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TRAPPING AND RE-EMISSION OF FAST DEUTERIUM IONS FROM NICKEL II

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ABSTRACT

Experiments on deuterium bombardment of nickel have been continued and measurements of gas release during and after bombardment have been compared. The results are consistent with the hypothesis that gas release from the solid is controlled by radiation damage sites produced by the incident ions slowing down in the metal. The population of these damage sites as a function of incident ion dose has been deduced.

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CONTENTS

1. INTRODUCTION

In a recent publication (Erents and McCracken 1969), referred to hereafter as I, experimental results were presented for the re-emission of deuterium from nickel at various temperatures during 18 keV deuterium ion bombardment. These results when compared with a simple diffusion model, indicated a much lower re-emission rate than expected from known diffusion coefficients. It was suggested that gas atoms are retained in radiation damage sites produced during bombardment and that these sites require a higher temperature for thermal release than for diffusion in an undamaged lattice. This hypothesis seemed to be confirmed by some preliminary thermal release spectra.

In the present paper we report further measurements on thermal release spectra from which the populations of gas atoms trapped in radiation damage sites have been deduced, and show that the results obtained of gas release during bombardment and isothermal release after bombardment are also consistent with the radiation damage model.

2. ION INJECTION AND RE-EMISSION

The techniques used for injection of deuterium ions into the thin-walled nickel tube target were described in I. This work showed that for all target temperatures between 243 - 373^{o}K the re-emission as a function of time during bombardment follows a similar pattern of a high trapping probability initially, followed by an increasing release rate which approaches 100% of the incident beam.

In most of the present experimental work bombardment has been carried out at 77^{o}K prior to thermal re-emission. The re-emission rate was recorded during bombardment, and the results in figure 1 show some interesting features. A quasi-saturation is reached at ≃ 15% re-emission after only a low dose ($<10^{17}$ ions cm^{-2}). This level continues up to a dose of $\sim 7 \times 10^{17}$ ions cm^{-2}, when the re-emission rate increases rapidly with increasing dose towards 90% re-emission after 5×10^{18} ions cm^{-2}.

Calculations using the thermal conductivity of nickel show that the front surface of the target cannot rise to more than $85^{O}K$ so that thermal diffusion will be negligible. Moreover release by erosion of the target into the initial ion range distribution cannot occur, since reported sputtering yields are too low. Thus the re-emission must be due to the process generally known as 'gas sputtering' cf. (Carter and Colligon 1968), whereby sufficient energy is transferred from the incident ions to the trapped atoms, to cause these trapped atoms to be released.

3. THERMALLY ACTIVATED GAS RELEASE SPECTRA

As described in I, after bombardment with a known incident dose of deuterium ions, the nickel tube was heated at a rate of $1.6^{O}k\ s^{-1}$ from $77^{O}K$ to $900^{O}K$ and the deuterium re-emission rate recorded as a function of temperature. After high incident doses the gas release spectra were observed to contain at least five peaks. A study of release spectra following incident doses ranging from 2×10^{16} ions cm^{-2} to 4.5×10^{18} ions cm^{-2} indicated that the positions of the peaks on the temperature scale did not shift appreciably with dose, and furthermore each of the five peaks could be clearly resolved, provided that the correct dose was chosen (figure 2). Peaks are resolveable at the following temperatures - $383^{O}K$, $335^{O}K$, $303^{O}K$, $263^{O}K$ and $220^{O}K$. They appear, and increase in magnitude, in this order with increasing dose.

It was suggested in I that the peak at $220^{\circ}K$ may be correlated with an interstitial diffusion process since release at this temperature is consistent with that expected for thermal diffusion of deuterium in an undamaged nickel lattice. It seems unlikely that there would be any transport mechanism which would be activated at a lower temperature. If the $220^{\circ}K$ peak does correspond to interstitial diffusion then the release at higher temperatures must essentially be single step, i.e. a single jump from a damage site into an interstitial position followed by rapid diffusion to the surface. In calculating the gas release spectra we therefore make the assumption that gas release at $220^{\circ}K$ is determined by diffusion and that at the higher temperatures gas release is a single step desorption process. The possibility that the $220^{\circ}K$ peak might also be the result of a single step process cannot, however, be over-ruled.

