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Self-diffusion in chromium

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Self-diffusion in chromium single crystals has been measured over the temperature range 1073 to 1446 K. These data, when combined with earlier measurements from this laboratory over the range 1370 – 2090 K, yield a plot of ln*D* vs $1/T$, which is straight over ten orders of magnitude in the diffusion coefficient *D*. The high values of the preexponential factor (1280 ± 230 cm^{2}s^{-1}) and activation enthalpy (4.58 ± 0.03 eV) are not readily interpreted in terms of a specific diffusion mechanism. They appear to be too high to be interpreted in terms of a monovacancy mechanism. The possible contribution of divacancies and self-interstitials are discussed.

I. INTRODUCTION

When measurements of the self-diffusion coefficient (*D*) in pure metals are made over a sufficiently large range in *D* ($> 10^5$), curvature in the Arrhenius plot is frequently observed.[1] Prior to 1978 the range of measured *D* for bcc transition metals had in general been small and curvature was only evident in vanadium[2–6] and the anomalous bcc metals, β-Ti (Ref. 7) and β-Zr (Refs. 8 – 10). Recent measurements in group-V metals, niobium[11] and tantalum,[12] and in the group-VI metals, molybdenum[13] and tungsten,[14] have shown curvature in all the Arrhenius plots. Earlier measurements of self-diffusion in chromium[15] displayed a straight Arrhenius plot, but the measurements extended only over a range of 10^6 in *D*. The present work has extended the chromium measurements to lower temperatures to explore for possible curvature in the Arrhenius plot.

Curvature in the Arrhenius plots is believed to result from the contribution of two mechanisms to diffusion[1,16,17] although single-mechanism theories have also been proposed.[18,19] Fitting of the self-diffusion data for the group-V and group-VI bcc metals to the sum of two exponentials yields the parameters shown in Table I. The activation enthalpies Q_i for the low- ($i = 1$) and high- ($i = 2$) temperature processes have been divided by the melting temperature (T_m) for that element. The pattern in the parameters of Table I that is evident for Ta, Nb, V, W, and Mo could be expected to extend to chromium. To estimate the parameters expected in this manner for chromium, which are given in the last line of Table I, mean values of $Q_2/Q_1 = 1.26$ and $D_2(T_m)/D_1(T_m) = 12$ were taken and the value of $D(T_m)$ was taken as 2.2×10^{-8} cm^{2}s^{-1} to match the high-temperature values of *D* found in the earlier work.[15] This estimate suggested that at 1143 K, for example, the value of *D* would be a factor of 4 above the extrapolation of the straight

TABLE I. Diffusion parameters for bcc refractory metals.

Element	D_{01} (cm^{2}s^{-1})	Q_1/T_m (cal K^{-1})	D_{02} (cm^{2}s^{-1})	Q_2/T_m (cal K^{-1})	Q_2/Q_1	$D_2(T_m)/D_1(T_m)$	$D(T_m)$ (cm^{2}s^{-1})	Reference
Ta	1.3×10^{-3}	28.2	1.0	33.4	1.25	23	2.3×10^{-8}	12
Nb	8.0×10^{-3}	30.4	3.7	38.1	1.25	10	1.8×10^{-8}	11
V	1.4×10^{-2}	31.2	7.5	39.8	1.27	7	1.7×10^{-8}	5
W	4.0×10^{-2}	34.0	46.0	43.0	1.27	13	1.9×10^{-8}	14
Mo	1.3×10^{-1}	36.1	139.0	45.3	1.26	10	1.8×10^{-8}	13
Cr	(9.0×10^{-1})	(39.8)	(1900.0)	(50.2)	1.26	12	1.8×10^{-8}	a

[a] Calculated as described in text.

Arrhenius line found in the earlier work.[15] A difference of this magnitude should be observable within the error of measurement of diffusion coefficients of the order 10^{-18} $\mathrm{cm^2 s^{-1}}$.

A survey in 1971 of self-diffusion in bcc metals[20] showed that the chromium self-diffusion data were best represented by a pre-exponential factor, $D_0 = 0.2$ $\mathrm{cm^2 s^{-1}}$ and an activation enthalpy, $Q = 3.2$ eV. Later work by Askill[21] on single-crystal chromium gave $D_0 = 1.6$ $\mathrm{cm^2 s^{-1}}$ and $Q = 3.5$ eV. Work at Argonne over a temperature range 1370–2090 K had produced significantly higher values of D_0 (970 $\mathrm{cm^2 s^{-1}}$) and Q (4.5 eV). The extension of these measurements to 1073 K was made both to confirm the high values of D_0 and Q and to allow for the examination of possible curvature in the $\ln D$ vs $1/T$ plot.

