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RADIATION DAMAGE AND GAS DIFFUSION IN MOLYBDENUM UNDER DEUTERON BOMBARDMENT

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RADIATION DAMAGE AND GAS DIFFUSION IN MOLYBDENUM UNDER DEUTERON BOMBARDMENT

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ABSTRACT

The trapping and thermal diffusion characteristics of deuterium from molybdenum have been shown to be critically dependent on the damage state of the material prior to implantation . It has been demonstrated that all deuterium may be removed from a sample at a temperature much lower than that required to anneal damage caused by the bombardment. Using this fact, measurements have been made of the rate of defect production for sites with binding energies above a certain value, determined by the molybdenum temperature during bombardment.

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1. INTRODUCTION

The release of gas from metals after implantation has been studied for many years[1]. A case of interest both from a fundamental point of view and from the application to controlled thermonuclear experiments is the bombardment of metals with hydrogen ions. This case is unique because of the high diffusion coefficient and high solubility of hydrogen in metals. In previous papers we have examined in detail the trapping and release of deuterium in nickel.[2,3] It was shown that the release rate is much less rapid than expected on the basis of thermal diffusion and there is considerable evidence that radiation damage by the incident ions produced trapping sites which inhibited subsequent diffusion by the implanted gas atoms. Similar evidence has been obtained for the helium tungsten system by Kornelsen[4] who was also able to identify the types of defect responsible for sites of different binding energies. In the investigation of nickel, estimates were made of the binding energies of different sites and their population as a function of incident ion dose. A similar study has now been made in molybdenum in which it is shown that the release rate is critically dependent on the damage and annealing history of the sample, and that under certain conditions release rates close to those predicted by thermal diffusion can be obtained.

2. EXPERIMENT

The experimental equipment is similar to that described previously (fig 1).[2,5] An ion beam in the energy range 5 to 35 keV is mass analysed and

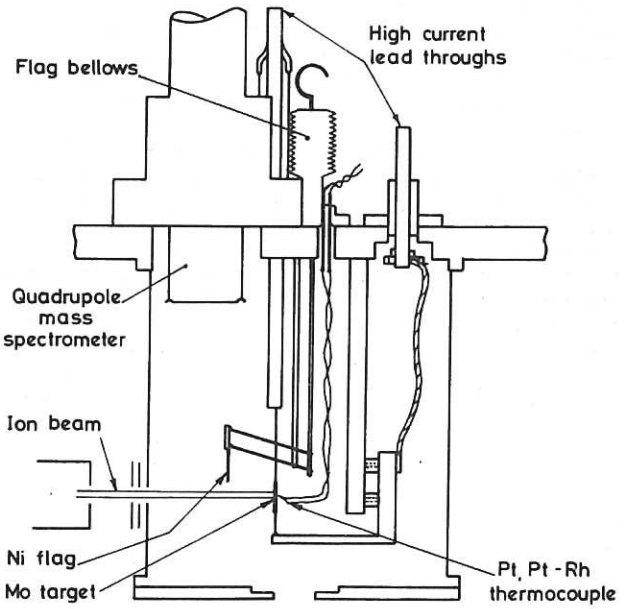

Fig 1 Schematic of target chamber.

focused on a target in the target chamber at a pressure $\sim 10^{-9}$ torr. The chamber is continuously pumped by an aperture of known pumping speed and the gas release is measured by a quadrupole mass filter. The target chamber is surrounded by an outer chamber which has a pumping speed for hydrogen of $\sim 10^4$ ℓ/sec, obtained by using a large titanium sublimation pump.

Measurements consist basically of observing the instantaneous release rate of deuterium from the surface as a function of time after the beam is turned on, for different target conditions. This is frequently followed by recording a post bombardment thermal desorption spectrum as the target temperature is increased linearly with time. The vacuum time constant of the system is 0.03 secs. The target consists of a strip of molybdenum (99.9%) 1 mm thick and 3 mm wide which is prepared by electropolishing and is heated directly by passing ac through it. It has been shown previously[6] that the target readily saturates so that there is an equilibrium between the rate of arrival of ions and the rate of re-emission of gas from the surface. The ion beam current is in the range 1-10 μA and the beam diameter is typically 3 mm. The area of the beam has an uncertainty of 20% leading to a systematic error in the estimates of ion dose per cm^2.

