A QUANTITATIVE STUDY OF VACANCY DEFECTS IN QUENCHED PLATINUM BY FIELD ION MICROSCOPY AND ELECTRICAL RESISTIVITY—II. ANALYSIS AND INTERPRETATION†

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In the previous paper (Part I) it was demonstrated by means of field ion microscopy that the measured ratio of divacancy concentration to monovacancy concentration \(c_{\text{div}}/c_{\text{mon}}\) in high purity platinum specimens quenched from 1700 °C was 0.06 ± 0.02. In the present paper (Part II), a detailed series of quantitative calculations was first performed which showed that this ratio was not affected by specimen storage and electropolishing procedures subsequent to the quench and hence represented a quenched-in value of \(c_{\text{div}}/c_{\text{mon}}\) equal to 0.06 ± 0.02 for a quench temperature of 1700°C are governed by the linear relationship

\[
E_{\text{v}}^{b} = \left[ (0.23 \pm 0.03) + 6.17 \cdot 10^{-4} \left( \frac{S_{\text{v}}^{b}}{k} \right) \right] \text{eV},
\]

where \(k\) is Boltzmann’s constant. This linear equation implies that the divacancy binding free energy \((G_{\text{v}}^{b})\) was 0.23 eV at \(T^* = 443.4°C\). This value of \(G_{\text{v}}^{b}\), calculated from our experimental data, depends only on a knowledge of the monovacancy migration energy and an approximate value of a frequency factor. The existing tracer diffusion data for platinum were re-examined in terms of a monovacancy and divacancy model in an attempt to decompose \(G_{\text{v}}^{b}\) into \(E_{\text{v}}^{b}\) and \(S_{\text{v}}^{b}\) terms, and it was concluded that the available data are not sufficiently accurate to make this decomposition significant.

EINE QUANTITATIVE UNTERSUCHUNG VON LEERSTELLENDEFETEN IN ABGESCHRECKTEM PLATIN MIT HILFE DER FELDIONENMIKROSKOPIE UND ELEKTRISCHER WIDERSTANDSMESSEGEN—II. ANALYSE UND INTERPRETATION

In der vorhergehenden Arbeit (Teil I) wurde mit Hilfe der Feldionenmikroskopie gezeigt, daß in hochreinen, von 1700 °C abgeschreckten Platinproben das Verhältnis von Doppeleerstellen-Konzentration zu Einfachleerstellen-Konzentration \(c_{\text{div}}/c_{\text{mon}}\) 0.06 ± 0.02 ist. In der vorliegenden Arbeit (Teil II) wird anhand ausführlicher quantitativer Berechnungen nachgewiesen, daß dieses gemessene Verhältnis nicht durch Probenaufbewahrung und Elektropolieren nach dem Abschrecken beeinflußt wird und somit \(c_{\text{div}}/c_{\text{mon}}\) bei der “Ausfrier”-Temperatur \((T^*)\) darstellt. Außerdem wird gezeigt, daß alle Kombinationen der Doppelleerstellen-Bindungsenergie \((E_{\text{v}}^{b})\) und Bindungsentropie \((S_{\text{v}}^{b})\), die zu dem eingescnrockneten Wert \(c_{\text{div}}/c_{\text{mon}} = 0.06 \pm 0.02\) für eine Abschrecktemperatur von 1700°C führen, durch die folgende lineare Beziehung beschrieben werden:

\[
E_{\text{v}}^{b} = \left[ (0.23 \pm 0.03) + 6.17 \cdot 10^{-4} \left( \frac{S_{\text{v}}^{b}}{k} \right) \right] \text{eV},
\]

Dabei ist \(k\) die Boltzmann-Konstante. Diese lineare Gleichung führt zu dem Ergebnis, daß die Bindungsentropie der Doppelleerstelle \((S_{\text{v}}^{b})\) bei \(T^* = 443.4°C\) 0.22 eV ist. Dieser aus unseren experimentellen Daten berechnete Wert von \(S_{\text{v}}^{b}\) hängt nur von der Kenntnis der Wanderungsentropie der Einfachleerstelle und einem Näherungswert des Frequenzfaktors ab. Die vorliegenden Tracer-Diffusionsdaten für Platin werden in Hinsicht auf ein Einfachleerstellen- und Doppelleerstellen-Modell erneut untersucht mit dem Ziel \(G_{\text{v}}^{b}\) in \(E_{\text{v}}^{b}\) und \(S_{\text{v}}^{b}\) zu erlegen; es zeigte sich, daß die verfügbaren Daten nicht genügend genau sind, um eine bedeutungsvolle Zerlegung zu erlauben.

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1. INTRODUCTION

In Part I(1) an experimental value was reported for the ratio of the divacancy to monovacancy concentration \((c_{2v}/c_{1v})\) for platinum specimens quenched from 1700 \pm 1°C. The main purpose of the present paper is to demonstrate that this ratio is a direct measure of the divacancy binding free energy \((G_{2v} b)\) at a characteristic "freeze-out" temperature \((T^*)\) as described in Part I and that the experimental value of \(c_{2v}/c_{1v}\) (i.e. \(0.06 \pm 0.02\)) can be used to determine a linear relationship between the divacancy binding energy \((E_{2v}^*)\) and binding entropy \((S_{2v}^*)\). The calculation of this relationship only requires a knowledge of the migration energy of a monovacancy \((E_{1v}^m)\) and an approximate value of a frequency factor \((\nu)\).