II. EXPERIMENTAL METHODS

The basic method used was to observe the diffusion from a thin surface layer of radiotracer by sectioning. The solution of the diffusion equation for these experimental conditions is

$$C_x = \frac{S}{(\pi D t)^{1/2}} \exp\left[\frac{-x^2}{4Dt}\right], \qquad (1)$$

where C_x is the specific activity of the tracer at a distance x from the surface, t is the time of anneal, D is the diffusion coefficient, and S is the activity per unit area at $x = 0$ and $t = 0$.

A. Materials

The chromium single-crystal disks measuring 1 cm in diameter and 0.30-cm thick were prepared by a strain-anneal technique. The high-purity chromium was obtained from the Chromalloy Corporation and had an impurity content of less than 120 parts per million by weight. This material was cast into an irregular rod shape in a nonconsumable arc furnace. The melt was made under a purified argon atmosphere in a noncontaminating water-cooled copper hearth. The polycrystalline casting was then jacketed in stainless steel and reduced in cross section to 1.27 cm by swaging at 850 °C. During this process approximately 15% strain was introduced into the specimen. After the steel jacket was removed the chromium was machined to the 1-cm diameter, electropolished, and annealed in a sealed rhenium crucible for 3 days at 1700 °C. The single-crystal disks were cut from the resulting single-crystal rod using a Buehler-Isomet low-speed diamond saw. The samples were then mechanically polished through Linde B, lightly electropolished in a chilled methanol-perchloric acid bath and thoroughly rinsed in methanol. Prior to the evaporation of radioactive chromium, ~ 1 μm was removed by ion sputtering in the apparatus described below.

The ^{51}Cr used as the radioisotope was prepared by irradiation of chromium metal (99.999% purity) in a neutron flux of 4×10^{14} n $\mathrm{cm^{-2} s^{-1}}$ for two weeks. The resulting specific activity of 2.7 C/gm provided sufficient counts in the thin $[< 0.1(Dt)^{1/2}]$ evaporated layers required by Eq. (1). The pressure in the chamber during the chromium evaporation was $< 10^{-5}$ Pa.

B. Diffusion measurements

The samples were placed in tantalum capsules which were closed by electron beam welding under a vacuum of 10^{-2} Pa. The flat polished surface of the samples was protected from damage by containing each sample in a molybdenum foil that was folded in the shape of a prism; this also prevented direct contact of the sample with the tantalum capsule. The capsules themselves were further encapsulated in quartz under a vacuum of 10^{-2} Pa and annealed in wire-wound furnaces. The temperatures were measured with Pt/Pt–10 at. % Rh thermocouples and the uncertainty in the temperatures was ± 2 K including the calibration errors. Time corrections for heat-up were applied. After annealing, the cylindrical surface of the samples was removed by spark cutting so that the penetration profile was not affected by vapor or surface transport.

The samples were sectioned by sputtering with argon ions, in equipment similar to that described in Ref. 22, but with a Kaufman-type ion source,[23] which generated a beam of argon ions uniform over ~ 2-cm diameter with energies up to 500 eV, and with current densities up to 2 $\mathrm{mA/cm^2}$. The surface of the sample was at an angle of 70° to the direction of the ion beam. The cylindrical side of the sample was protected by a graphite sleeve. The samples were rotated at 15 revolutions per minute. The sputtered chromium was collected with $\sim 90\%$ efficiency on a defined area of a 5-cm-wide Mylar ribbon held in a collecting device. The Mylar ribbon could be advanced in this "cameralike" device from outside the sputtering apparatus, so that up to 30 consecutive sections could be taken without interruption of the ion beam. The sputtering rate was kept constant by controlling the beam current. The uniformity of the rate was checked at various voltages on a neutron-irradiated chromium sample. The sputtering rates could be varied from 15 to 300 Å/min.