3.1 Theoretical Considerations

Theoretical thermal release spectra have been calculated by two methods. In the first an analogue technique was used, while in the second a direct calculation was made of the sum of a number of theoretical spectra. The two methods are now considered.

(a) Analogue The electrical analogue for the isothermal release of gas from sites of a single activation energy Q, is simply the discharge of a capacitor C through a fixed resistor R', the system having a time constant $\tau = CR' = \tau_0 \exp(Q/RT)$ where R is the gas constant and $1/\tau_0$ is the frequency factor.

To obtain gas release spectra the target is heated at a rate $b^{\circ}K$ per second. The 'time constant' τ now varies with time

$$\tau = \tau_0 \exp\left(Q/(R\,[T_0 + bt])\right) \qquad \ldots (1)$$

where T_o is the initial target temperature.
If therefore we maintain C fixed and vary R′ exponentially with reciprocal time we obtain from a discharging capacitor a direct output which represents the variation in gas release rate with time. By connecting a number of circuits with different parameters in parallel and summing the currents from each, the thermal release spectra of gas from a number of sites can be simulated. Good fitting to experimental curves was obtained for up to four peaks. A more detailed description of the analogue technique is to be published.

(b) Digital The drawbacks in the analogue method are the difficulty in simulating diffusive release and the complexity of dealing with more than three or four peaks. The problem can also be solved by taking the analytical form of the release rate and summing it for different activation energies Q and initial populations N_o. This was done using a simple digital computer program on an interactive basis. The theoretical spectra can be quite quickly fitted to the experimental ones and hence values of Q, N_o and τ_o obtained.

Considering first the single step release, the integral equation for N(t) is

$$N = N_o \exp\left\{-\frac{1}{\tau_o}\int_0^t \exp\left(-\frac{Q}{RT}\right) dt\right\} \qquad \ldots (2)$$

where the target temperature $T = (T_o + bT)$. Using the approximate solution for the integral given by Grant and Carter (1965) we obtain an expression for the release rate

$$\frac{dn}{dt} = \rho_{si} = \frac{N_{oi}}{\tau_o} \exp\left\{-\frac{RT^2}{\tau_o Q_i b} \exp\left(-\frac{Q_i}{RT}\right) - \frac{Q_i}{RT}\right\} \qquad \ldots (3)$$

The case for diffusive release during a linear increase in target temperature with time has been solved by Farrell and Carter (1967); the release rate is given by

$$\rho_d = \frac{A}{T^3} \exp \left\{ \frac{Q_d}{2RT} - P^2 \frac{bQ_d\tau_o}{2RT^2} \exp \left(\frac{Q_d}{RT} \right) \right\} \qquad \ldots (4)$$

where $$A = \frac{N_d Pb \ Q_d}{2R} \cdot \left(\frac{\pi R}{2\tau_o bQ_d} \right)^{-\frac{1}{2}}$$

and N_d is the initial number of trapped atoms in sites of activation energy Q_d located a distance P lattice planes from the surface.

To obtain a complete gas release spectrum for a system with diffusive and single step re-emission we simply sum the ρ_{si} and ρ_d from equations (3) and (4) for the various Q_i and Q_d. By inserting the known factors b and P and adjusting the population densities N_{oi}, N_d, the activation energies Q_i and τ_o, the theoretical spectra can be fitted to those obtained experimentally.