The use of the value of \(c_{2v}/c_{1v}\) to determine the quantity \(G_{2v} b\) required proof that the measured \(c_{2v}/c_{1v}\) was not changed from its quenched-in value at \(T^*\) as a result of the specimen storage and electropolishing procedures which followed the quench from 1700 \pm 1°C. Hence, a detailed series of calculations was first made (Section 2) which monitored the ratio \(c_{2v}/c_{1v}\) during the total specimen thermal history. The main conclusion of these calculations was that the value of the ratio \(c_{2v}/c_{1v}\) for the specimens electropolished by procedure \(B\) (Section 2.3.2 of Part I) was not changed by this treatment or any other steps involved in their thermal history, and therefore could be used to determine \(G_{2v} b\) at \(T^*\).

Finally, in an attempt to decompose \(G_{2v} b\) into \(E_{2v} b\) and \(S_{2v} b\) terms, the available tracer diffusion data for platinum were re-examined critically (Section 4.2) and it was concluded that the existing data are not sufficiently accurate to allow a significant decomposition.

2. THE RATIO \(c_{2v}/c_{1v}\) AS A FUNCTION OF THE TOTAL THERMAL HISTORY OF A SPECIMEN

The total thermal history of a specimen consisted of the following three stages:

1. A quench from 1700 \pm 1°C \((T_p)\) to \(-5°C\).
2. The storage of the specimens in bulk form at \(\approx 20°C\) for a maximum of 30 days.
3. The preparation of a sharply pointed FIM tip from a bulk specimen by either electropolishing procedure \(A\) or \(B\) (see Sections 2.3.1 and 2.3.2 in Part I) followed by further storage at either \(\approx 20\) or \(-50°C\).

The above three stages are illustrated schematically in Fig. 1.

2.1 Redistribution of a closed assembly of monovacancies and divacancies during the quench

The first stage consisting of a quench from 1700 \pm 1°C to \(-5°C\), was schematized as a quench to 20°C (see Fig. 1) for the analysis. In the analysis for the defect redistribution we treated the assembly of monovacancies and divacancies as a closed system, hence it was necessary to specify a value of the total vacancy concentration \((c_t)\) for the calculations. Thus, we first present a brief physical argument to demonstrate that the relevant value of \(c_t\) is the measured quenched-in value \((c_t^*)\) and that the thermal equilibrium value at 1700°C need not be known.†

The best value of \(c_t^*\) reported in Part I is a lower limit to the actual thermal equilibrium value at 1700°C because of the loss of vacancies to sinks which must occur in any real quench(2) from a temperature which was so close to the melting point (1769°C). The largest percentage of the total loss occurs at elevated temperatures and after this initial loss \(c_t\) is then approximately a constant for the remainder of the quench (see Seidman and Balluffi(18,4) for a treatment of the diffusional aspects of this problem). The temperature at which the losses become negligible is higher than the critical temperature \((T^*)\) at which a closed assembly of monovacancies and divacancies can no longer maintain itself in quasi-equilibrium. The reason for this fact is that the diffusion distance between dislocations is appreciably greater than the diffusion distance between two monovacancies, so that the assembly is able to maintain itself in local equilibrium long after the vacancy losses to dislocations have become negligible. Thus, the calculated ratio \(c_{2v}/c_{1v}\) at the end of a quench for a closed assembly is characteristic of an open assembly, if the value of \(c_t\) employed in the calculation is the one measured after the quench.

† It is also to be noted that this approach avoids the problem of assigning exact values to \(E_{1v}^m\), \(S_{1v}^m\), \(S_{2v}^m\) and \(E_{2v}^m\) in the expression for \(c_t\) [see equations (2)-(5) of Part I] at the initiation of the analysis.
The analysis starts with the approximate equations:

\[
\frac{dc_{1v}}{dt} = -2K_{1}c_{1v}^{2} + 2K_{2}c_{2v}, \quad (1)
\]

\[
\frac{dc_{2v}}{dt} = K_{1}c_{1v}^{2} - K_{2}c_{2v}, \quad (2)
\]

where the \( K_{n} \)'s are given by:

\[
K_{1} = 84\nu \exp \left( -E_{1v}^{m}/kT \right) \quad (3)
\]

\[
K_{2} = 14\nu \exp \left( S_{2v}^{b}/k \right) \exp \left[ -(E_{1v}^{m} + E_{2v}^{b})/kT \right], \quad (4)
\]

and \( t \) is time. The quantities \( E_{1v}^{m} \) and \( E_{2v}^{m} \) are the monovacancy and divacancy migration energies, respectively, and \( \nu \) is a frequency factor which includes an entropy of migration factor. The free energy \( G_{2v}^{b} \) is given by:

\[
G_{2v}^{b} = E_{2v}^{b} - TS_{2v}^{b} \quad (5)
\]

where \( E_{2v}^{b} \) and \( S_{2v}^{b} \) are defined by equations (5) and (6) of Part I. The total vacancy concentration is given by:

\[
c_{t} = c_{1v} + 2c_{2v}, \quad (6)
\]

and since \( c_{t} \) is constant for a closed assembly, it follows that:

\[
\frac{dc_{1v}}{dt} = -2\frac{dc_{2v}}{dt}. \quad (7)
\]

Fujiwara was the first to solve the coupled nonlinear differential equations (1) and (2) under idealized quenching conditions employing computer techniques. We have also solved these equations employing a computer, but have used the following expression for the thermal history during quenching which was derived from the experimentally determined quenching curve shown in Fig. 1 of Part I:

\[
T(t) = 1700 \exp \left\{ -[(13x)^{3} + 5(10x)^{4} + (10x)^{6} + (10x)^{8}] \right\} \text{sec}, \quad (8)
\]

where \( x = (t + 2 \cdot 10^{-3}) \text{sec}. \)

