybdenum increases the nature of the blistering changes radically and four different characteristic forms of surface blistering have been identified at temperatures of 300 K, 800 K, 1100 K, and 1600 K. The mechanism of the change in blistering is not understood but may be due either to changes in the mechanical properties of the metal or to changes in the size and distribution of the initial bubble formation in the metal before blistering occurs.

The blistering phenomenon must be confined to light ions. With heavier ions, because of the combination of higher sputtering coefficient and lower range, the surface is eroded and gas released before sufficiently large concentrations have built up to produce blistering. With helium the probability of blistering is increased because of the low solubility resulting in no loss of gas by permeation. This contrasts with the case of hydrogen where there is considerable gas release due to permeation [(17)], and accounts for the fact that blistering occurs at much lower doses in helium ($\sim$ 5 x 10^{17} ions cm^{-2}) than in hydrogen ($\sim$ 10^{19} ions cm^{-2}) [(17)]. The bursting of blisters and the cracking of the surface by gas pressure must lead to surface erosion which in practice will be superimposed on the erosion by atomic sputtering processes. Whether erosion due to blistering is measured in any conventional sputtering experiment will depend on whether or not the critical dose has been exceeded. It would be of interest to compare the rate of erosion of a surface at doses lower and higher than the critical dose.

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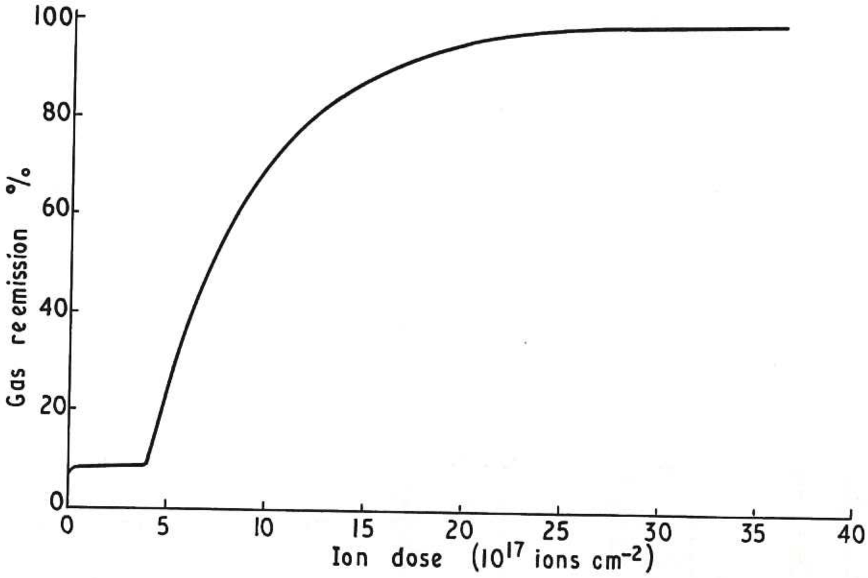
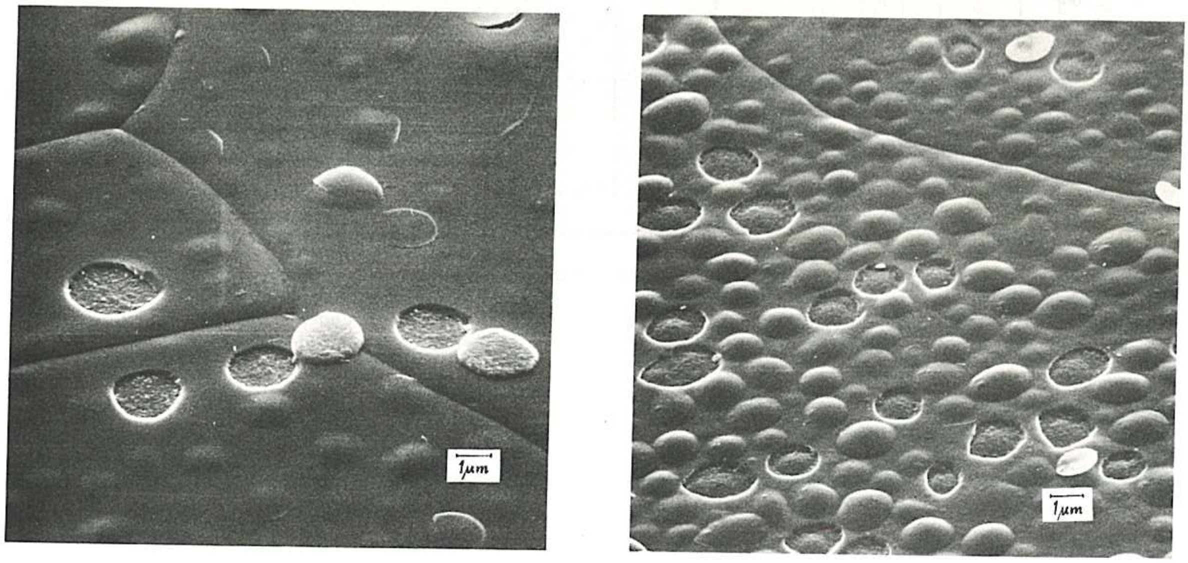