In practice approximate values of the peak temperatures were estimated from examination of all the curves. Then a value of τ_o was obtained by fitting one spectrum, enabling values of Q_i and Q_d to be deduced which could then be adjusted slightly to get peak positions correct. Finally with Q_i and τ_o fixed the N_{oi} were adjusted to fit each of the fifteen spectra individually. Typical examples of the fits obtained are shown in figure 3 and the values of the activation energies were $Q_d = 8.9$ k cal mole^{-1}, and $Q_i = 5.7 \pm 0.3$, 6.8 ± 0.3, 7.2 ± 0.3, and 8.6 ± 0.3 k cal mole^{-1}. A value of $\tau_o = 10^{-4}$ s was required to fit all the single step data.

A number of the release spectra showed evidence of sites with even higher activation energies, but the population of these sites was too small to make analysis reliable.

4. EFFECT OF ION DOSE ON SITE POPULATION

The parameters N_{oi} and N_d used to fit the experimental thermal release curves give directly the population density in each of the five trapping sites. The results are presented in figure 4 as a function of dose.

The general trend, noted previously, of a build-up to saturation of the highest temperature peaks first is clearly seen. The 383°K peak increases immediately while the 335°K peak does not increase until after a dose of $\sim 3 \times 10^{15}$ ions cm^{-2}. The 303°K peak appears after a dose of 1.0×10^{17} ions cm^{-2} and the lower temperature peaks appear at about 5×10^{17} ions cm^{-2}. The sharp break point at 6.6×10^{17} ions cm^{-2} in the curve in figure 1 corresponds to the saturation in the 303°K peak and the rise in the 263 and 220°K peaks after this dose.

An interesting result is obtained from figure 4 when a calculation of the saturation number of trapped atoms in each site is made. Both sites associated with the high temperature release (383°K and 335°K) saturate with a similar number, $\sim 1 \times 10^{17}$ ions cm^{-2}. The next two types of site, corresponding to peaks at 303°K and 263°K in the release spectra, saturate again with an equal number, but with about five times as many trapped atoms as the first sites, $\sim 5.0 \times 10^{17}$ ions cm^{-2}. The trapping centres associated with the 220°K peak are approaching saturation after the maximum incident dose used, with about 7.0×10^{17} ions cm^{-2} trapped.

These figures would be more meaningful if considered in terms of atomic densities. These may be deduced from range distribution data, and it may be assumed that damage and range distributions are similar (Sanders and Sigmund 1967). No direct measurements of range distributions for deuterium ions in nickel have been made, but theoretical calculations of light ion range distributions (Schiott 1967) are in quite good agreement with experimental results for deuterium ions in aluminium and gold (Freeman and Latimer 1967) and so these have been used to estimate the range distributions in nickel. From this the total number of lattice atoms within the range of the incident ions has been estimated as 1.4×10^{18} atoms cm^{-2}. This figure will probably increase due to range broadening at high dose, but neglecting this it is estimated that the sites corresponding to the $383^{\circ}K$ and $335^{\circ}K$ peaks each saturate at a deuterium concentration of ~ 7 atomic %. The three lowest temperature peaks saturate at trapped gas concentrations of approximately 37, 37 and 50 atomic %. At the maximum possible concentration therefore the total number of trapped atoms is 1.4 times that of the nickel atoms which surround them. The different activation energies observed may therefore be a result of atoms clustering as well as being due to location in various types of radiation damage site.

The fact that in the thermal release spectra sites with lower and lower activation energies appear as the incident dose is increased could be explained either by (a) the fact that these new sites are being produced by the increasing radiation damage, or (b) that the radiation damage is saturated at much lower doses and it is simply the increased gas concentration which causes the atoms to occupy the lower sites, or to change the activation energy by the interaction of close neighbours.

The total number of deuterium ions trapped during bombardment may be obtained by integration from the results in figure 1. These can then be compared directly with the number released during thermal re-emission, both by direct integration of the thermal release spectra, and as a cross-check, with the sum of the populations for the five different sites shown in figure 4. The results are shown in figure 5, and there is seen to be good agreement between the estimates of the number trapped from the two experiments, indicating that all atoms trapped are released by the subsequent thermal desorption.