The variable parameters in this model which affect the quenched-in ratio \( c_{2v}/c_{1v} \) are \( E_{1v}^{m} \), \( \nu \), \( S_{2v}^{b} \) and \( E_{2v}^{m} \), because \( T_{q} \) and \( c_{t} \) are fixed by the experimental conditions. Since our objective was to determine \( E_{2v}^{b} \) from the value of \( c_{2v}/c_{1v} \), we calculated the sensitivity of this ratio to the remaining variable parameters for \( S_{2v}^{b} = 0 \) and showed that for all reasonable values of \( E_{1v}^{m} \) and \( \nu \) the value of \( c_{2v}/c_{1v} \) was essentially determined by \( E_{2v}^{b} \). A value of \( E_{1v}^{m} \) equal to 1.38 eV is favored as a best value by both Jackson and Schumacher et al., and the range 1.33–1.43 eV covers most of the numbers reported in the literature. Hence we calculated the quenched-in ratio \( c_{2v}/c_{1v} \) for \( E_{1v}^{m} = 1.33, 1.38 \) and 1.43 eV at constant values of \( \nu \). The range considered for \( \nu \) was from \( 10^{12} \) to \( 10^{14} \text{sec}^{-1} \) and it is noted that this 100-fold variation for \( \nu \) is appreciably greater than the possible range of this parameter expected in practice. The results of these calculations are displayed in Table 1. The numbers

<table>
<thead>
<tr>
<th>( E_{1v}^{m} ) (eV)</th>
<th>( E_{2v}^{b} ) (eV)</th>
<th>( \nu ) (sec(^{-1}))</th>
<th>( c_{2v}/c_{1v} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33</td>
<td>0.05</td>
<td>10^{12}</td>
<td>0.004</td>
</tr>
<tr>
<td>1.38</td>
<td>0.05</td>
<td>10^{12}</td>
<td>0.0039</td>
</tr>
<tr>
<td>1.43</td>
<td>0.05</td>
<td>10^{12}</td>
<td>0.0038</td>
</tr>
<tr>
<td>1.33</td>
<td>0.10</td>
<td>10^{14}</td>
<td>0.005</td>
</tr>
<tr>
<td>1.38</td>
<td>0.10</td>
<td>10^{14}</td>
<td>0.0059</td>
</tr>
<tr>
<td>1.43</td>
<td>0.10</td>
<td>10^{14}</td>
<td>0.0065</td>
</tr>
<tr>
<td>1.33</td>
<td>0.20</td>
<td>10^{12}</td>
<td>0.044</td>
</tr>
<tr>
<td>1.38</td>
<td>0.20</td>
<td>10^{12}</td>
<td>0.04</td>
</tr>
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<td>1.43</td>
<td>0.20</td>
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<td>0.039</td>
</tr>
<tr>
<td>1.33</td>
<td>0.30</td>
<td>10^{12}</td>
<td>0.158</td>
</tr>
<tr>
<td>1.38</td>
<td>0.30</td>
<td>10^{12}</td>
<td>0.139</td>
</tr>
<tr>
<td>1.43</td>
<td>0.30</td>
<td>10^{12}</td>
<td>0.124</td>
</tr>
</tbody>
</table>

Table 1. The ratio of divacancies to monovacancies frozen-in at low temperatures after a quench from \( T_{q} \) for a closed system of monovacancies and divacancies with \( E_{1v}^{m} = 1.38 \) eV and \( S_{2v}^{b} = 0 \) for various values of the parameters \( \nu \) and \( E_{2v}^{b} \).

listed in Table 1(a) demonstrate that for \( E_{1v}^{m} = 1.33–1.43 \) eV (\( \nu = 10^{13} \text{sec}^{-1} \)), the ratio \( c_{2v}/c_{1v} \) is rather insensitive to the value of \( E_{1v}^{m} \) when compared to its strong dependence on \( E_{2v}^{b} \). Thus, it is concluded that it is satisfactory procedure for the purposes of Section 2 to employ one set of "best" values (\( E_{1v}^{m} = 1.38 \) eV and \( \nu = 10^{13} \text{sec}^{-1} \)) for the calculation of \( c_{2v}/c_{1v} \) as a function of \( E_{2v}^{b} \).

To emphasize the strong effect of \( E_{2v}^{b} \) on the ratio \( c_{2v}/c_{1v} \) at constant \( \nu \) and \( S_{2v}^{b} \), we have plotted this ratio in Fig. 2 as a function of \( T(\text{C}) \) for \( E_{1v}^{m} = 1.38 \) eV, \( S_{2v}^{b} = 0 \) and \( \nu = 10^{12} \text{sec}^{-1} \). Figure 2 illustrates the following three important characteristics of a quench:

1. At elevated temperatures, during a rapid quench, the assembly is able to maintain itself in a quasi-equilibrium state and the ratio \( c_{2v}/c_{1v} \) obeys the
The ratio of divacancy to monovacancy concentration \( c_{2v}/c_{1v} \) vs. temperature during a quench from 1700°C for various values of \( E_{2vb} \) is shown in Fig. 2. The curves were calculated using equations (1)–(7) for a closed system of monovacancies and divacancies for an experimental quenching rate which was given by equation (8). The total concentration employed was the value of 2.64 \( \times \) 10^{-4} at. fr. reported in Part I.