Fig.1 Helium re-emission during bombardment of molybdenum by 20 keV He^+ ions.



(a) 6×10^{17} ions cm^{-3}

(b) 1.2×10^{18} ions cm^{2}

Fig.2 Blistering of a molybdenum surface after bombardment with 36 keV He^+ ions.

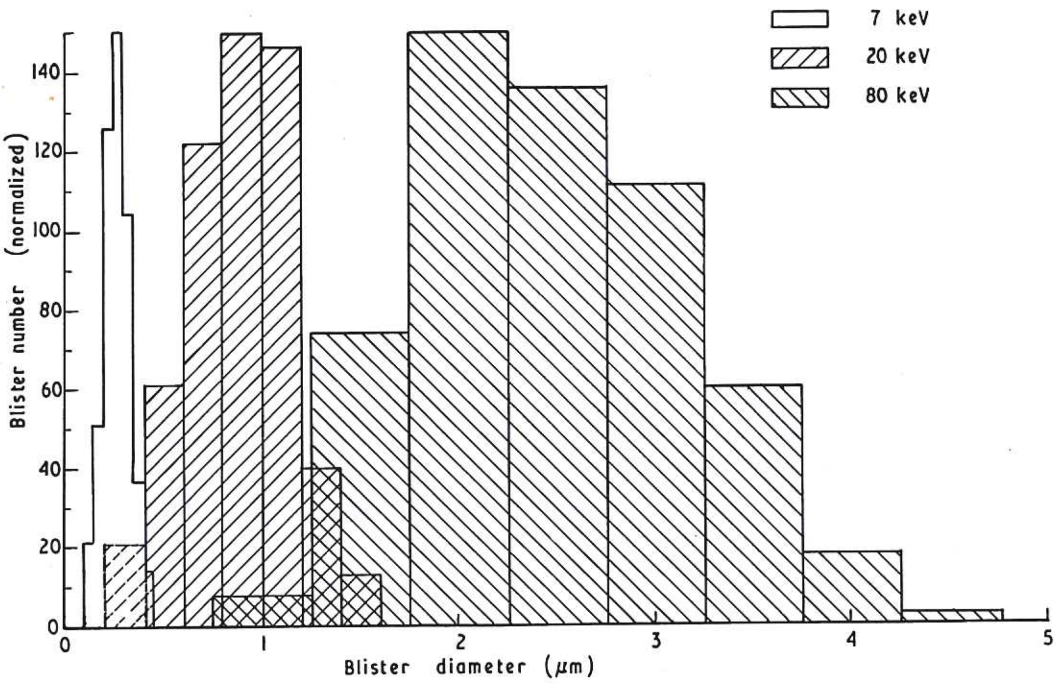
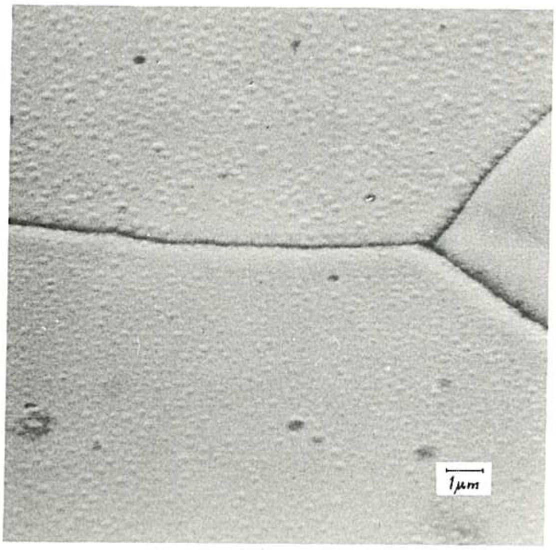
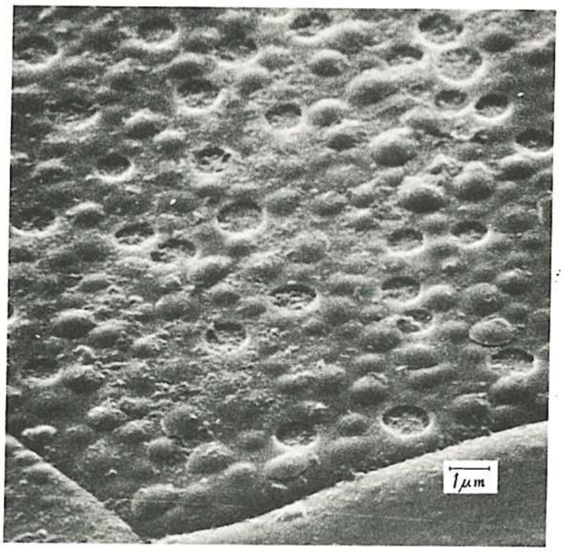