5. PRE-BOMBARDMENT EXPERIMENTS

In order to test whether lattice damage by another ion could affect the deuterium desorption spectra, a series of experiments were carried out in which the nickel target was pre-bombarded with 18 keV H_2^+ ions prior to deuterium bombardment and subsequent deuterium thermal release. A typical result is shown in figure 6. The thermal release spectra have higher populations in the sites of lower activation energy than occur without the pre-bombardment but no new types of site are created. In general the results are similar to that obtained if a deuterium dose equal to the sum of the hydrogen plus deuterium dose had been given.

6. RE-EMISSION DURING BOMBARDMENT AT HIGH TEMPERATURE

Curves for the re-emission rate of deuterium atoms during ion bombardment of higher temperature targets were presented in I. However these results were analysed on the basis of diffusion theory. In view of the gas release spectra and the model of damage sites proposed it is probable that re-emission is also controlled by a single step rather than a diffusion process. If one step theory is applicable then for any one site

$$\ell n\ (1 - J/J_0) = -t/\tau$$

where J is the release rate and J_0 is the incident ion flux. Although the system is complicated by a number of sites, in fact reasonable values of τ were obtained from plots of $\ell n(1 - J/J_0)$ against t. The activation energy was deduced by plotting $\ell n\ \tau$ against $1/T$ as shown in figure 7. This gives only an approximate method of estimating Q but the value obtained of 7.2 ± 1.0 k cal mole^{-1} and the value $\tau_0 \sim 10^{-4}$ s are seen to be in good agreement with the values obtained from the thermal release measurements.

7. ISOTHERMAL RELEASE AFTER BOMBARDMENT

Further evidence about the release mechanism can be obtained from isothermal gas release after bombardment. For single step release from sites of unique activation energy an exponential decay in gas release rate with time is expected. Figure 8 shows the experimental results obtained after bombardment and gas release at a constant temperature of 323°K. After separation of the components three distinct linear regions are visible, from which time constants of 2 s, 9 s and 64 s have been deduced. Assuming the value of $\tau_0 = 10^{-4}$ s from the previous results, the corresponding activation energies for isothermal release have been calculated to be 6.4, 7.3 and 8.6 k cal mole^{-1} respectively - in good agreement with the three highest activation energies of 6.8, 7.2 and 8.6 k cal mole^{-1} calculated from the thermal desorption spectra. Re-emission corresponding to the peaks at 263°K and 220°K is probably too fast to be observed at 323°K.

Isothermal release has also been observed at other target temperatures. Measurements made at $273^{\circ}K$ are also shown in figure 8. Here only two time constants are discernable corresponding to activation energies of 5.9 and 7.0 k cal mole^{-1} for $\tau_0 = 10^{-4}$ s, in reasonable agreement with the activation energies of 5.7 and 6.8 k cal mole^{-1} obtained from the thermal desorption spectra.

Isothermal release has also been studied by Martin and Lewin (1966) after hydrogen and helium bombardment of stainless steel at low energies. They attempted to interpret the release in terms of diffusion but the results were not in good agreement with the predictions of the diffusion model. Although it is unlikely that in their experiment the incident ions would have had sufficient energy to create major lattice damage, it is possible that damage was created over a long period of time, possibly by heavy ion impurities, and this could produce enough sites for efficient trapping of hydrogen or helium. Attempts have been made to replot their results on the single step desorption model but without any information on τ_0 no definite conclusions could be drawn.

8. CONCLUSIONS

Evidence for the existence of trapping sites, caused by radiation damage and with well-defined activation energies, has been observed in three separate types of equipment; re-emission during bombardment, isothermal release after bombardment and analysis of thermal release spectra after bombardment. The thermal release spectra following bombardment at $77^{\circ}K$ indicate at least four types of damage site with activation energies of 5.7, 6.8, 7.2 and 8.6 k cal mole^{-1}. The results are all summarised in Table I and there is seen to be quite good agreement between these experiments.