3. RESULTS

(i) Dose dependence

The release rate of the implanted gas during bombardment was found to be a function of the previous history of the sample - in particular on the amount of damage or annealing which the target had been subjected to. Results for the sample in different conditions are shown in fig 2. The curve (a) is for a sample in which the damage is saturated by prolonged ion bombardment so that

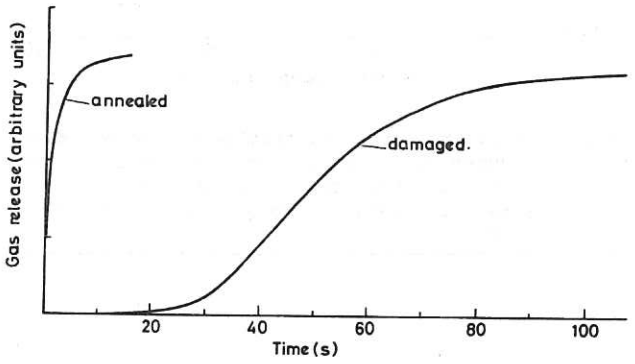

Fig 2 Gas release during 20 keV D^+ implantation of damaged and annealed Mo, at 523°K.

further damage causes no further change in the release behaviour. Gas implanted during the damaging stage is thermally released as described in (iii). Curve (b) is fully annealed as described later (ii). It is seen that the release rate is changed by more than two orders of magnitude from the damaged to the fully annealed states. Both of these states are completely reproducible in the same sample.

(ii) Damage annealing

The effect of temperature on the annealing of the sample is illustrated in fig 3. A target is damaged to saturation by a long period of bombardment with deuterons - typically 800 μA- min per cm^2 at 400K. The sample is then annealed for 10 minutes at successively higher temperatures and in between each anneal the target is bombarded for a short time at 2.5 μA in order to produce a characteristic re-emission curve as in fig 2. (The anneal removes the gas implanted during the damaging stage.) The number of ions trapped in the target during this test bombardment was measured by integrating the thermal release curve and this was used as a measure of the number of damage sites remaining in the sample. As seen in fig 3 there was a marked annealing effect at $\sim$ 1500K and the target was fully annealed at 1700K. The time and temperature agrees well with the recrystallization time for cold worked molybdenum specimens.[7]

(iii) Post implantation thermal desorption

For the annealing tests to be meaningful it is clear that the gas injected during the short test

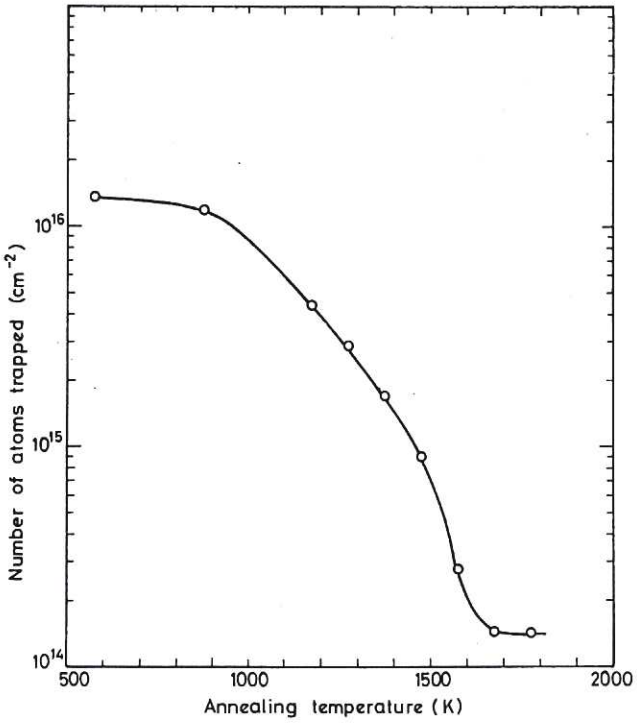

Fig 3 Annealing curve for molybdenum after damage induced by 20 keV D^+ ions. Annealing time 10 mins. Ordinate is the gas desorbed after a test implantation to gas saturation at 523K.