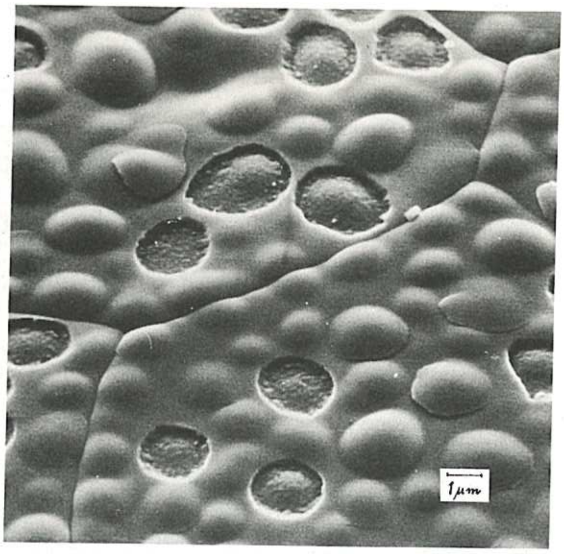
Fig.3 The sign distribution of helium blisters produced in molybdenum surfaces after bombardment with helium ions of various energies.



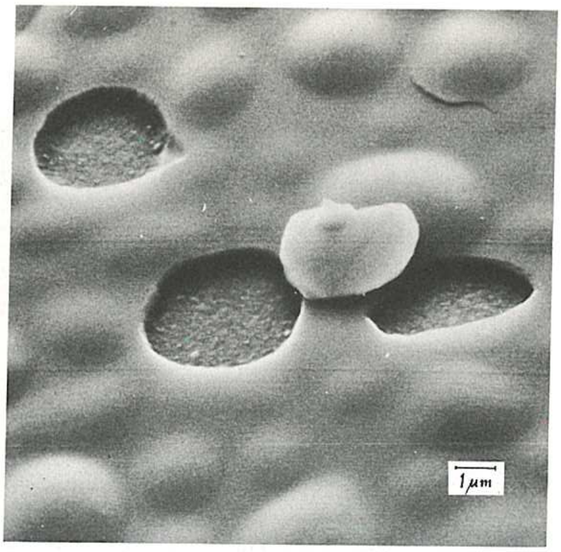
(a) 7 keV



(b) 20 keV



(c) 50 keV



(d) 80 keV

Fig.4 Blistering of a molybdenum surface after bombardment with helium ions of different energies.