TABLE I

	τ_0	Q_1	Q_2	Q_3	Q_4
Thermal Release Spectra	10^{-4}	5.7 ± 0.3	6.8 ± 0.3	7.2 ± 0.3	8.6 ± 0.3
Isothermal Release	(10^{-4})	5.9 ± 0.2	7.0 ± 0.01 6.4 ± 0.15	7.3 ± 0.6	8.6 ± 0.2
Bombardment Induced Release	$10^{(-3.7 \pm 0.8)}$			7.2 ± 1.0	

The values of τ_0 obtained both from the thermal release spectra and from bombardment induced release are of the order of 10^{-4} s. This is of the same order as that obtained by Cavaleru, Comsa and Iosifescu (1968) by analysis of release data for other systems. The alternative interpretation, that the width of the release spectra is due to a large number of unresolved peaks, does not explain the individual components of the isothermal release curves.

The observation of a number of discrete activation energies and release temperatures much higher than expected on the basis of simple diffusion, supports the hypothesis that the damage sites act as trapping centres for the diffusing deuterium atoms. As the incident ion dose increases, first one occupied damage site appears and saturates, followed by the others in turn. This suggests the possibility that the production of some types of occupied damage site depend on the presence of others.

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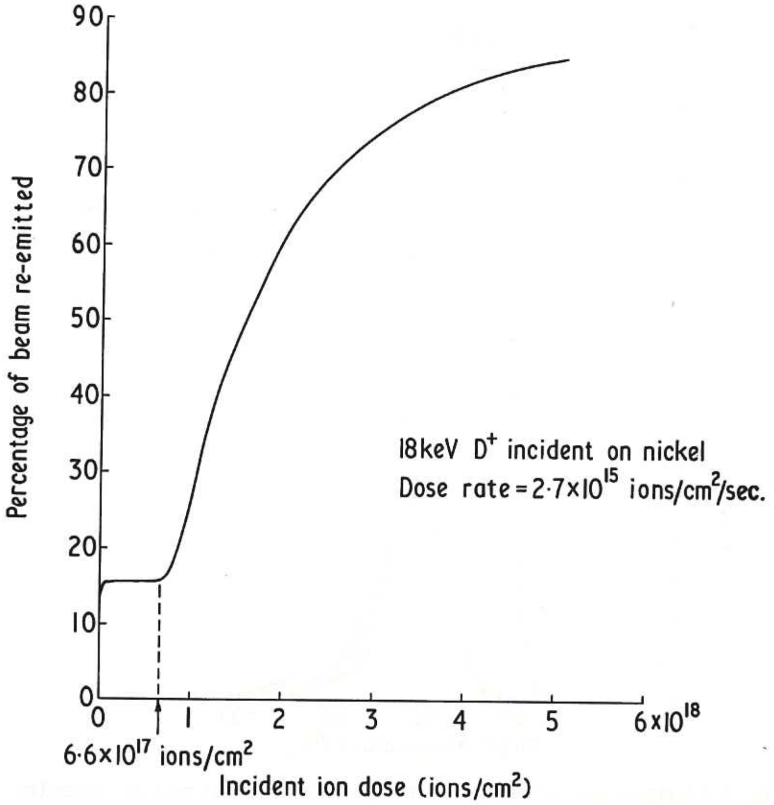

Fig. 1 Percentage of beam re-emitted from nickel at −196°C as a function of total ion dose.