The second step in the thermal history consisted of the specimen storage in bulk form at ~20°C (see Fig. 1) for a maximum period of 30 days. Prior results of isochronal recovery experiments on bulk specimens quenched from 1700°C indicated that there were no appreciable losses of vacancies to sinks until ~180°C (see Jackson’s Fig. 7 and Schumacher et al.’s). Hence, it was concluded that the specimen storage in bulk form at room temperature did not cause a change in the value of \( c_{2v}/c_{1v} \) frozen in at \( T^* \).

The differential equations governing the redistribution of monovacancies and divacancies are given by equations (1) and (2) with the \( K_1 \)’s described by equations (3) and (4). The quantity \( c_{2v} \) can be eliminated from equation (1) employing equation (6) to obtain

\[
\frac{1}{2K_1} \frac{dc_{1v}}{dt} = \left( c_{1v} + \frac{K_2}{4K_1} \right)^2 - \alpha^2
\]

where

\[
\alpha^2 = \frac{(K_2^2 + 8K_1K_1')}{16K_1}
\]

Next, making the substitution

\[
u = c_{1v} + \frac{K_2}{4K_1}
\]

and casting the differential equation in integral form yields

\[
\int_{u^*}^{u(t)} \frac{du}{u^2 - \alpha^2} = -2K_1 \int_0^t dt
\]

where the quantity \( u^* \) at \( t = 0 \) is determined from the value of \( c_{1v} \) at \( T^* \) (see Fig. 2). The integration of equation (13) yields

\[
c_{1v}(t) = \left[ 1 + \frac{(u^* - \alpha)}{(u^* + \alpha)} \exp (-4\alpha K_1t) \right] \left[ 1 - \frac{(u^* - \alpha)}{(u^* + \alpha)} \exp (-4\alpha K_1t) \right]^{-\frac{K_2}{4K_1}}
\]

for the time dependence of \( c_{1v} \) at constant \( T \) and \( c_t \).

Equation (14) was evaluated at \( T = 20°C \) for \( c_t = 2.64 \cdot 10^{-4} \) at.fr., \( E_{1v}^m = 1.38 eV, \nu = 10^{13} \text{sec}^{-1} \) and for \( E_{2v}^b = 0.40, 0.30, 0.20, 0.10 \text{ and } 0.05 \text{ eV}. \)

The calculations showed that there was absolutely no redistribution of the monovacancy–divacancy assembly for a holding time of 30 days at ~20°C. This result held for all five values of \( E_{2vb} \) employed. Hence, it was concluded that the specimen storage in bulk form at room temperature did not cause a change in the value of \( c_{2v}/c_{1v} \) frozen in at \( T^* \).
2.3 Redistribution of an open assembly of monovacancies and divacancies during the electropolishing procedure

The third stage in the thermal history (see Fig. 1) of one group of specimens consisted of the preparation of a sharply pointed tip (~100 Å radius) by electropolishing at ~20°C and subsequent storage at either ~20 or ~50°C (see Section 2.3.2 in Part I). As a result a surface was introduced which was in the immediate vicinity of the monovacancy-divacancy population which was subsequently examined by the FIM pulse dissection technique. Thus, monovacancies and divacancies may have diffused out of the sharply pointed tip to its surface during the electropolishing and subsequent storage. In order to analyze this possibility quantitatively, a model was constructed based on the following assumptions:†

1. The FIM tip was approximated by a sphere of radius $R$.
2. The surface of the sphere was the only sink present for both monovacancies and divacancies and it maintained the defect concentrations in local equilibrium during the holding period.
3. The initial distribution of monovacancies and divacancies was uniform throughout the tip.
4. The initial value of $c_1$ was taken as the experimental value of $2.64 \times 10^{-4}$ at.fr.
5. The concentration gradient had no angular dependence.

The coupled nonlinear partial differential equations governing this situation are:

$$\frac{\partial c_{1v}}{\partial t} = D_{1v} \left[ \frac{\partial^2 c_{1v}}{\partial r^2} + \frac{2}{r} \frac{\partial c_{1v}}{\partial r} \right] - 2K_1c_{1v}^2 + 2K_2c_{2v}$$

$$\frac{\partial c_{2v}}{\partial t} = D_{2v} \left[ \frac{\partial^2 c_{2v}}{\partial r^2} + \frac{2}{r} \frac{\partial c_{2v}}{\partial r} \right] - K_1c_{1v}^2 - K_2c_{2v}$$

where the $K_n$'s are defined by equations (3) and (4) and the $D_{1v}$'s and $D_{2v}$'s by:

$$D_{1v} = a^2 \nu_{1v} \exp \left(-E_{1v}^m/kT \right)$$

$$D_{2v} = a^2 \nu_{2v} \exp \left(-E_{2v}^m/kT \right)$$

where $a$ is the lattice parameter, and $\nu_{1v}$ and $\nu_{2v}$ are the frequency factors for monovacancy and divacancy migration respectively which include entropy of migration terms. Equations (15) and (16) were solved numerically on a computer at fixed values of $R$ and $T$ to obtain $c_{1v}(r, t)$ and $c_{2v}(r, t)$. These latter quantities were then integrated over the volume of the sphere to obtain their mean values as a function of holding time at a particular $T$. The following values of the variable parameters were employed: $E_{1v}^m = 1.38$ eV, $\nu_{1v} = \nu_{2v} = 10^{13}$ sec$^{-1}$, $E_{2v}^b = 0.40$, 0.30, 0.20, 0.10 and 0.05 eV and $S_{2v}^b = 0$. These values are identical to those used previously in Sections 2.1 and 2.2. The only additional parameter to be specified was $E_{2v}^m$. A value of 1.11 eV for $E_{2v}^m$ has been suggested by both Jackson$^7$ and Schumacher et al.$^8$, although effective energies as low as ~1.0 eV have been measured in recovery experiments for specimens quenched from near the melting point (Pollak$^9$ and Schumacher et al.$^8$).