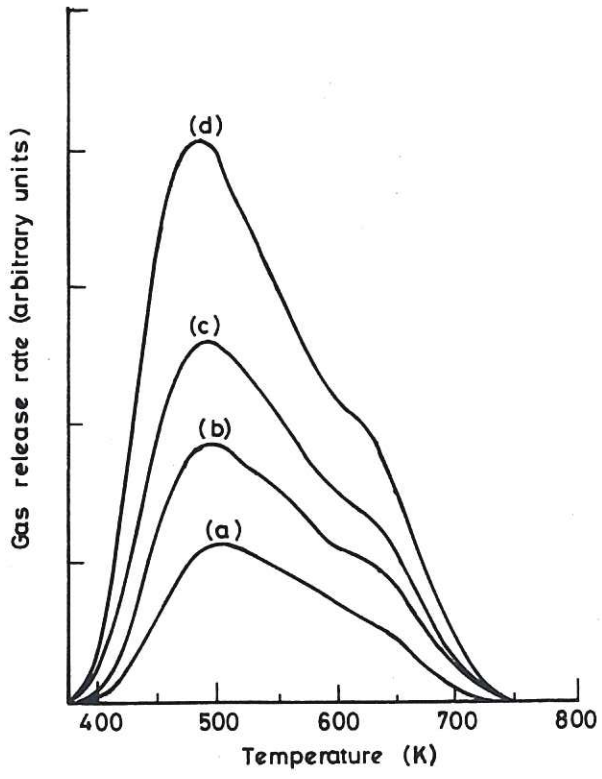

Fig 4 Post bombardment thermal release of gas from Mo after implantation of 20 keV D^+ ions at 373K. Incident dose
(a) 1.9×10^{16} ions cm^{-2}
(b) 4.7×10^{16} ions cm^{-2}
(c) 9.5×10^{16} ions cm^{-2}
(d) 1.9×10^{17} ions cm^{-2}

implantations between anneals must be completely removed during the annealing process. Post implantation thermal release spectra using a linear temperature ramp were therefore measured for initially annealed specimens after a variety of implantations, as shown in fig 4. It is clear that all gas is released from the target at temperatures above 750K and hence the annealing curve shown in fig 3 is meaningful above that temperature.

It is clear from the thermal desorption spectra that there is an increasing population of atoms in damaged sites with increasing dose and it is assumed that this is due to the increasing number of sites. It is also clear that there is some thermal desorption at the implantation temperature as release is observed immediately after implantation stops for some seconds. In fact in an earlier investigation[8] implantation was carried out at 77K and a continuous thermal desorption spectrum was observed from 100K to 700K. The major peaks were then observed between 150K and 250K. An attempt was made to analyse the present spectra in terms of individual peaks in the same way as was previously done for deuterium implanted in nickel.[3] However it was found necessary to introduce at least 6 peaks to obtain good agreement between theoretical and experimental results and since they were not at all well resolved it was virtually impossible to do this in an unique way. Thus the attempt to obtain individual site populations was abandoned.

(iv) Damage production rate

The fact that gas can be released at a much lower temperature than that at which the damage is annealed suggests a technique for measuring damage rates. An annealed target is damaged by ion bombardment for a fixed time at a temperature below the annealing temperature. Then by heating the damaged target just above the gas release temperature (750K in this case) the gas implanted during damage production is removed. The target is then bombarded with a short test dose at a well defined temperature and the re-emission rate during implantation is measured. Finally the target is heated and the thermal desorption spectrum is obtained. From integration of the re-emission curve during implantation and the thermal desorption curve an estimate is made of the number of atoms trapped in the lattice. Since the number trapped in an annealed target is normally small (cf fig 2) all these trapped atoms can reasonably be assumed to be trapped at damage sites. Furthermore if the test implantation is continued until the target is saturated then it is probable that all damage sites which can be occupied at that temperature are filled. Thus the number of atoms desorbed, which can be quite accurately measured absolutely, is a direct measure of the number of damage sites produced in the lattice.

