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VACANCY MIGRATION ENTHALPY IN TUNGSTEN AT HIGH TEMPERATURES*

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ABSTRACT

The curvature found in the Arrhenius plot for tungsten self-diffusion has been commonly interpreted in terms of simultaneous diffusion by two different defect processes. An alternative interpretation has been in terms of the temperature dependence of the migration enthalpy and/or the formation enthalpy for single vacancies. In order to study the magnitude of the temperature dependence for the migration enthalpy, the present interrupted quenching experiments studied the annealing of a supersaturation of vacancies at high temperatures in tungsten. The temperature dependence of H_{1v}^{m} found in the present experiments is insufficient to explain the Arrhenius curvature found for self-diffusion in tungsten. However, the curvature could be explained if the formation enthalpy, H_{1v}^{f} had a temperature dependence of similar magnitude.

I. INTRODUCTION

When accurate measurements of tracer self-diffusion coefficients, D_T, of metals are made over a wide enough range of temperature the data usually deviate from straight Arrhenius plots. The curvature of the Arrhenius plots has been commonly interpreted in terms of two mechanisms of diffusion [1,2]. The considerable evidence for diffusion by single vacancies being responsible for the low temperature mechanism has been extensively reviewed [1-4]. In fcc metals the deviation of the high temperature data from a straight extrapolation of a fit to the low temperature data has been attributed to divacancies [1-4]. However in bcc metals where the Arrhenius curvature is more readily observed [4-7] the identification of the high temperature mechanism has proven difficult [7,8].

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An alternative explanation for the curvature in the Arrhenius plots has been the suggestion by Gilder and Lazarus [9] that the entire curvature is due to a temperature dependence of the activation energy for a single diffusion mechanism. While this explanation has not found wide acceptance [2-4] the statistical fit of all tracer self-diffusion data is equally good to the model of Gilder and Lazarus as to the two mechanism model. In order to understand what defects are responsible for the Arrhenius curvature in self-diffusion it would help to have experimental defect studies made over a similar wide range of temperatures. Unfortunately the temperature ranges of defect studies have been severely limited. Equilibrium defect experiments, differential dilatometry and PAS, have been limited to temperatures $\gtrsim 0.8\ T_m$. Quenched-in resistivity studies examine lower temperatures $\sim 2/3\ T_m$ but are limited at higher temperatures because of defect loss during quenching. Annealing studies with both PAS and resistivity commonly follow the annealing of defects produced by quenching or electron irradiation [10]. Annealing of such defects occurs at Stage III temperatures which are far below the temperatures used in diffusion experiments. What is clearly desirable are experiments which examine defect properties over a range of temperatures similar to that used when observing the Arrhenius curvature found for diffusion data. We report here one such experiment on tungsten using interrupted quenching techniques.

II. EXPERIMENTAL PROCEDURE

The experimental procedure has been outlined more fully elsewhere [11] and only a short description will be given here. The tungsten wire samples (54 μm diam., RRR ~1350 kindly supplied by Professor H. Schultz, MPI, West Germany) were subjected to the following temperature vs time profile: The sample was first equilibrated at a temperature $T_{eq} = 2900$ K, then radiation quenched to an annealing temperature T_a, which was maintained for a time t_a, after which the sample was radiation quenched to room temperature. The quenched-in resistivity was subsequently measured at 4 K. By varying t_a alone the relaxation time τ for the excess vacancy concentration could be determined and by further varying T_a the temperature dependence of τ could be determined and an apparent migration enthalpy calculated.

In order to benefit from previous carefully established techniques, the present set-up copied, as closely as possible, conditions established by (8, 12, 13). The temperatures T_{eq} and T_a were determined according to the resistivity scale for tungsten [13]. Direct quenching ($t_a = 0$) was used to confirm that the present procedure closely duplicated that of earlier work [8,12] and the slope of the quenched-in resistivity in an Arrhenius plot yielded a vacancy formation enthalpy of 3.6±0.2 eV. In addition, direct quenching was also used at regular intervals in the experiment to verify that the sample had neither been contaminated nor had its dislocation substructure been changed.

III. EXPERIMENTAL RESULTS

In the present work two samples were measured. The characteristic decay times $\tau_{1/2}$ (the time for the excess vacancy concentration to decay to

TABLE I. Characteristic decay time, $\tau_{1/2}$ for the quenched-in resistivity of tungsten for 2900K obtained from the interrupted quench data at the tabulated anneal temperatures.