In view of this all calculations were performed for $E_{2v}^m$ equal to both 1.11 and 1.0 eV, even though it is highly probable that 1.0 eV does not correspond to the migration energy of the divacancy.

Some of the calculated results are given in Fig. 3 which shows plots of the normalized ratio $c_{2v}(t)/c_{2v}(0)$ vs. time at 20°C for the two values of $E_{2v}^m$ for a specimen with a 100 Å tip radius. The initial values of $c_{1v}$ and $c_{2v}$ were obtained from Fig. 2. The following results were obtained at 20°C:

1. For $E_{2v}^m = 1.11$ eV the initial value of $c_{2v}$ decreased by only ~4.5 per cent (see Fig. 3) and $c_{1v}$ remained completely unchanged after a total holding time of 600 hr.
2. For $E_{2v}^m = 1.0$ eV the initial value of $c_{2v}$ decreased by ~51.5 per cent (see Fig. 3) and $c_{1v}$ remained unchanged after a total holding time of 600 hr.
3. The percentage decrease in $c_{2v}$ for both values of $E_{2v}^m$ was independent of $E_{2v}^b$ (see Fig. 3).

At $T = -50°C$ the calculations showed that:

† It is readily shown (see next section) that any losses which occurred during the relatively short electropolishing period were negligible and that we need consider only the storage period after the tip was formed.
both $c_{1v}$ and $c_{2v}$ were completely unchanged after a total holding time of 600 hr for $E_{2v}^m$ equal to either 1.11 and 1.0 eV. In terms of the experimental results (Table 3 in Part I) this implied that for specimens 7 and 8 the measured value of $c_{1v}/c_{1e}$ was characteristic of that at $T^*$. For specimen 6 (Table 3 in Part I) the possibility arises that if $E_{2v}^m$ is as small as 1.0 eV, then there would have been a zone denuded of divacancies next to the original electropolished surface. But it is noted that $\sim 50-100 \, \AA$ of material was removed from this specimen during the low temperature field evaporation process which was used to bring the tip to its final end form. Hence, the denuded material was probably removed prior to the pulse dissection examination for vacancies. Thus, it is believed that even for the improbable case of $E_{2v}^m = 1.0 \, \text{eV}$, the material examined for vacancies had a value of $c_{2v}$ which was close to that present originally at $T^*$. We note that the experimental result that there are no significant differences between the divacancy concentrations measured in specimens 6-8 (Table 3 in Part I) is consistent with this conclusion.

2.4 Redistribution of an open assembly of mono vacancies and divacancies during the electropolishing procedure A

The situation during electropolishing procedure A was more complicated, since appreciable defect redistribution may have occurred during the relatively high temperature electropolish.

We first show that rapid redistribution without losses occurred during electropolishing in regions well away from the surface and that a quasi-equilibrium monovacancy–divacancy population typical of the electropolishing temperature must have been established in those regions. Equation (13) was used to calculate the time required to reach the quasi-equilibrium values of $c_{1v}$ and $c_{2v}$ at 325°C for $c_{1} = 2.64 \times 10^{-4}$ at.fr. The times required were $\sim 6-7$, $\sim 2$, <1 and <1 sec for $E_{2v}^m$ equal to 0.40, 0.30, 0.20 and 0.10 eV, respectively. Since each of these times is less than, or equal, to the shortest total polishing time at 325°C or greater (see Table 2 of Part I), it can be assumed that in the absence of any diffusional losses to sinks the assembly achieved quasi-equilibrium conditions for all values of $E_{2v}^m$ considered.

We next attempt to estimate the losses which occurred to the surface during the electropolishing operation which consisted of periodically dipping the sharply tipped specimen into the molten salt bath to a depth of approximately 1 mm. Each “dip” consisted of rapidly inserting the specimen into the bath and then quickly removing it after a period of time that was less than 1 sec. A relatively large amount of material was removed in each dip and after a considerable number of dips a satisfactory specimen tip was obtained. Satisfactory tips were generally obtained by this procedure after a total immersion time of 5–30 sec.

Since the defects became sufficiently mobile to escape from the tip at temperatures near the bath temperature of 325°C, it becomes necessary to estimate the amount of defect migration which could have occurred during the complex heating and cooling history of the specimen tip during the periodic dipping process.

First of all, it is easily shown that no significant losses could have occurred to the surface while the specimen tip was immersed in the salt bath during the polishing. During this period the surface was moving rapidly inwards due to the removal of material by the electropolishing. For this situation we employ an approximate model consisting of a semi-infinite region possessing a flat surface which is moving inward with a constant normal velocity, $v$. Each defect is assumed to diffuse independently, i.e. defect interactions are ignored. (This latter approximation is justified by the results below.) Taking the situation in the steady state at 325°C, it may be shown$^{190}$ that the widths of the zones denuded of monovacancies or divacancies are given approximately by

$$\bar{x}_{1v} = \frac{D_{1v}}{v},$$

and

$$\bar{x}_{2v} = \frac{D_{2v}}{v}.$$  (20)

The velocity $v$ was measured experimentally and was found to be $\gtrsim 2 \times 10^{-4} \, \text{cm sec}^{-1}$. Using the previous expressions for the defect diffusivities, equations (19) and (20) predict denuded zones of negligible width; i.e. $\bar{x}_{1v}$ and $\bar{x}_{2v}$ are of the order of a few angstroms or less.

