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PAS DETERMINATION OF THE VACANCY FORMATION ENTHALPY IN TUNGSTEN*

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DISCLAIMER

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PAS DETERMINATION OF THE VACANCY FORMATION ENTHALPY IN TUNGSTEN*

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A measurement of the vacancy formation enthalpy in 99.999 wt.% pure tungsten under thermal equilibrium conditions was made using the positron annihilation spectroscopy (PAS) Doppler-broadening technique. Temperatures were measured by optical pyrometry, with calibrations against a W(Re) thermocouple, the tantalum melting point, and the power delivered to the sample. A trapping-model analysis of the PAS data from the temperature range 300-3633 K yielded a vacancy formation enthalpy of 3.76 ± 0.39 eV. Comparisons are made between the present result and the other available results on vacancy formation in tungsten.

1. INTRODUCTION

Tungsten is the most extensively investigated refractory body-centered cubic (bcc) metal in terms of its atomic defects and their relationship to the mechanisms of atomic transport. A variety of methods, including radiotracer self-diffusion, post-quench resistometry, transmission electron microscopy, and field ion microscopy, and positron annihilation spectroscopy (PAS), have been used in these investigations. The radiotracer data have yielded a self-diffusion coefficient which exhibits a linear Arrhenius behavior at low temperatures, but which is enhanced with increasing magnitude as the melting temperature is approached [1]. A combination of post-quench resistometry [2,3] and equilibrium PAS [4] measurements of vacancy formation and migration in tungsten have confirmed that the low-temperature self-diffusion occurs via atomic exchange with monovacancies, in accord with other metals. However, the atomic-defect mechanism responsible for the strong diffusion enhancement observed at high temperatures in the refractory bcc metals is presently unknown (see [5] for a recent review). The present PAS Doppler-broadening study of tungsten was carried out to determine whether the description of the equilibrium vacancy ensemble that has been deduced from the results of recent quenching studies [2,3] is indeed representative of the equilibrium state, particularly at the highest temperatures where the self-diffusion is strongly enhanced.

2. EXPERIMENTAL PROCEDURE

The sample was fabricated from 99.999 wt.% pure tungsten in the form of a cylinder (0.5 cm diameter, 5.4 cm height), with axial holes spark eroded in both ends. The bottom hole was used as the black-body cavity for temperature measurement; the top hole contained the ^{58}Co positron source implanted into six small disks made of the sample material. A total of about 10^{14} atoms (≲ 10 μCi) of ^{58}Co were ion-implanted into the tungsten, which ensured that the sample purity was not compromised by the source. The source hole was filled with a plug of the sample material and electron-beam welded around the top rim. The sample-source assembly is shown in Fig. 1. This assembly was suspended vertically in an electron-beam furnace within

Fig. 1. Gamma-radiograph of the sample-source assembly.

an ultra-high vacuum (UHV) chamber. The large sample dimensions were necessitated by a combination of the minimum diameter needed for viewing by the pyrometers, the minimum aspect ratio of the black-body hole to ensure an emissivity near unity, and a sufficient wall thickness to maintain sample integrity under evaporation losses at high temperatures. Such dimensions, however, required a large heating-power input (≤ 3 kW) to the sample, which had to be dissipated within the UHV chamber in order to maintain a good vacuum and to allow for a small (~ 5 cm) separation between the sample (at ≤ 3695 K) and the Doppler-broadening detector (at 78 K) for reasonable PAS count rates. This was enabled by the use of a thin double-walled, water-jacketed copper can, which surrounded

the sample and electron-beam furnace, but which allowed for adequate pumping. This copper can also allowed for sample temperature measurement through its top and bottom axial holes, and in addition served to reduce the effects from any visible radiation scattered into the pyrometer from an object other than the sample, such as the furnace filaments.

Sample temperatures were measured by (1) an infrared pyrometer for temperatures below 2000 K, (2) a disappearing-filament optical pyrometer for temperatures above 1100 K, and (3) the power delivered to the sample by the high-voltage furnace for temperatures above 1200 K. The uncertainties in the measured temperatures were ±15 K below 3000 K, and ±30 K above. The pyrometers were calibrated against a W(5% Re)/W(26% Re) thermocouple below 1900 K by remotely inserting the thermocouple into the top hole of a dummy Ta sample with the same dimensions as the W sample. After removal of the thermocouple, the Ta sample was melted in situ for a further calibration point. The radiation from the black-body hole passed through the bottom aperture in the copper can, and was reflected from a stainless-steel mirror through a sapphire window in the UHV chamber, which allowed for transmission of both the infrared and visible radiation into the respective pyrometers. The input-power versus sample-temperature calibrations were made on the actual sample, using the previously calibrated optical pyrometer; these followed the T^4 law within a small offset error (e.g., 16 W out of 3 kW at 3695 K), which confirmed the pyrometer calibration. A final check of the temperature calibration was made by melting the tungsten sample in situ; agreement within 30 K of the accepted value (3695 K) was obtained. Owing to evaporation coating of the stainless-steel mirror at sample temperatures above 3400 K, the input-power calibration was used exclusively for temperature measurements in this range.