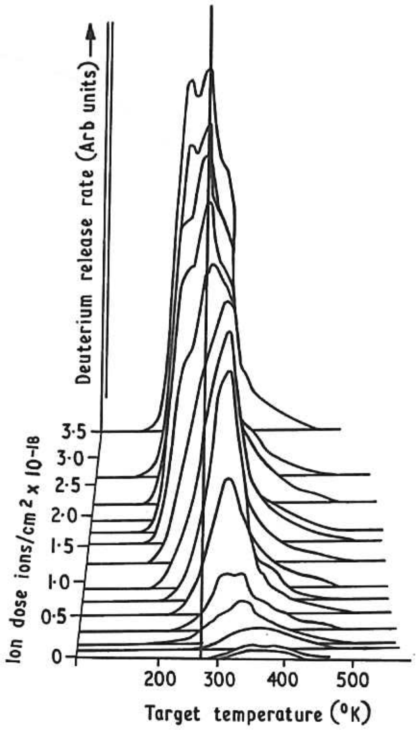

Fig. 2 Deuterium gas release spectra following bombardment of nickel at 77°K.

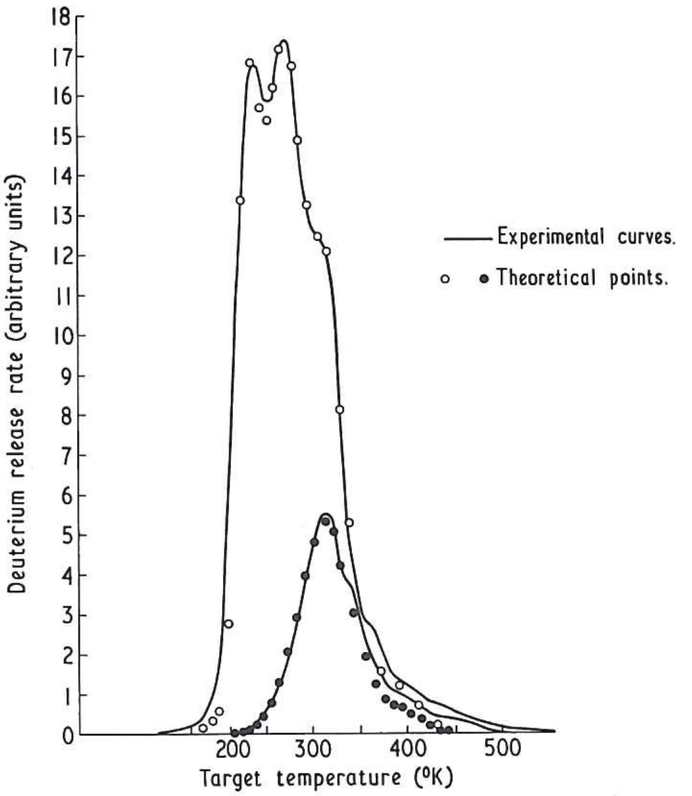

Fig. 3 Comparison of experimental and theoretical release spectra

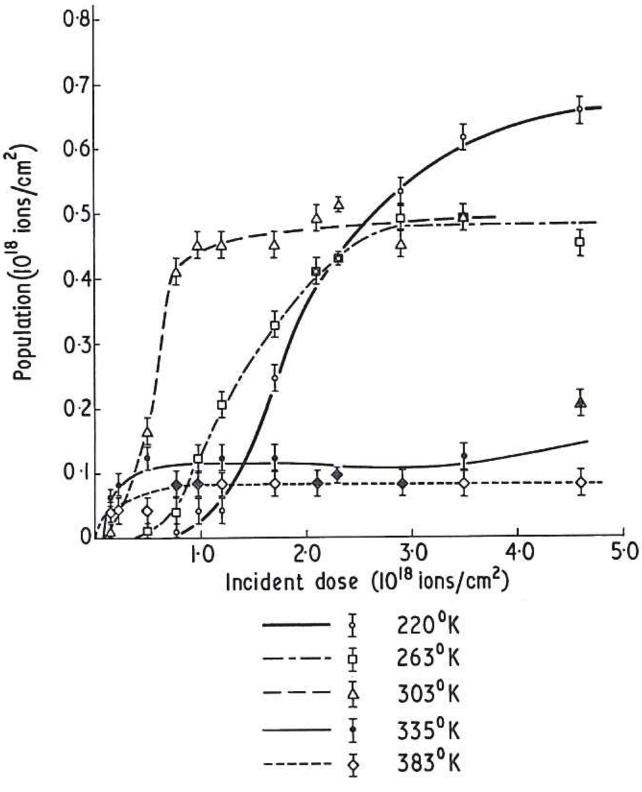

Fig. 4 Population distribution of individual sites as a function of incident ion dose.

