DETERMINATION OF THE VACANCY FORMATION ENTHALPY IN CHROMIUM BY POSITRON ANNIHILATION*

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DETERMINATION OF THE VACANCY FORMATION ENTHALPY IN CHROMIUM BY POSITRON ANNIHILATION*

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Doppler broadening of the positron annihilation lineshape in 99.99 at.% pure chromium was measured over the temperature range 296 - 2049 K. The chromium sample was encapsulated in sapphire owing to its high vapor pressure near melting. Saturation-like behavior of the lineshape was observed near the melting temperature (2130 K). A two-state trapping model fit to the data yielded a vacancy formation enthalpy of 2.0 ± 0.2 eV. This result is discussed in relation to extant empirical relations for vacancy migration and self-diffusion in metals and to data from previous self-diffusion and annealing experiments in chromium. It is concluded that the observed vacancy ensemble is unlikely to be responsible for the measured self-diffusion behavior. The implications of the present results in terms of our understanding of mechanisms for self-diffusion in chromium and other refractory bcc metals are discussed.

1. INTRODUCTION

The self-diffusion behavior of Cr appears superficially to be rather different than that of the other refractory bcc metals, V, Nb, Ta, Mo and W. Radiotracer data for these latter metals generally show curvature in the Arrhenius plot of their self-diffusion coefficient, which is thought to result from the contributions of two separate diffusion mechanisms, one predominant at low temperatures and characterized by the activation enthalpy Q_1, the other becoming important with increasing temperature near the melting point and characterized by the activation enthalpy Q_2. See reference [1] for a review of the self-diffusion properties of these metals. For the refractory bcc metals that exhibit such curvature, it is generally true that $Q_2/Q_1 \approx 1.26$ [2]. But the Arrhenius plot of the self-diffusion coefficient for Cr is linear over ten orders of magnitude, and the activation enthalpy obtained, 4.58 eV, is considered by comparison to those of the other Group VI-B metals Mo and W to be too large to interpret in terms of monovacancy diffusion [2]. For Mo and W, a combination of post-quench resistometry and equilibrium PAS measurements of vacancy formation and migration have confirmed that the low temperature self-diffusion is due to atomic exchange with monovacancies, while the high-temperature mechanism remains uncertain. The present paper describes positron annihilation Doppler-broadening measurements made on Cr over the temperature range 296 K to 2049 K. These measurements were carried out in order to determine the vacancy formation enthalpy in Cr and to investigate whether the equilibrium vacancy ensemble sampled by positrons is related to the observed self-diffusion behavior in this metal.

2. EXPERIMENTAL PROCEDURE

The cylindrical sample (0.5 cm diameter, 0.6 cm height) was prepared from 99.99 at.% Cr obtained from the Materials Preparation Center, Ames Laboratory, Iowa State University. About nine microcuries of ^{58}Co were electrodeposited on a Cr disk, which was then placed in a Cr can sealed with a screw-top lid. Because of the high vapor pressure of Cr (~ 1 torr at 2100 K), the sample/source assembly was encapsulated, first in a sapphire can with a lid, which was in turn placed in a Mo can which was then electron-beam welded shut. The sample was annealed in situ for 2 hours at 1700 K prior to the start of the experiment; all temperature measurements were made with a W(5% Re)/W(26% Re) thermocouple. To allow for subsequent data stabilization, the 497 keV line from ^{103}Ru was recorded simultaneously with the 511 keV annihilation spectrum, using the microscopic spectrum method [3]. A more complete description of the experimental procedure will be given elsewhere [4].

3. RESULTS AND DISCUSSION

The Doppler-broadening lineshape parameter data were analyzed with a simple two-state trapping model. The data fall along a sigmoidal curve, as seen in Fig. 1, in which the solid line is the trapping-model fit to the data. Saturation-like behavior is observed near the melting temperature,