Results for such an experiment are shown in fig 5 for a molybdenum target bombarded by deuterons at three different energies. Initially the damage increases linearly with dose and a measurable amount of damage is produced in a few seconds at the current density used of $\sim 25\ \mu A/cm^2$. As the dose increases the rate of damage decreases and the target reaches a saturation level. This saturation level is apparently higher for larger incident ion energies. The initial linear increase is a measure of the number of trapping sites which have been produced by a given dose ie a given number of incident ions. Thus the slope of the curve can be directly converted to damage rate in terms of defects/incident ion.

In this way the damage rate has been plotted as a function of energy as shown in fig 6. In addition to the three energies directly measured, the threshold for defect production has also been plotted

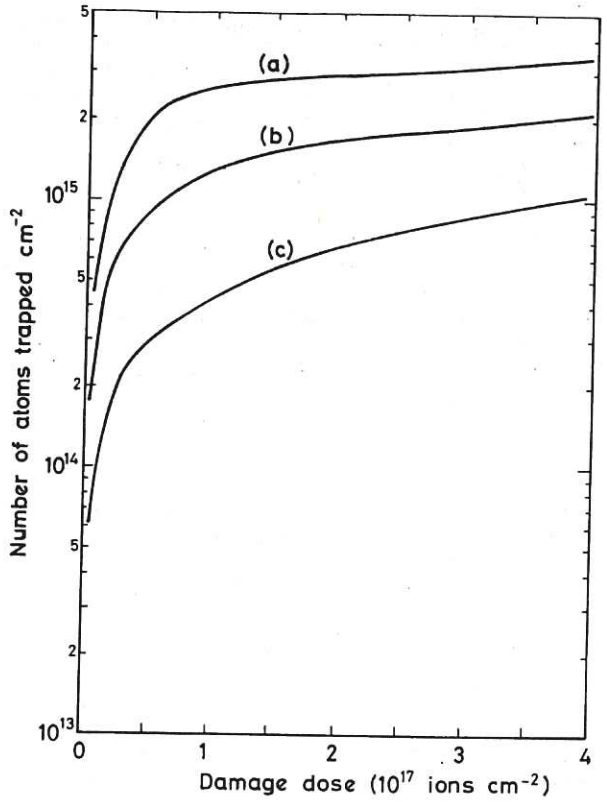

Fig 5 Trapping sites produced by D^+ ions in molybdenum. The ordinate is the gas desorbed after a test implantation at 623K.
(a) 35 keV (b) 20 keV (c) 7 keV

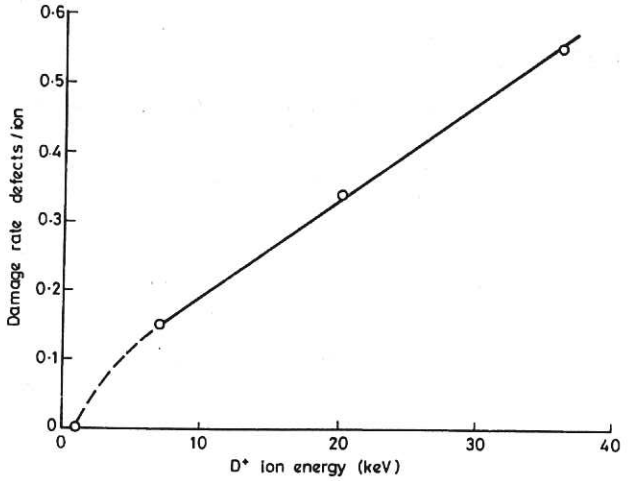

Fig 6 Rate of production of defects in Mo under bombardment by D^+ ions. Defects measured at 623K by implantation and subsequent thermal desorption of a test desorption of a test dose of D^+ ions.

assuming a displacement energy of 40 eV. It is seen that the damage rate increases roughly linearly with energy, and that the damage rate is remarkably low. Even at 30 keV the rate is less than 0.5 defects/ion. This low defect production rate is consistent with the fact that atoms do diffuse out of an annealed sample - for if the defect production rate was greater than unity then one would expect most incident ions to be trapped. No attempt has been made to calculate the defect production rate directly but it is generally accepted that with light ions the primary energy loss mechanism is electronic and that the proportion of the total energy lost by nuclear collisions is small.