The section thickness was determined from the sputtering rate and the individual sputtering times. The sputtering rate for each sample was determined from the weight loss measured with a Mettler ME 22 electronic balance and the sample diameter measured with a traveling microscope. The uncertainty introduced by this technique is greatest for the lowest diffusion coefficient (±20%). In order to ensure that the layers removed by sputtering were parallel to the initial surface, all samples were sputtered to a depth of 10^{-4} cm prior to evaporating the radioactive chromium. The sputtering conditions for the sectioning remained the same so one would expect isoactivity contours to be followed. Interference microscopy of the surfaces before and after sputtering revealed no obvious changes in the planeness of the surface. After sputter sectioning the samples, the Mylar ribbon was cut into sections, folded, placed into vials, and counted in a well-type NaI(Tl) scintillation counter. Counts were taken from a window around the 0.32-MeV γ peak.

C. Other observations

The surface of samples annealed at 1142 and 1185 K appeared to have oxidized. The surface of the 1185-K sample was cleaned by a light mechanical polishing and the penetration profile is shown in Fig. 1. Poor definition of the $X = 0$ plane in-

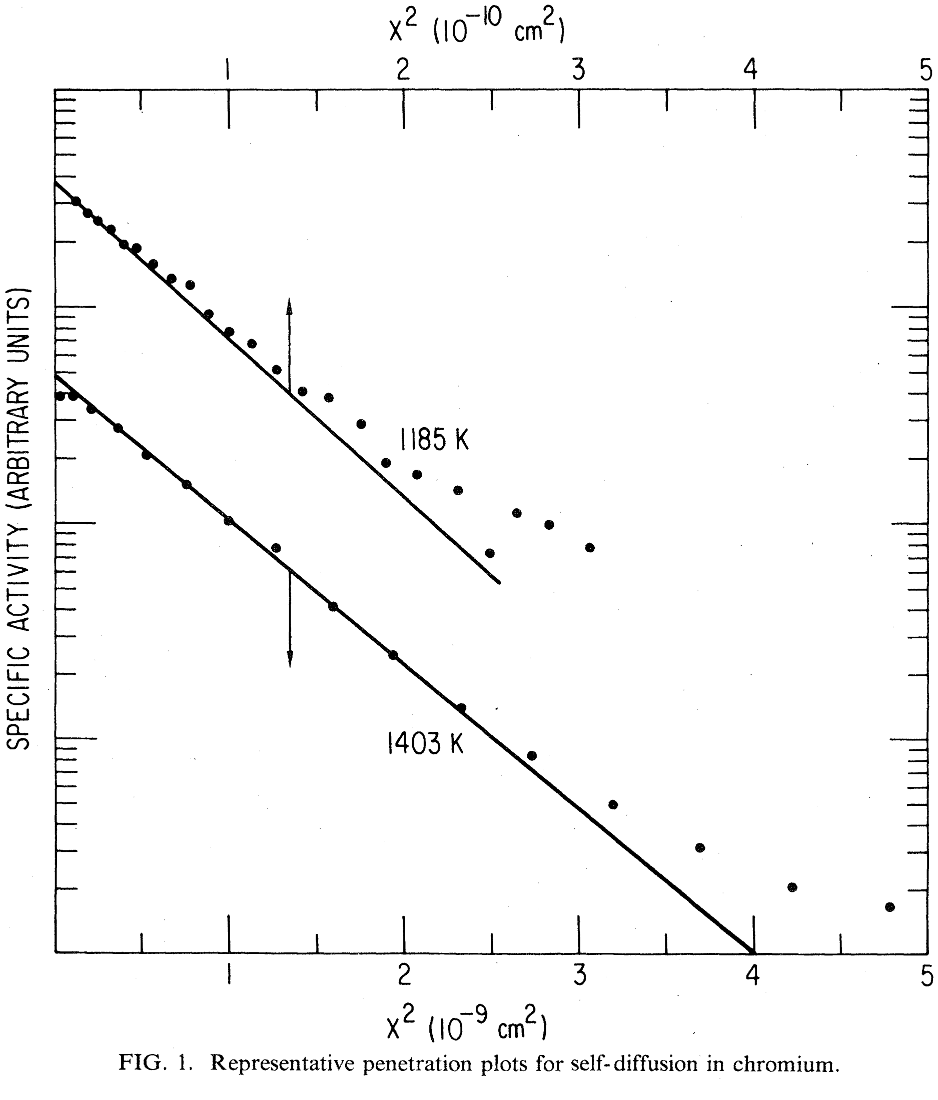

FIG. 1. Representative penetration plots for self-diffusion in chromium.

creased the error associated with the slope of this profile. Earlier measurements of chromium self-diffusion[15] using the same annealing procedure, indicated that the tantalum capsule acted as a "getter" for oxygen and it is not clear why there were "oxide" problems with these two anneals. The sample annealed at 1142 K yielded a profile of constant concentration and could not be used.