The only remaining source of denudation is therefore the defect loss which could have occurred to the fixed surface during the time that the specimen tip cooled down from 325°C in air after its sudden removal from the salt bath following its final “dip”. An approximate treatment of this problem has been given elsewhere$^{190}$ and we shall only summarize the results here. Computer calculations of the thermal history of the specimen tip during the cooling period were first carried out. The width of the denuded zone for either defect was then estimated by integrating
the defect diffusion distance over $t$ according to

$$\bar{x}_{1v} = 2[\int D_{1v}(t) \, dt]^{1/2};$$

(21)

and

$$\bar{x}_{2v} = 2[\int D_{2v}(t) \, dt]^{1/2};$$

(22)

Calculations based upon equation (21) indicate negligible denudation for the slower diffusing monovacancy. However, equation (22) predicted denudation widths for the faster diffusing divacancies as large as several hundred angstroms and we therefore predict that appreciable divacancy losses may have occurred.

The experimental results appear to be in qualitative agreement with the above predictions. Only one divacancy was detected among the 321,298 sites examined in the specimens prepared by procedure $A$ (see Table 2 in Part I). This should be contrasted with the 8 divacancies detected among the 593,794 sites examined (see Table 3 in Part I) in the specimens prepared by procedure $B$.

It is concluded generally that the ratio $c_{2v}/c_{1v}$ measured for the specimens polished by procedure $A$ (Nos. 1–5 in Table 2 of Part I) was not characteristic of the value frozen-in at $T^*$ during a quench, but that its value was appreciably decreased as a result of preferential diffusional losses of divacancies to the surface during the high temperature polishing treatment (see Fig. 1). Furthermore, we conclude that our combined calculations and experimental results are completely consistent with a divacancy which is more mobile than the monovacancy as discussed in Part I.

3. THE DIVACANCY BINDING ENERGY

The results of the calculations presented in Section 2 demonstrate that the quenched-in value of $c_{2v}/c_{1v}$ determined for specimens 6–8 (Table 3 in Part I) can be used to determine $E_{2v}^b$ via the method discussed in Section 2.1. All the calculations performed up to this point were made on the basis of an assumed value of $S_{2v}^b = 0$, but it is clear that the equilibrium value of $c_{2v}/c_{1v}$ at $T_e$, as well as the quenched-in value at room temperature, is really determined by $G_{2v}^b$. Hence, a search was made for all possible combinations of $E_{2v}^b$ and $S_{2v}^b$ which gave a quenched-in value of $c_{2v}/c_{1v} = 0.06$ for the parameters $c_{1v}^* = 2.64 \cdot 10^4$ at.fr., $E_{1v}^m = 1.38$ eV and $\nu = 10^{12}$ sec$^{-1}$. Some typical results are shown in Fig. 4, for $E_{2v}^b = 0.40$, 0.23, 0.11 and 0.05 eV. These calculations showed that the following linear relationship exists between $E_{2v}^b$ and $S_{2v}^b$,

$$E_{2v}^b = \left[ (0.23 \pm 0.03) + 6.17 \cdot 10^{-2} \left( \frac{S_{2v}^b}{k} \right) \right] \text{eV},$$

(23)

which is shown plotted in Fig. 5 for a wide range of possible values of $E_{2v}^b$ and $S_{2v}^b$.

4. DISCUSSION

4.1 The relationship between the divacancy binding energy ($E_{2v}^b$) and binding entropy ($S_{2v}^b$)

The linear relationship between $E_{2v}^b$ and $S_{2v}^b$ obtained in Section 3 implies that for all combinations, of these two quantities which lead to a fixed $c_{2v}/c_{1v}$ for a quench from a single temperature $G_{2v}^b$ is a constant which is characteristic of a single $T^*$. This can be seen by noting that under the above conditions equation (5) reads

$$G_{2v}^b(T^*) + T^*S_{2v}^b(T^*) = \text{const.}$$

(24)

Hence, a simple calculation showed that $T^* = 443$°C and that $G_{2v}^b(443)$°C = 0.23 eV for our experiments. We note that the further decomposition of $G_{2v}^b$ into $E_{2v}^b$ and $S_{2v}^b$ terms requires a knowledge of a second value of $G_{2v}^b$ for a different $T^*$. This could be accomplished experimentally by quenching from the same $T_q$ at a faster quenching rate than the one employed or alternatively quenching from a different $T_e$. The main experimental problem with the latter procedure would involve obtaining a statistically significant value of $c_{2v}/c_{1v}$ if $T_q$ were decreased appreciably below 1700°C.