The temperature at which the measurements of damage production rate are made is obviously critical. This was chosen for practical reasons to be sufficiently high that diffusion out of the sample was rapid, so that there were no atoms which were simply diffusion trapped. However since there are a range of defect binding energies only those sites which have a binding energy above a given level can be occupied at any given temperature. Thus the measurements outlined above measure only the number of sites with binding energies for deuterium above a certain value. There will be many more sites with energies below this value which are not detected. Obviously it would be useful to repeat the measurements over a range of temperatures.

(v) Temperature effects

As discussed above temperature has an important effect on release rate both through the temperature dependence of diffusion rate and due to the range of binding energies of the deuterium atoms at different types of defect. Measurements of the number of atoms trapped in the surface have therefore been made both for an initially fully annealed sample and for a sample which had been damaged to saturation. The results are presented in fig 7.

In the case of the damaged sample, since the test implantation continued until the target saturated, these figures represent the maximum number of trapping sites which can be occupied at any particular temperature. The number of these sites increases as the temperature decreases down to the lowest temperature investigated of 293K. The concentration of damage sites is then 3.5×10^{16} cm^{-2}, or assuming a damage range equal to the ion range ($\sim$ 1000 Å) the concentration is 3.5×10^{21} cm^{-3}. This is of course extremely large and suggests that there may be many deuterium atoms trapped per defect site.

The result for the annealed sample does not necessarily represent atoms trapped at residual defects but, at least at high temperatures, may be

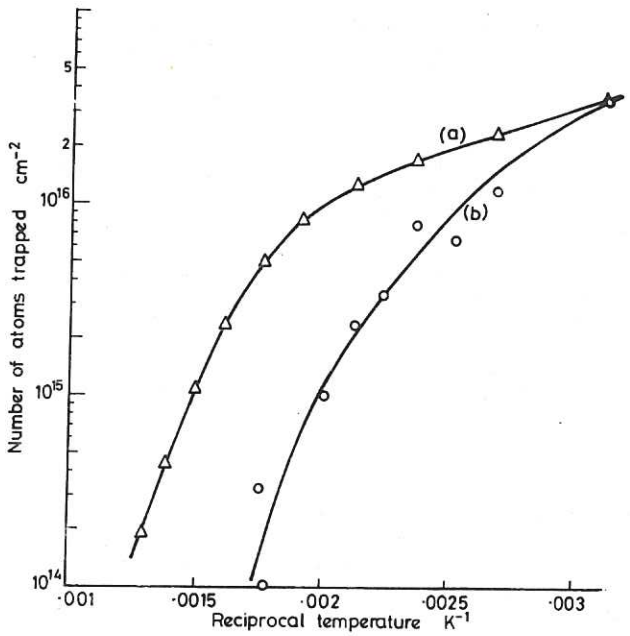

Fig 7 Number of atoms trapped in Mo during bombardment by 20 keV D^+ ions at various temperatures
(a) Mo initially damaged by 3×10^{17} ions cm^{-2}
(b) Target annealed at 1770K for 10 mins between runs

simply the number of atoms which are present in interstitial sites and have not diffused out within the time taken to make the measurement. However as temperature decreases the time to reach saturation increases as the diffusion coefficient decreases. Thus at lower temperatures there is a significant amount of damage introduced in the sample in the time required to make the measurement (the sample is annealed between measurements at different temperatures). At the lowest temperatures the number of atoms trapped was virtually identical to that in the damaged sample thus indicating that the target had been saturated and the number of atoms trapped was determined by the trapping sites only.