Autoradiographs of each sample surface were made after the last section had been taken. The radiographs revealed up to 200 spots and examination of the sample surface at 500× indicated flaws at the majority of the points where the spots occurred. The flaws, which had a range of sizes up to $\sim 5\times 10^{-3}$ cm, were not always observable after polishing but could be seen on all samples following a high-temperature anneal or after sputtering the surface. Not all the flaws had the same appearance; some appeared to be small voids while others may have been small oxide particles.

The samples were weighed before and after the anneal so that the evaporation rate of the chromium sample could be determined. The molybdenum foils which held the samples in the tantalum capsules were counted in the scintillation counter. This showed that at the highest anneal temperatures at least half of the radioactive chromium ended the anneal on the molybdenum foil. At the lowest anneal temperatures there was no measurable evaporation. Placing chunks of chromium in the capsule for the 1320-K anneal, carried out subsequent to those at 1228, 1403, and 1446 K, effectively eliminated this problem.

III. EXPERIMENTAL RESULTS

Representative penetration plots [log specific activity versus x^2, to match Eq. (1)] obtained as described above are shown in Fig. 1. In addition to the Gaussian portion predicted by Eq. (1), the plots have a "tail" which becomes more and more important as the annealing temperature decreases. The tail is surely associated with short-circuiting diffusion caused by the imperfections indicated in the autoradiographs; a contribution from diffusion along dislocations cannot, however, be excluded. Even though the exact mechanisms responsible for the tails cannot be specified, their presence requires fitting[24] the penetration plot to an equation,[25]

$$C_x = A\exp(-Bx^2) + C\exp(-Px^{6/5})\ , \tag{2}$$

where $B = 1/4Dt$, and the second term gives the "short-circuiting diffusion coefficient" D', given by

$$D'\delta = 0.66P^{-5/3}\left[\frac{4D}{t}\right]^{1/2}\ , \tag{3}$$

with δ the width of the fast-diffusing path. Because of the possible presence of several different kinds of short-circuiting paths, D' cannot be analyzed further.

In addition to the tails, problems were encountered with the evaporation of chromium in the samples annealed at 1446, 1403, and 1228 K, as mentioned above. Corrections for evaporation were made to the diffusion coefficients obtained from the slope B of Eq. (2) using the equation given by Ghoshtagore.[26] This equation is applicable to diffusion from a thin film into an evaporating solid and assumes constant evaporation throughout the diffusion anneal. In the present experiments it was difficult to establish experimentally whether this was indeed the way evaporation took place, or whether there was an initial rapid evaporation followed by negligible losses. The calculations showed that if the evaporation occurred only during the first quarter of the anneal, the fraction of radioactivity retained would have been lower than that observed. A slower evaporation rate suggests that the rate was controlled by some sink for the chromium vapor, such as diffusion of chromium into the molybdenum foil. Crude chemical etching experiments on the molybdenum foil confirmed that the chromium had indeed diffused into the foil.

A knowledge of the weight loss during the anneal, surface area of sample, relative fraction of activity retained in the sample, the slope B from Eq. (2), and the anneal time, allowed upper and lower limits to be placed on the diffusion coefficients for these three temperatures. The Ghoshtagore equation established an upper limit within a few percent. The lower limit is poorly defined but necessarily has to be above the uncorrected value obtained using the slope B from Eq. (2).

The values of D calculated from Eq. (2) are given in Table II. The uncertainties quoted are the Pythagorean sum of uncertainties arising from the determination of the slope B, the section thickness, and the temperature. The values of D quoted for the anneals at 1446, 1403, and 1228 K are the arithmetic mean between the uncorrected value as calculated from B [Eq. (2)], and the upper limit determined in the Ghoshtagore fit. The uncertainty in this procedure was added to the uncertainty as described above and constituted the major part of the error bars on these points.

TABLE II. Self-diffusion in chromium.