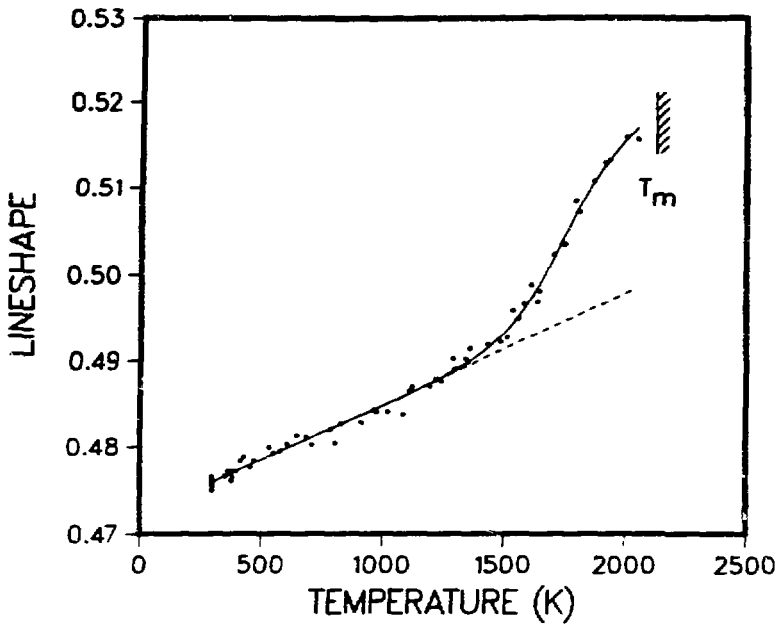

Fig. 1. Doppler-broadening lineshape for chromium as a function of temperature between 296 K and 2049 K. The two-state trapping model fit to the data up to near the melting temperature (T_m = 2130 K) is shown, along with a dashed-line extension of the Bloch-state fit.

similar to that seen for the other Group VI-B metals Mo and W [5,6]. The vacancy formation enthalpy obtained from this fit is H_v^F = 2.0 ± 0.2 eV, with χ^2 = 1.12 for 58 degrees of freedom. This value is consistent with the result of Campbell and Schulte [7], H_v^F = 2.27 ± 0.13 eV, obtained from an empirical rule involving the onset temperature of positron trapping rather than from a trapping-model fit to their data, which were limited to lower temperatures than the present data. The present data yielded an onset temperature of 1530 ± 30 K, in good agreement with that of Campbell and Schulte [7], 1560 ± 30 K. A detailed investigation of the χ^2-sum surface of the present data was undertaken using both simulated and real data. It was found that if only data up to the inflection point of the sigmoidal curves were available, the χ^2-sum surface is highly skewed and at best permits the establishment of an upper limit for H_v^F. For the full data, however, the χ^2-sum surface near the minimum was nearly quadratic. The trapping probability for the positron at the melting point in Cr was determined to be 0.87, in comparison to about 0.9 for Mo and W [5,6].

The equilibrium vacancy ensemble observed by PAS in Cr does not seem to be responsible for the diffusion behavior measured by radiotracer techniques, which after all appears to be dominated by a high-temperature mechanism by comparison with the results for other refractory bcc metals [1,2]. The present value for H_v^F (2.0 eV) could only be consistent with a vacancy model for the observed diffusion (with activation enthalpy 4.58 ± 0.03 eV [2]) if the vacancy migration enthalpy were about 2.6 eV. However, this value would indicate vacancy migration at temperatures well above those found by PAS for the complete annealing of any vacancy defects introduced by electron irradiation in Cr [8]. Indeed, a comparison of the observed temperature (550 K) for the dominant post-irradiation vacancy annealing stage [8] and an empirical correlation [9] between such temperatures and vacancy migration enthalpies would indicate a vacancy migration enthalpy in Cr of ~1.4 eV. Furthermore, if it is assumed that the measured self-diffusion activation enthalpy for Cr, 4.58 eV, is characteristic of a high-temperature mechanism by analogy with the results for the other refractory bcc metals, then the

empirical rule observed by Mundy et al. [2], $Q_2/Q_1 = 1.26$, could be used to estimate a self-diffusion activation enthalpy representative of monovacancies, $Q_1 = 3.6$ eV. Using this and the present result for H_v^F, a monovacancy migration enthalpy can be estimated as $H_v^M = Q_1 - H_v^F = 1.6 \pm 0.2$ eV, which is consistent with that deduced above from the electron-irradiation results [8]. The inability to explain the measured diffusion behavior in Cr in terms of the equilibrium vacancy ensemble observed with PAS, therefore, seems clear. Whether an interstitialcy mechanism, as suggested for the other Group VI-B metals W and Mo [1], is responsible for the observed diffusion behavior remains to be seen; more direct experiments to attempt to answer this question are presently underway in our laboratory.

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