4. DISCUSSION

The results obtained considerably clarify the situation regarding release of hydrogen from metals during surface bombardment. It is now clear for example why the diffusion model discussed previously[2] does not fit the results in practice even qualitatively. In the case of an already damaged target incident ions may go into the lattice and stay there permanently without contributing to the diffusive flow and there will be a finite dose required to saturate the trapping sites before any diffusive flow will be observed. For a fully annealed target where the diffusion coefficient is high, diffusive release may occur in a time short compared with that required to produce a significant number of damage sites and in this case the release should follow the diffusion model. The agreement though not completely satisfactory is not unreasonable, fig 8. The diffusion coefficient obtained is a factor of 5 lower than that obtained in conventional thermal diffusion experiments[9] at 600K though a factor of 200 lower at 473K where trapping may be significant.

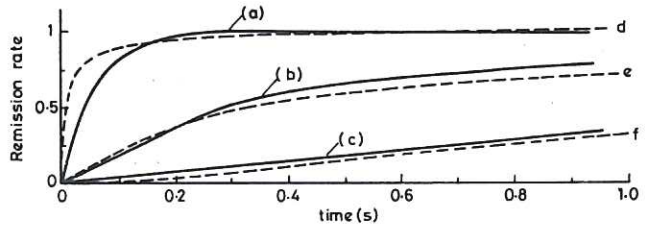

Fig 8 Deuterium re-emission rate from annealed Mo during bombardment by 20 keV D^+ ions.

——— experimental ------ calculated

(a) 600K	$D = 1 \times 10^{-8}$ cm^2 sec^{-1}
(b) 523K	$D = 2.8 \times 10^{-10}$ cm^2 sec^{-1}
(c) 473K	$D = 4.4 \times 10^{-11}$ cm^2 sec^{-1}

The presence of trapping sites has been deduced in direct measurements of thermal diffusion coefficients particularly in the case of iron[10,11,12] and also in the case of tungsten.[13] In the case of iron the effect is particularly important below 500K with activation energies varying between 2 and 16 kcal/mole in different samples. The trapping sites have been attributed to microcracks, pores and occluded impurities and have been shown to be strongly dependent on the mechanical and thermal history of the iron. In tungsten it was found that there could be two kinds of site, one interstitial and another of unknown nature. The concentration of interstitial hydrogen was $\sim 10^{-3}$ of the total hydrogen concentration. An analysis of diffusion in the two types of site was given which provided a qualitative explanation of the diffusion behaviour observed.

The filling of damage sites with hydrogen atoms and their subsequent thermal desorption appears to be a potentially powerful technique for detection of lattice defects in metals. Provided that the test hydrogen implant is small so that it produces little damage itself or else it is implanted at an energy below that required to cause a lattice displacement ($\sim$ 1000 eV for H^+ on Mo) then the sensitivity of the technique might be as high as 1 defect in 10^6 lattice atoms. A similar technique to examine defects has been suggested by Kornelsen[4] with helium ion implantation. The advantage of hydrogen over helium is that the hydrogen can be desorbed at a temperature well below that at which the damage anneals, whereas this is not the case for helium. On the other hand the disadvantage of hydrogen is that surface adsorption is a competing process for hydrogen trapping and may lead to large backgrounds if UHV techniques are not employed during implantation.

5. CONCLUSIONS

The diffusion of hydrogen in metals is critically dependent on the amount of damage in the lattice. The effective solubility of hydrogen is similarly affected. In molybdenum the effects are particularly of importance at temperatures below 750K.

Measurements have been made of the rate of defect production by incident ions of a type of trapping site with a binding energy above a certain critical value. This value is determined by the temperature at which the experiment is carried out and examination of a wide range of temperatures should be investigated in the future.

These experiments show that hydrogen implantation is a potentially valuable tool for measuring defect concentrations although the interpretation of the types of defect detected has not yet been made. The technique should be equally applicable to damage produced by radiation other than ions eg to electrons and neutrons.

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