The Doppler-broadening data were acquired using a Ge(Li) detector with a resolution of 1.5 keV at 497 keV. The data acquisition system has been described in detail elsewhere [6]. Data stabilization was enabled [7] by the simultaneous recording of the 497 keV line from ^{103}Ru along with the 511 keV positron annihilation spectrum. Prior to the PAS measurements reported here, the tungsten sample was annealed in situ for > 2 h at 3125 K in the UHV system.

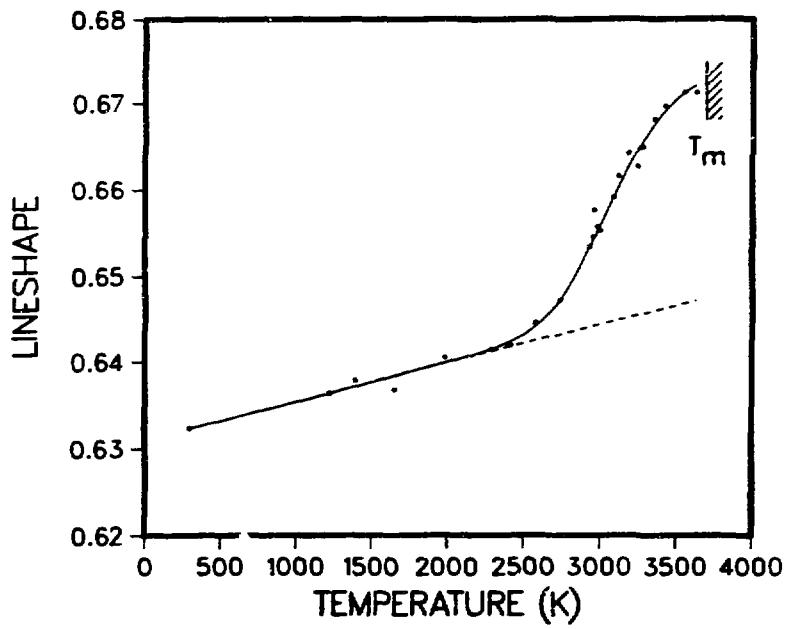

Fig. 2. Doppler-broadening lineshape for tungsten as a function of temperature between 300 K and 3633 K. The two-state trapping model fit to the data up to near the melting temperature (T_m = 3695 K) is shown, along with a dashed-line extension of the Bloch-state fit.

3. RESULTS

The measured Doppler-broadening lineshape as a function of temperature between 300 K and 3633 K is shown in Fig. 2. These data were analyzed according to the simple two-state trapping model, in which it is assumed that the positron exists in either the free (Bloch) state in the perfect lattice or the vacancy-trapped state and that the characteristic lineshapes resulting from annihilation in these states are linearly dependent upon temperature. The results of this analysis are $H_v^F = 3.76 \pm 0.39$ eV and $T_o = 3116 \pm 30$ K, where H_v^F is the vacancy formation enthalpy and T_o is the temperature at which 50% of the positrons annihilate from a vacancy-trapped state.

4. DISCUSSION

Radiotracer self-diffusion data for tungsten taken over a wide range of temperatures [1] indicate that the self-diffusion coefficient is enhanced at the melting temperature by about a factor of ten over that extrapolated from the low-temperature diffusion behavior. Such strong Arrhenius-plot curvature is rather typical of the self-diffusion behavior in the refractory metals [5]. Post-quench resistivity measurements [2] of the vacancy formation (3.6 eV) and migration (1.8 eV) enthalpies have confirmed that the low-temperature diffusion mechanism (with activation enthalpy 5.45 eV [1]) is atomic exchange with monovacancies, and have further suggested that the strong high-temperature enhancement in the self-diffusion coefficient may be a result of atomic transport via an interstitialcy mechanism. This description has gained additional support from combined post-quench resistivity and field ion microscopy [3] measurements, which yielded a value for the divacancy binding enthalpy (about 0.7 eV) and, in combination with the previous quenching results [2], indicated that the nearest-neighbor divacancies observed by field ion microscopy have a mobility that is slightly less than or about equal to that for the monovacancy. This combination of a rather low divacancy concentration (no more than 1-10% of the total vacancy concentration at T_m) and low (or at least not enhanced) divacancy mobility cannot explain the strong high-temperature enhancement of self-diffusion. The present equilibrium PAS results lend further support to this picture, while confirming the results from the nonequilibrium quenching studies on tungsten. The equilibrium value of $H_v^F = 3.76 \pm 0.39$ eV obtained from temperatures between 300 K and 3633 K agrees within experimental precision with that from the quenching studies [2,3], 3.6 ± 0.1 eV, but would allow for at most a small divacancy contribution at the highest temperatures consistent with the field ion microscopy results [3]. A previous PAS measurement of $H_v^F = 4.0 \pm 0.3$ eV [4] in tungsten, based primarily on lower-temperature data than the present work, is also consistent with this picture for the equilibrium vacancy ensemble in tungsten.

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