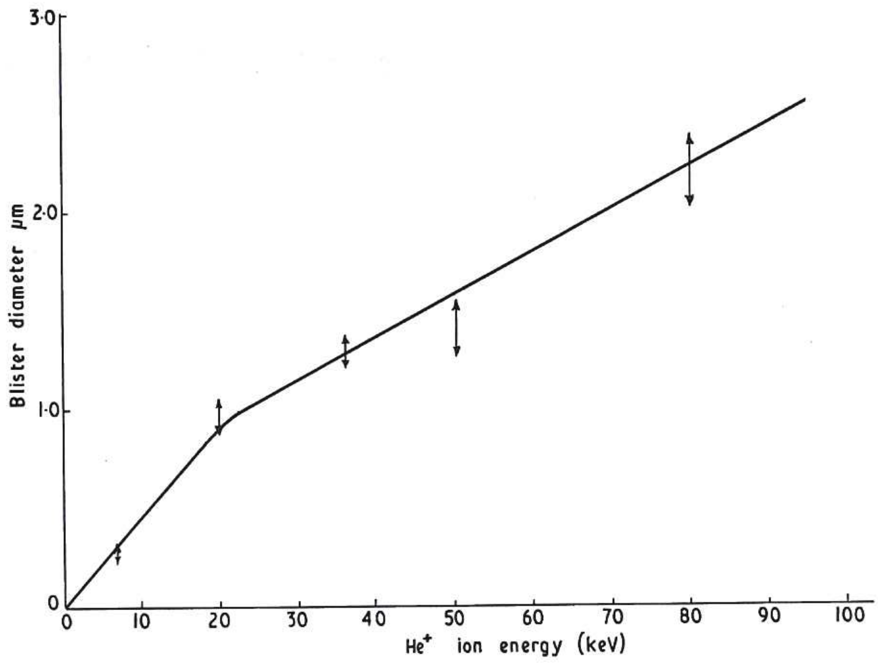
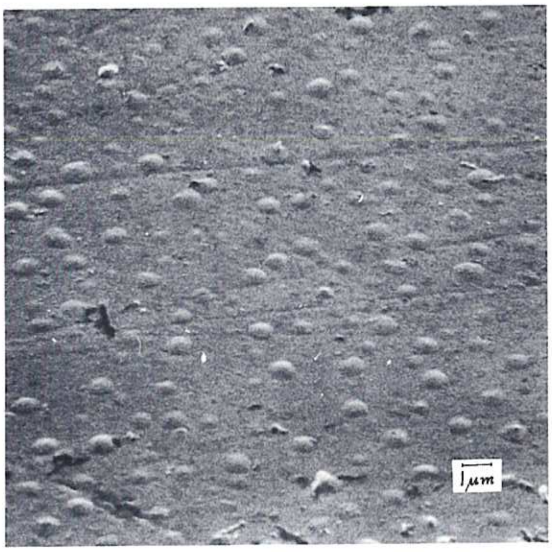
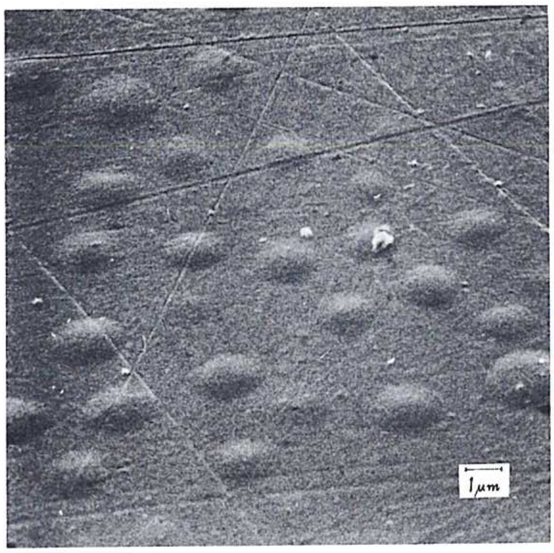


Fig.5 Most probable molybdenum blister size as a function of helium incident ion energy.



(a)



(b)

Fig.6 Blistering of (a) platinum and (b) nickel surfaces after bombardment with 36 keV He^+ ions.