Anneal temperature T_A(K)	$\tau_{1/2}$ (ms)	
	Sample 1	Sample 2
2600	--	82.35
2300	249.5	273.8
2100	613.3	--
1900	1839.	1934.
1550	20187.	--

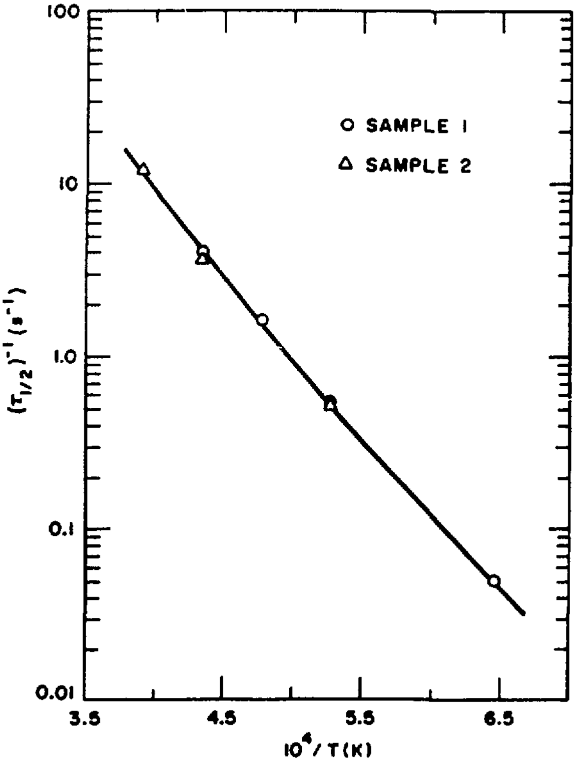

Fig. 1. Arrhenius plot of the inverse of the characteristic decay time, $(\tau_{1/2})^{-1}$, as a function of inverse temperature.

half its original value) are given in table 1. In figure 1 an Arrhenius plot of $(\tau_{1/2})^{-1}$ is shown. A least-squares analysis of the data gave the result: $H^m(T) = H_{2200} + k_B\ (T-T_{2200})$, where $H_{2200} = 1.89\pm0.03$ eV, $\alpha = 3.8 \pm 1$, or H^m (2600K) = 2.02±0.05 eV and H^m (1550K) = 1.68±0.06 eV.

IV. DISCUSSION

The present work has resulted in an apparent migration enthalpy. We shall now consider the question as to whether this result applies to monovacancies or divacancies or possibly a mixture of these defects.

The ratio of vacancies, migrating to the sinks as divacancies, to those migrating as monovacancies can be estimated as [11]

$$R \approx \frac{\nu_{2v}(T_a)\ C_{2v}(T_a)}{\nu_{1v}(T_a)\ C_{1v}(T_a)} \left[\frac{C_{1v}(T_{eq})}{C_{1v}(T_a)} + 3\right] \qquad (1)$$

where $\nu_{iv}(T_a)$ $(i = 1,2)$ are the jump rates and $C_{iv}(T)$ are the equilibrium concentrations for the vacancies, respectively. If it is assumed that the self-diffusion data [7]:

$$D^{SD} = D_{01}\ \exp(-Q_1/k_BT) + D_{02}\ \exp(-\ Q_2/k_BT) \qquad (2)$$

for tungsten can be interpreted as a monovacancy mechanism at low temperatures (Q_1, D_{01}) and a mono/divacancy mechanism at high temperatures, where Q_2 and D_{02} accounts for the divacancy contribution, then one obtains:

$$R \approx \frac{f_1 D_{02}\ \exp(-\ Q_2/k_BT)}{f_2 D_{01}\ \exp(-\ Q_1/k_BT)} \left[\frac{C_{1v}(T_{eq})}{C_{1v}(T_a)} + 3\right] \qquad (3)$$