Temperature (K)	Annealing Time (sec)	Section Thickness (Å)	D ($\mathrm{cm^2\,s^{-1}}$)
1446	8.8×10^{3}	567	$(1.0\pm0.3)\times10^{-13}$
1403	8.8×10^{3}	419	$(2.7\pm0.9)\times10^{-14}$
1320	8.0×10^{3}	102	$(3.8\pm0.3)\times10^{-15}$
1228	8.8×10^{4}	174	$(2.3\pm0.7)\times10^{-16}$
1185	4.0×10^{5}	62	$(3.7\pm1.9)\times10^{-17}$
1104	1.2×10^{6}	30	$(2.6\pm0.4)\times10^{-18}$
1073	2.5×10^{6}	18	$(9.0\pm3.4)\times10^{-19}$

The diffusion coefficients of Table II are plotted vs $1/T$ in Fig. 2 together with the earlier measurements.[15] A weighted least-squares fit to all 38 points gives the Arrhenius relation

$$D=[(1.3\pm0.2)\times10^{3}\ \mathrm{cm^2\,s^{-1}}]\times\exp\left[\frac{-4.58\pm0.03}{kT}\ \mathrm{eV}\right],$$

with $\chi^2=1.41$.

IV. DISCUSSION

The present data together with those of Ref. 15 do not agree with the parameters for self-diffusion in chromium proposed by Neumann[20] or Askill.[21] The agreement of the present data with those of Ref. 15 is within the error bars in the overlap region. However, a small systematic discrepancy between the two sets of data, which cannot be assigned to errors in the measurement of temperature, manifests itself in the following ways:

(i) a fit to the seven points of the present work alone yields $D_0=46\ \mathrm{cm^2\,s^{-1}}$, $Q=4.20\pm0.05$ eV with $\chi^2=0.31$;

(ii) the value of χ^2 is 2.54 if the present seven points are fitted to the line of Ref. 15;

(iii) the deviations of the present seven points about Eq. (4) are systematic (negative at high, positive at low temperature).

A fit of all 38 points to the sum of two exponentials decreases somewhat the systematic deviation of the present seven points, but does not provide positive proof of the existence of a curved $\ln D$ vs $1/T$ plot because the contribution of a second exponential is so small that no minimum χ^2 fit with physically reasonable parameters for the second exponential could be found.

The curvature that is frequently found when D is measured over a wide range of temperature in the fcc metals is commonly interpreted[1,16] in terms of a single-vacancy mechanism dominant over most of the temperature range with an increasing contribution from divacancies at high temperatures. This interpretation has been reinforced by the formation and migration enthalpies for defects which have been obtained from other techniques.[27,28] Recently some of this information has been obtained from the group-V and -VI bcc metals. The positron annihilation spectroscopy (PAS) experiments on W and Mo (Ref. 29) yielded values of the single-vacancy formation enthalpy (W: $H_{1v}^{F}=4.0\pm0.3$ eV, Mo: $H_{1v}^{F}=3.0\pm0.2$ eV) in good agreement with the enthalpies obtained from the measurements of quenched-in resistivity [W: $H_{1v}^{F}=3.67\pm0.2$ eV,[30] Mo: $H_{1v}^{F}=3.2\pm0.2$ eV (Refs. 31–34)]. The resistivity work also yielded values for the migration enthalpy [W: $H_{1v}^{M}=1.78\pm0.1$ eV,[30] Mo: $H_{1v}^{M}=1.35$ eV (Ref. 34)]. The sum of H_{1v}^{F} and H_{1v}^{M} is in excellent agreement with the activation enthalpy for the low-temperature diffusion process [W: $Q_1=5.45\pm0.5$ eV,[13] Mo: $Q_1=4.53\pm0.2$ eV (Ref. 14)]. Although the evidence is not as strong for the group-V bcc metals, the PAS results[29] suggest that the low-temperature process could be associated with single vacancies.