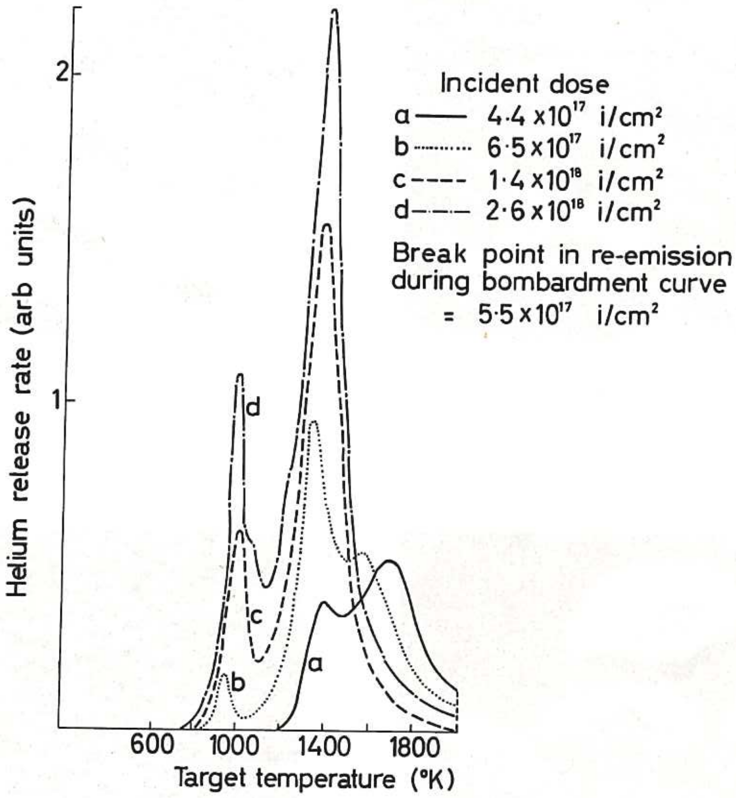
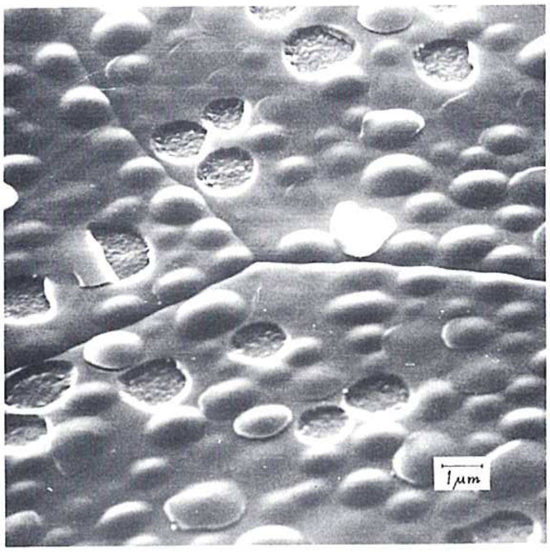
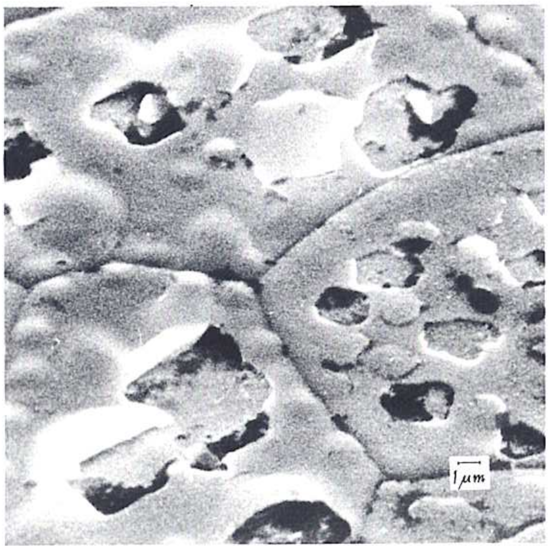


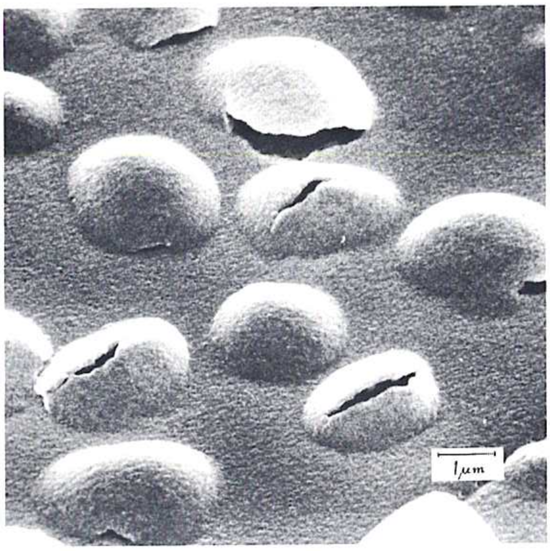
Fig.7 Thermal release spectra of helium from molybdenum following 36 keV He^+ bombardment.



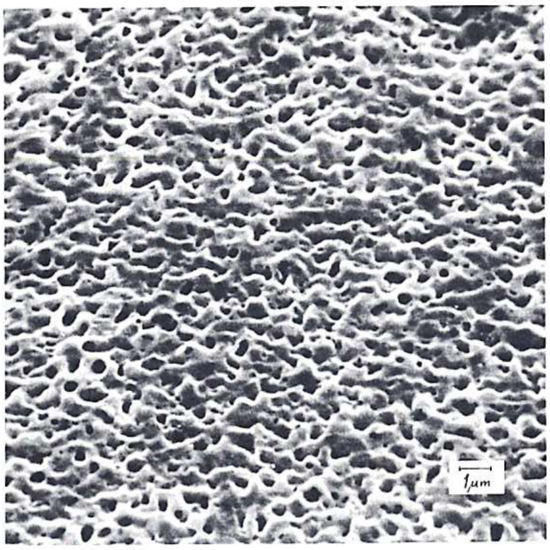
(a) 300 K



(b) 800 K



(c) 1100 K



(d) 1600 K

Fig.8 Blistering of molybdenum surfaces after bombardment with 26 keV He^+ ions at different temperatures.