where f_1 and f_2 are the correlation factors. From equation 3 we find that the divacancy flux is dominant for all temperatures T_a used in the present experiment. [R ~ 28 at 2600K and increases to 10^4 at 1550K.] Thus if it is assumed that the high temperature mechanism is due to mass transport by divacancies, then the migration enthalpy determined in the present experiment is that of a divacancy. However, this result would imply (assuming for a bcc that $Q_2 \approx 2\ H^f_{1v} + H^m_{2v} - H_b$) a value of $H_b \geq 2$ eV, which is substantially larger than the experimental result of Park et al. [8] of $H_b \approx 0.7 - 1.0$ eV. Similarly, theoretical calculations by Johnson [14] suggests a binding energy of a divacancy in the second nearest neighbor configuration to be 0.78 eV. We may, therefore, conclude that the high temperature transport mechanism is unlikely to be due to divacancies. The same conclusion was also reached, but for different reasons, by Park et al. [8].

If one adopts the binding energy found by Park et al. [8] in the interpretation of the present data, then the divacancy concentration becomes low, and we therefore suggest that the present experiment has lead to the determination of the monovacancy migration enthalpy. The present result of H^m_{1v} = 1.68±0.06 eV at 1550K agrees with that of Rasch et al. [12] of 1.70±0.1 eV (when corrected according to the temperature scale of Mundy [13]) obtained by the change of slope method at ≈ 900K. Rasch et al. [12] calculated that for their directly quenched samples the average number of vacancy jumps for recovery was about $2x10^6$, and using the same expression we obtain about 10^8 for the present samples. If it is assumed that the sinks in the present samples were dislocations only, then the density would be 10^7 dislocations cm^{-2}. It would thus appear that quenching to an intermediate temperature in vacuum introduces less stress in the sample and keeps the sink density low.

The present experiments have determined that the migration enthalpy of defects in tungsten increase in value from 1.68±0.06 eV at 1550K to 2.02±0.05 eV at 2600K. This temperature dependence is the result of the variation with temperature of the migration enthalpy of a single diffusion process. The temperature dependence of H^m_{1v} expressed in terms of α gives $\alpha \sim 3.8$ and is considerably greater than earlier estimates of $\alpha \sim 0.2$ [1,15-17]. In itself this temperature dependence is insufficient to explain the change in the activation enthalpy determined from the self-diffusion data. Over the temperature range of 1550 to 2600K the migration enthalpy change ΔH^m_{1v} = 0.34 eV whereas the change in activation enthalpy for self-diffusion ΔQ = 0.9 eV. If the temperature dependence of H^f_{1v} was of similar magnitude to that for H^m_{1v} then the curvature of the Arrhenius plot for tracer self-diffusion in tungsten could be simply explained by the temperature dependence of the activation enthalpy for diffusion by single vacancies.

Experimental evidence for a temperature dependence of H^f_{1v} is difficult to obtain for two reasons. First, as mentioned already, the experiments determining H^f_{1v} are limited to rather narrow temperature ranges, and secondly their uncertainties (0.2-0.4 eV) will be similar to or larger than the expected effects. Extension of the temperature range could, for example, be achieved by comparing PAS results to those from quenched in resistivity. However, such a comparison not only is a comparison among values for H^f_{1v} obtained at ≈ 3100K for PAS [18] and values centered at ≈ 2800K for the quenched experiment [12] but also a comparison between a thermal equilibrium experiment with a nonequilibrium experiment. Thus at present a temperature dependence of H^f_{1v} similar to that of H^m_{1v} cannot be ruled out. There has been some theoretical work[19] on the subject of the temperature dependence of H^f_{1v} and H^m_{1v} for the alkali metals. Both H^f_{1v} and H^m_{1v} were found to be temperature dependent and the sum of the H^f_{1v} and H^m_{1v} matched rather closely the change of activation enthalpy for self-diffusion found in experimental measurements [5,6,20].

While a comparison of the diffusion properties of alkali metals to those of a refractory bcc metal may appear a large leap, it should be remembered that there are more similarities than simply their common bcc structure. The magnitude of tracer self-diffusion at the melting temperature is similar for all bcc metals and a comparison of the diffusion parameters for all bcc metals shows a common pattern. The temperature dependence of the isotope effect for tracer self-diffusion is also closely similar for sodium,[5] α and δ-iron [21], chromium [22] and niobium [23]. Fits of all experimental data for tracer self-diffusion can be fit statistically with equal quality to a temperature dependent single defect process or the combination of two defect processes.

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