The values of Q_1/T_m given in Table I range from 28 to 36 T_m (cal $\mathrm{K^{-1}}$) and are considerably lower than the $49.7T_m$ found for the chromium self-diffusion enthalpy given by Eq. (4). The entropy of activation for chromium obtained on the assumption of single vacancies, $\Delta S=13k$, is also much greater than the entropies of activation (1—4k) for the low-temperature mechanism in the other bcc transition metals given in Table I. The entropies of activation ΔS were obtained from the equation

$$D_0=\gamma a^2\nu f\exp(\Delta S/k)\,, \tag{5}$$

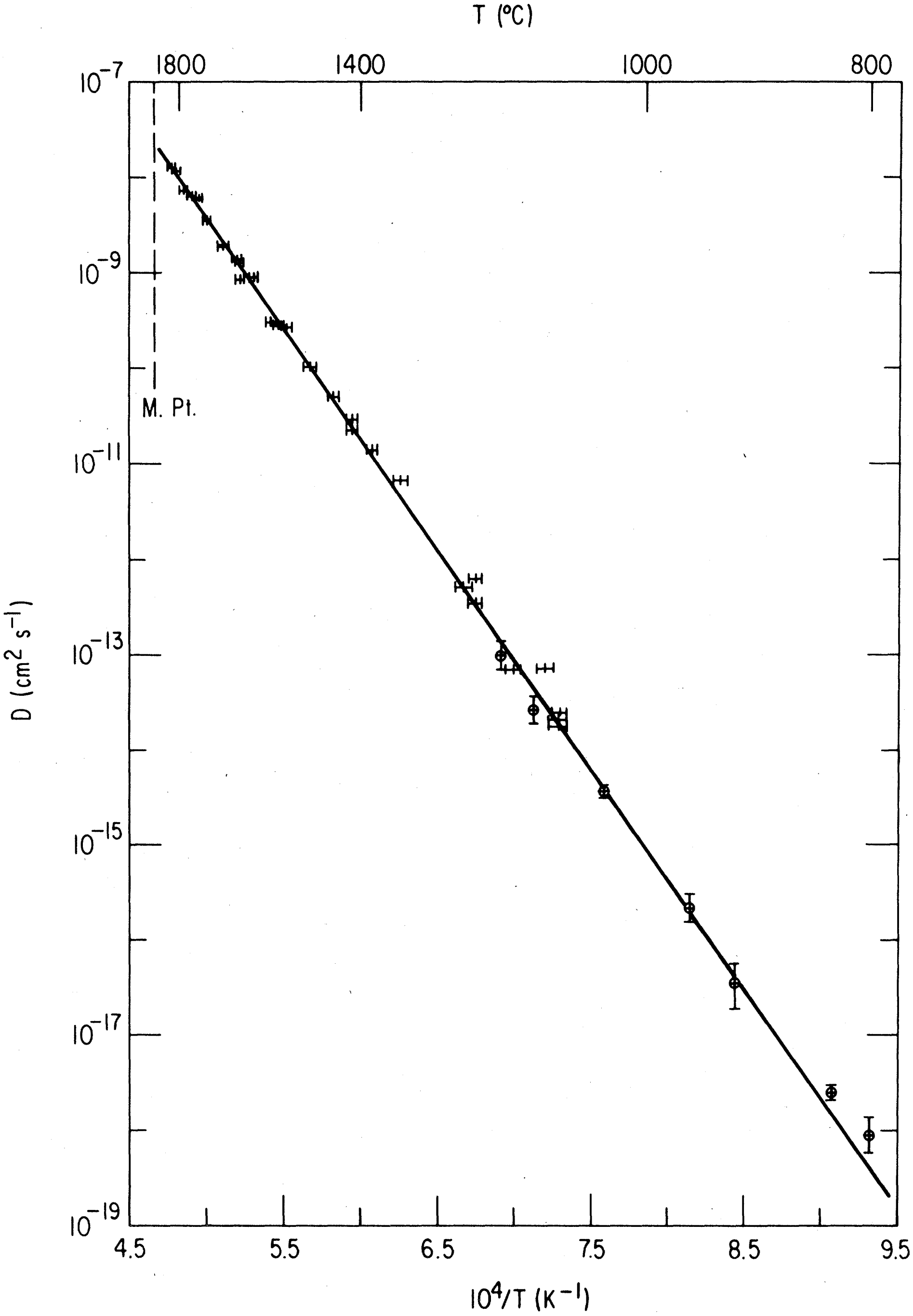

FIG. 2. Arrhenius plot for self-diffusion in chromium. The high-temperature data from previous experiments at this laboratory (Ref. 15) show a larger temperature error due to the use of a vacuum furnace for the diffusion anneals. The present data are denoted by Φ.

where γ is a geometrical constant that depends on the unit-cell geometry and the assumed jump mechanism, ν is an average vibration frequency, and k is Boltzmann's constant. We assumed for chromium $\gamma = 1$, $f = 0.727$, $a = 2.885 \times 10^{-8}$ cm, and $\nu = 4 \times 10^{12}$ s^{-1}.