There have been no experimental determinations, to date, of $S_{2v}^b$ for any metal and the theoretical situation is in a rather uncertain state. Schottky
S?&k

Fig. 5. The divacancy binding energy ($E_{2v}^b$) vs. the quantity $S_{2v}^b/k$ where $S_{2v}^b$ is the divacancy binding entropy and $k$ is Boltzmann's constant. The linear relationship between $E_{2v}^b$ and $(S_{2v}^b/k)$ was obtained from Fig. 4 by finding the locus of all combinations of $E_{2v}^b$ and $S_{2v}^b$ which lead to a value of $c_{2v}/c_{1v} = 0.06$ at room temperature.

et al.\textsuperscript{(11)} have calculated values of $S_{2v}^b$ for copper, silver and gold of $-1.8k$, $-1.8k$ and $-2.2k$, respectively. Burton\textsuperscript{(12)} has employed a method originally developed by Land and Goodman\textsuperscript{(13)} to calculate $S_{2v}^b$ for a divacancy in solid argon and obtained a value of 0.34$k$. In addition, Burton\textsuperscript{(14)} has criticized the Einstein approximation employed by Schottky et al. in their calculations of $S_{2v}^b$ for the noble metals. In view of this controversial theoretical situation we have chosen not to decompose our measured value of $G_{2v}^b$ on the basis of a theoretical value for $S_{2v}^b$.

4.2 A re-examination of the tracer diffusion data in terms of a monovacancy and divacancy model

The only equilibrium data involving vacancy type defects available for platinum are the results of two high temperature tracer diffusion experiments. The first of these experiments was performed by Kidson and Ross\textsuperscript{(15)} using the sectioning technique\textsuperscript{(16)} and they obtained the following expression for the tracer diffusion coefficient ($D_T$)

$$D_T = 0.33 \exp (-2.96 \pm 0.06 \text{ eV}/kT) \text{ cm}^2 \text{sec}^{-1}$$

in the temperature range 1325–1600°C (see Fig. 6). The second experiment was performed by Cattaneo et al.\textsuperscript{(17)} in the temperature range 1250–1725°C (see Fig. 6) employing the residual surface activity technique.\textsuperscript{(18)} They obtained a value of

$$D_T = (0.22 \pm 0.03) \exp (-2.89 \text{ eV}/kT) \text{ cm}^2 \text{sec}^{-1}$$

from their data. Both of these sets of data are plotted in Fig. 6 and it is noted that the overall extent and quality of the combined data are not particularly good when compared, for example, to the self-diffusion data for gold (see Wang et al.'s\textsuperscript{(18)} Fig. 12 and Seeger and Mehrer's\textsuperscript{(19)} Fig. 1). Peterson in his review article\textsuperscript{(20)} favors the Kidson and Ross data over the Cattaneo et al. data and in a conversation with the authors Peterson has made the point that the vast majority of the inaccurate tracer diffusion experiments have employed the residual surface activity technique. In view of these facts, we regard as unsatisfactory the fitting of these data to a common curve with equal weight given to each data point.

We have discussed the tracer diffusion data in some detail, since Schumacher et al.\textsuperscript{(18)} have analyzed the combined data discussed above in terms of a monovacancy and divacancy defect model. They suggest that the data exhibit a "slight curvature in the Arrhenius plot" and attribute this "nonlinearity on the high-temperature side" to the "divacancy contribution of self-diffusion and a temperature dependence of the activation energies and entropies". While we agree that divacancies can make a contribution to self-diffusion at elevated temperatures, we do not feel that the existing tracer diffusion data provide any reliable evidence for curvature in the Arrhenius plot or furthermore allow a decomposition of $G_{2v}^b$ into values of $E_{2v}^b$ and $S_{2v}^b$.

The conclusion that the existing tracer diffusion data are not precise enough to allow a reliable determination of $E_{2v}^b$ and $S_{2v}^b$ was demonstrated by calculating $D_T$ for the parameters suggested by Schumacher et al. and other sets of $E_{2v}^b$ and $S_{2v}^b$ values consistent with our equation (23). [We note that the parameters suggested by Schumacher et al. are consistent with equation (23) within the estimated experimental error of 0.03 eV.] The expression for $D_T$ in terms of a monovacancy and divacancy defect model including a temperature dependence of the activation energies and entropies (see Seeger and Mehrer\textsuperscript{(21)} for a review of this subject) is given by

$$D_T = D_{10} \exp \left( \frac{-Q_1}{kT} \right) \exp \left[ 2x \ln \left( \frac{T}{T_0} \right) \right] \exp \left[ -2x \left( \frac{T - T_0}{T} \right) \right] \left[ 1 + D_{21} \exp \left( \frac{-Q_{21}}{kT} \right) \right]$$

\[ (27) \]
Fig. 6. The tracer diffusion coefficient ($D_T$) vs. $(1/T) \text{K}^{-1}$ for all data available for platinum. The solid curves were calculated for a monovacancy and divacancy defect model which included a temperature dependence of the activation energies and entropies, and was described by equations (27)-(34). The values of the different parameters employed to calculate $D_T$ for the various sets of $E_{2v}^b$ and $S_{2v}^b$ are listed in Table 2.

where

$$D_{10} = a v_{1v}^0 f_{1v}^0 \exp \left( \frac{S_{1v}^m}{k} \right) \exp \left( \frac{S_{1v}^f}{k} \right),$$  \hspace{1cm} (28)

$$Q_1 = E_{1v}^f + E_{1v}^m$$  \hspace{1cm} (29)

$$\alpha = \frac{1}{2}(\alpha_m + \alpha_F)$$  \hspace{1cm} (30)

$$Q_{21} = E_{1v}^f - E_{1v}^m + E_{2v}^m - E_{2v}^b,$$  \hspace{1cm} (31)

and

$$D_{21} = \frac{4f_{2v}^b}{f_{1v}} \exp \left( \frac{S_{2v}^f - S_{2v}^b}{k} \right) \frac{v_{2v}^0}{v_{1v}^0} \exp \left( \frac{S_{2v}^m}{k} \right) \exp \left( \frac{S_{2v}^f}{k} \right).$$  \hspace{1cm} (32)

