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THERMAL DESORPTION SPECTROSCOPY (TDS) OF HYDROGEN FROM NIOBIUM*

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INTRODUCTION

Thermal desorption spectroscopy is often used to determine the activation energy of desorption of an adsorbate on a substrate as well as the order of the kinetics. In the case of flash desorption of an adsorbate from a surface obeying second order kinetics, a plot of $\text{Log}(\theta_0 T_p^2)$ vs. $1/T_p$ (where θ_0 is the initial surface coverage and T_p is the temperature of the maximum desorption rate, i.e., the "desorption temperature") will yield a straight line, the slope of which is determined by the chemisorption energy. However, Davenport et al.¹ argued on the basis of a simple theoretical model that in the case of a system with hydrogen absorbed into the bulk in quasiequilibrium with adsorption sites on the surface, a similar plot, where the coverage θ_0 must now be replaced by the initial concentration x_0 , will yield a slope determined by the heat of solution. In the following experiments we have tried to verify the functional dependence of the desorption temperature on hydrogen loading as outlined above. Deviations from these theoretical predictions were observed, and numerical kinetic simulations were made to aid in understanding them.

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EXPERIMENTAL METHOD

Samples consisted of thin foils (50 μm , MARZ grade) of niobium, 5 mm wide by 20 mm long. They were spot welded onto 2 mm diameter tungsten rods as supports in an ultrahigh vacuum system with a base pressure in the low 10^{-10} Torr range. The samples were cleaned by resistive heating to over 2300 K in the ultrahigh vacuum after baking them in 10^{-6} Torr oxygen at 2000 K. This treatment removes the interstitial impurities.² The frequent heating and cooling of the sample caused recrystallization and grain growth. Using an attached low-energy electron diffraction apparatus we observed that the grains were all aligned with their (110) planes parallel to the surface. The experimental results can therefore be taken as characteristic of the (110) plane of Nb. For the desorption experiments the samples were heated by a dc current which was programmed to vary in such a way as to provide a linear time dependence of the sample temperature for heating rates up to $\sim 200^\circ/\text{sec}$. The hydrogen desorption was monitored using the output of a UTI mass analyzer 100C tuned to the H_2 peak.

The sample was allowed to accumulate hydrogen at pressures which varied from 5×10^{-10} Torr to 1×10^{-4} Torr for periods of time usually shorter than 2 minutes. The pressure drop during absorption and the area under the resulting desorption peaks correlated well and, knowing the volume of the vacuum system, could be used to estimate the absolute amount of hydrogen absorbed or adsorbed by the sample.

EXPERIMENTAL RESULTS

The data obtained in this manner are shown in Figure 1. The data are plotted so that, according to the discussion of Davenport et al.¹, they should fall on a straight line with a slope equal to $2E_s/k_B$ where E_s is the heat of solution per hydrogen atom. There are two features of the desorption data which are in disagreement with the predicted behavior. First, the slope is such that if it is given by $2E_s/k_B$ then the value of E_s is found to be 12.8 rather than the accepted value³ of 8.6 Kcal/mole of hydrogen atoms. Second, it may be seen (especially from the 200 K s^{-1} data) that at high hydrogen loadings the desorption-peak temperature T_p , falls with increasing loading to a minimum value and then rises again. As we shall see below, the occurrence of such a minimum is a feature of the kinetic model upon which Davenport et al. based their discussion although the analytic approximations they used caused them to overlook its existence.

Fig. 1. The variation of the temperature of the maximum hydrogen desorption rate, T_p , with the amount of hydrogen loading for a (110) niobium surface for two rates of heating. The amount of hydrogen loading is characterized by the integrated desorption rate, A . The numbers indicate the approximate loading in monolayers of hydrogen atoms.

DISCUSSION

To help understand the origins of the discrepancies mentioned above we numerically solved the kinetic equations of the model used by Davenport et al.¹ (albeit with various approximations): bulk hydrogen sites "communicate" with a set of surface sites which "communicate" with the vacuum (the single-site model). We also numerically calculated the properties of models with two types of surface sites (two-site models). The kinetic equations of the single-site model for desorption into the vacuum are:

$$d\theta/dt = -K\theta^2 - \nu\theta(1-x) + \beta x(1-\theta) \quad (1)$$

$$N_2 dx/dt = \nu\theta(1-x) - \beta x(1-\theta) \quad (2)$$

where x and θ are bulk and surface concentrations and K , β , and ν are temperature-dependent rate constants, N_L is the number of layers of sites in the bulk. Using rate constants consistent with experimental data on hydrogen uptake kinetics⁴ and heat of solution³ E_s , the numerical calculations yield the results in Figure 2, which are qualitatively like the experimental data. The slope of the linear region is $\approx 2E_s/k_B$ in agreement with the results of Davenport et al.¹, and quasiequilibrium between bulk and surface sites was found to occur over the entire range of loading as they had assumed. The calculated minimum desorption peak temperature, ≈ 570 K, is less than the experimental value, ≈ 680 K, but agreement is achieved by reducing the pre-experimental factor of the rate constant K from $1 \times 10^{14} \text{ s}^{-1}$ to $5 \times 10^{12} \text{ s}^{-1}$. (Such a minimum was not predicted by Davenport et al. because of their assumptions that $\beta x \ll 1$.) It was not possible to choose parameters consistent with the experimental uptake kinetics and the heat of the solution which would yield quantitative agreement between the value of the slope calculated with the single-site model and the experimental value. Numerical simulations based on two different two-site models also failed to match the experimental value. The origin of the discrepancy remains unknown.

Fig. 2. The dependence of the temperature of the maximum hydrogen desorption rate, T_p , upon hydrogen loading (characterized by the integrated hydrogen desorption rate, A) as calculated with the single-site model. The numbers indicate the approximate loading, in monolayers of hydrogen atoms.

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