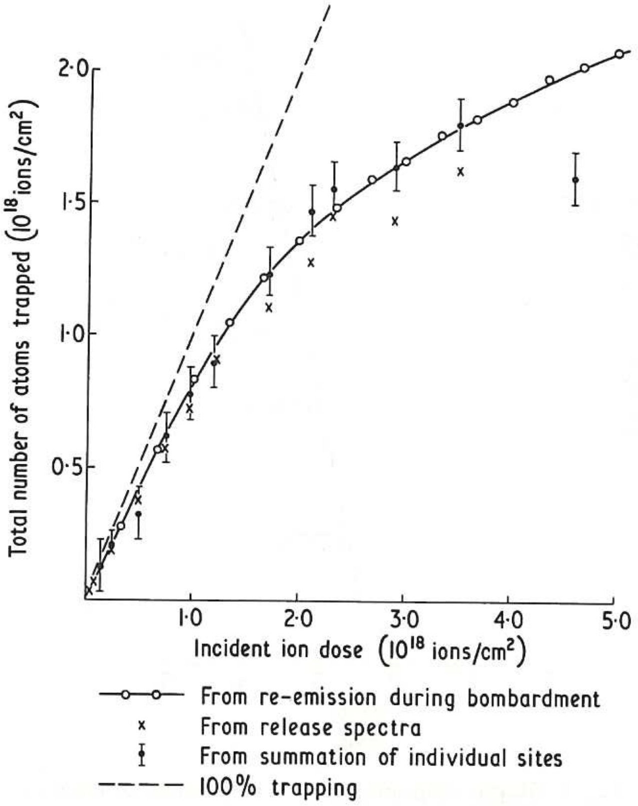

Fig. 5 Comparison of results for deuterium trapped from re-emission during bombardment, and from thermal release spectra.

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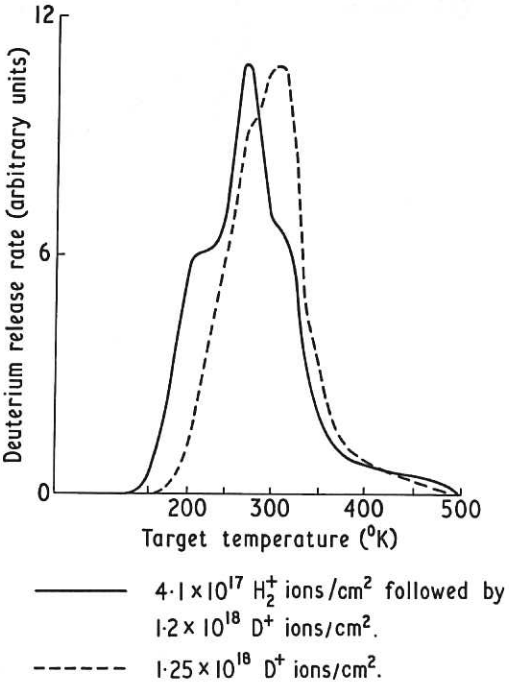

Fig. 6 Effect of prior proton bombardment on the deuterium gas release spectra.