The $f_{1v}$ are the correlation factors for tracer diffusion ($f_{1v} = 0.781^{(22)}$ and $f_{2v} = 0.475^{(23)}$), $S_{2v}^m$ the entropies of migration, $v_{2v}^0$ the frequency factors and $\frac{1}{2}(\alpha_m + \alpha_F)$ the temperature dependence of the migration and formation energies and entropies. The expressions used for the temperature dependence of the energies and entropies are identical to the ones employed by Schumacher et al. and are given by expressions of the form

$$E(T) = E(T_0) + a k(T - T_0),$$  \hspace{1cm} (33)

and

$$S(T) = S(T_0) + a k \ln \left( \frac{T}{T_0} \right)$$  \hspace{1cm} (34)

where $T_0$ is a reference temperature which was set equal to 300°K. The quantity $\alpha$ was assumed to be identical for both monovacancies and divacancies.

The values for the different sets of the five variables [equations (28) and (32)] used to calculate $D_T$ are listed in Table 2. The fourth column contains the best values given by Schumacher et al., and the remaining columns are for other values of $E_{2v}^b$ and $S_{2v}^b$ which are consistent with our equation (23).

It is noted that changing $E_{2v}^b$ and $S_{2v}^b$ only affects $Q_{21}$ and $D_{21}$ in equation (27), and, as seen below, the
### Table 2. Values of the five basic parameters of the monovacancy and divacancy defect model for different combinations of $E_{zvb}^b$ and $S_{zvb}^b$

<table>
<thead>
<tr>
<th>$E_{zvb}^b$ (eV)</th>
<th>$S_{zvb}^b$</th>
<th>$D_{11}$ (cm$^2$ sec$^{-1}$)</th>
<th>$Q_1$ (eV)</th>
<th>$S_{zvb}^b$</th>
<th>$D_{11}$ (eV)</th>
<th>$S_{zvb}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0†</td>
<td>-3.72k</td>
<td>0.14</td>
<td>2.87</td>
<td>0.14</td>
<td>118.46</td>
<td>0.14</td>
</tr>
<tr>
<td>0.08†</td>
<td>-2.925k</td>
<td>0.14</td>
<td>2.87</td>
<td>0.14</td>
<td>54.33</td>
<td>0.14</td>
</tr>
<tr>
<td>0.11†</td>
<td>-2.5k</td>
<td>0.14</td>
<td>2.87</td>
<td>0.14</td>
<td>35</td>
<td>0.14</td>
</tr>
<tr>
<td>0.15†</td>
<td>-1.3k</td>
<td>0.14</td>
<td>2.87</td>
<td>0.14</td>
<td>10.53</td>
<td>0.14</td>
</tr>
<tr>
<td>0.23†</td>
<td>0.0k</td>
<td>0.14</td>
<td>2.87</td>
<td>0.14</td>
<td>0.82</td>
<td>0.14</td>
</tr>
<tr>
<td>0.4†</td>
<td>2.75k</td>
<td>0.14</td>
<td>2.87</td>
<td>0.14</td>
<td>0.187</td>
<td>0.14</td>
</tr>
</tbody>
</table>

† The values of $E_{zvb}^b$ and $S_{zvb}^b$ in this column are consistent with equation (23).

The values in this column are from Table 2 of Schumacher et al.†† [We note that the $E_{zvb}^b$ and $S_{zvb}^b$ values are consistent with equation (23) within the estimated experimental error of 0.03 eV.] There appear to be two arithmetic errors in Schumacher et al.'s Table 2. The first one is that the values which they list for $v_{zvb}$ exp ($S_{zvb}^b/k$) and $S_{zvb}^b/k$ are not consistent with $D_{11} = 0.14$ cm$^2$ sec$^{-1}$. The second one is that the value of $D_{11}$ calculated from the listed quantities which comprise this expression [equation (32)] does not correspond to 35. Nevertheless, we have taken $D_{11} = 0.14$ cm$^2$ sec$^{-1}$ and $D_{21} = 35$.

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**Fig. 7.** The tracer diffusion coefficient ($D_T$) vs. $(1/T^\circ K)$ in the temperature range 1665–1769°C (the melting point). The calculated curves for $D_T$ are for a monovacancy and divacancy model described by equations (27)–(34) employing various sets of $E_{zvb}^b$ and $S_{zvb}^b$ values which are consistent with equation (23). This temperature range is an extremely important one with respect to the monovacancy–divacancy defect model, since it is the regime which is the most sensitive to the values of $E_{zvb}^b$ and $S_{zvb}^b$.

The tracer diffusion coefficient ($D_T$) in going from the values $E_{zvb}^b = 0.4$ eV and $S_{zvb}^b = -2.75k$ to $E_{zvb}^b = 0$ and $S_{zvb}^b = -3.72k$ is only <11 per cent, hence values of $D_T$ accurate to better than 5 per cent between $\sim 1600^\circ$C and $T_m$ would be extremely useful in decomposing $G_{2v}^b$. Figures 6 and 7 show that in this crucial regime there is a paucity of data and that the absolute values of $D_T$ which are available in this important high temperature regime have an absolute accuracy of only ±13.6 per cent [equation (26)]. In view of this situation we must conclude that the existing data for $D_T$ are not sufficiently accurate to allow a significant decomposition of $G_{2v}^b$ into $E_{zvb}^b$ and $S_{zvb}^b$ terms.

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REFERENCES