The value of $Q = 49.7T_m$ found for chromium is in better agreement with the values of Q_2/T_m found for the other group-VI bcc metals (Table I). If one associates this process with the migration of a divacancy, the entropy obtained from the preexponential factor ($11k$) is also in better agreement with that obtained for the high-temperature mechanism in W ($8k$) and Mo($9k$). However, there are problems with associating the high-temperature diffusion process with divacancies.[13,14] The formation enthalpy for quenched-in defects (W, 3.67 eV; Mo, 3.2 eV) was obtained for quenches from the temperature range (W, $T_Q > 2500$ K; Mo, $T_Q > 2000$ K) where the high-temperature diffusion process is dominant. As already noted, this formation enthalpy can be associated with single vacancies. However, this implies[30] that the high-temperature defect is in low concentration and has high mobility so that only the quenched-in single vacancies are observed. The PAS experiments[29] examined equilibrium defects, and the onset temperatures (W, $T_3 \sim 2640$ K; Mo, $T_3 \sim 2120$ K) indicate that the defect properties obtained are from the temperature range where the high-temperature diffusion process is dominant. The good agreement between the enthalpy found from the PAS (Ref. 29) and the resistivity measurements[30–34] could also be explained if the high-temperature defect were in low concentration and with high mobility. Such a defect could be a divacancy or an interstitial as proposed for the high-temperature mechanism in copper.[35] The large values of the formation entropies for interstitials would fit with the rather large preexponential factors found for the high-temperature mechanisms in the bcc transition metals (Table I). The low values of the isotope effect for self-diffusion in chromium[15] could also be interpreted in terms of motion by a dumbbell-type interstitial. Thus self-diffusion in chromium could take place via interstitial motion, but there is little confirming evidence.

The lack of curvature of the $\ln D$ vs $1/T$ plot found for chromium is in strong contrast to the curvature found in all the other bcc transition metals. The contribution from a low-temperature process suggested by the pattern in Table I (see Introduction) is certainly not present. A minimum contribution can be estimated on the basis that one would expect the activation enthalpy to be $\sim 79\%$ of that for the high-temperature process. For chromium such a value (3.6 eV) would agree with the value of Q_1 suggested by recent PAS experiments on chromium[36] (3.5 eV). A two-exponential fit of the combined set of chromium data (Ref. 15 and present work) with a fixed value of $Q_1 = 3.6$ eV has a $\chi^2 = 1.29$ compared to $\chi^2 = 1.41$ for the single exponential fit of Eq. (4), however, one finds then that $D_{02}/D_{01} \gtrsim 5 \times 10^4$. The curvature of $\ln D$ vs $1/T$ plots in bcc transition metals is more prominent than that for fcc metals because the ratio for D_{02}/D_{01} is greater; for fcc metals[1] D_{02}/D_{01} ranges from 14 to 120, for group-V metals,[14] $D_{02}/D_{01} \sim 500$, and for tungsten and molybdenum $D_{02}/D_{01} \sim 1100$. The present data on chromium self-diffusion would thus require a ratio of D_{02}/D_{01} well over an order of magnitude greater than even the other group-VI bcc metals, if the assumption of $Q_1 = 3.6$ eV were correct.

The measurements of the isotope effect (E) in chromium self-diffusion[15] showed a strong temperature dependence. A strong temperature dependence of E has usually been accompanied by an observable curvature in the $\ln D$ vs $1/T$ plot and interpreted as resulting from contributions from two diffusion processes (single plus divacancy).[1,16,37] The temperature dependence of E found for chromium[15] is in strong contrast to the straight line $\ln D$ vs $1/T$ plot, which has been confirmed by the present work.

V. CONCLUSIONS

We have the following.

(1) The combined set of chromium self-diffusion data is best fit by the single Arrhenius line,

$$D = [(1.3 \pm 0.2) \times 10^3\,\mathrm{cm^2\,s^{-1}}] \times \exp(-4.58 \pm 0.03\ \mathrm{eV}/kT)\ .$$

(2) The possibility of two diffusion processes would require a larger ratio of preexponential factors than commonly found for self-diffusion in metals.

(3) The atomic mechanisms of diffusion responsible for chromium self-diffusion cannot be defined at the present time.

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