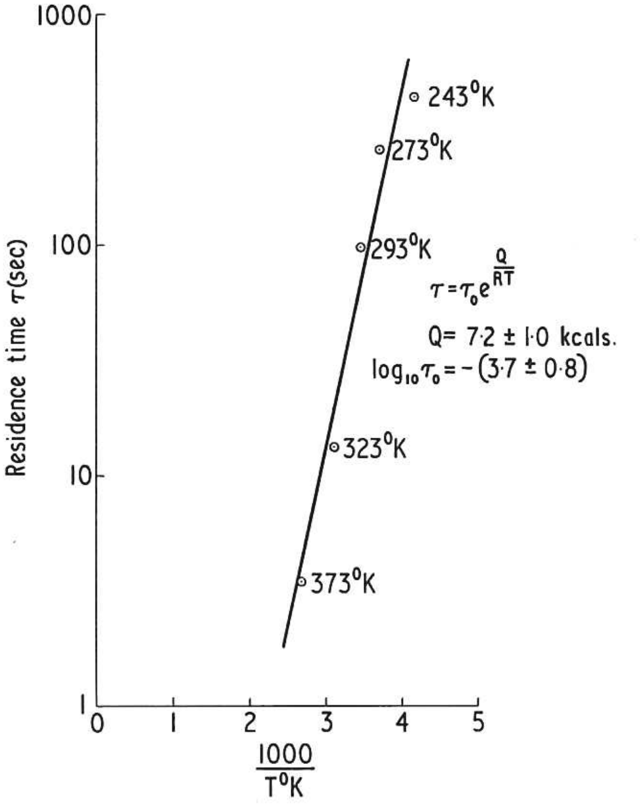

Fig. 7 Single step analysis for deuterium re-emission from nickel, during bombardment.

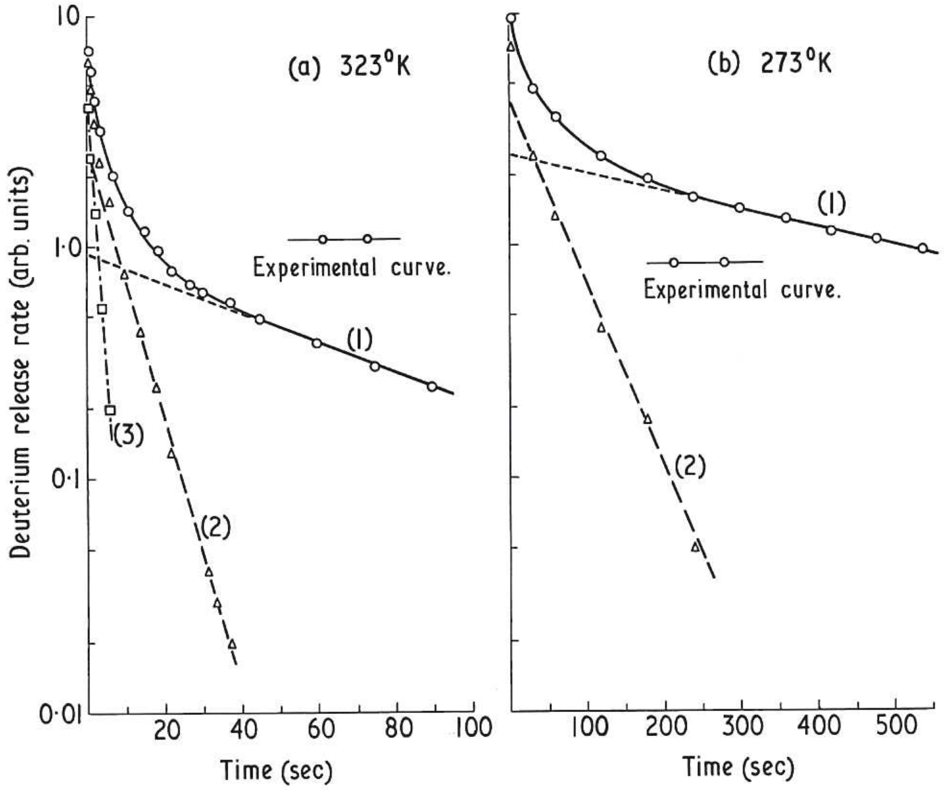

Fig. 8 Isothermal re-emission of deuterium from nickel.