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► **To cite this version:**

M. Wada. ON THE THERMALLY ACTIVATED FIELD EVAPORATION OF SURFACE ATOMS. Journal de Physique Colloques, 1984, 45 (C9), pp.C9-89-C9-94. 10.1051/jphyscol:1984916 . jpa-00224394

HAL Id: jpa-00224394

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Submitted on 4 Feb 2008

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ON THE THERMALLY ACTIVATED FIELD EVAPORATION OF SURFACE ATOMS

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Résumé - La dépendance thermique des champs d'évaporation des métaux dans une gamme de 20 K à 150 K a été examinée en termes de processus d'activation thermique.

Abstract - Temperature dependence of the evaporation fields of metals in a range from 20 K to 150 K was examined in terms of the thermally activated process.

Surface atoms of metals are desorbed by a high positive electric field. This is known as the field evaporation and it can be directly observed by a field ion microscope. In a previous study /1/, the temperature dependence of the evaporation field was examined in a range from 20 K to 150 K for Fe, Ni, Cu and Pd by directly observing the evaporation of atomic planes. However, when the obtained dependence was incorporated with the charge-exchange model of the field evaporation /2/, unrealistically large activation energies were resulted. In this study, this problem was examined further and a possibility of a short-range surface migration of atoms prior to the evaporation as a rate-controlling process was discussed. A full account of this study will be published in Surface Science.

Fig. 1 shows the temperature dependence of the evaporation field normalized to the extrapolated value at 0 K. In the experiment, the corresponding applied voltage was determined by observing the evaporation of atomic planes at a constant rate of 0.1 layer/s in the FIM. Imaging gases were about 10^{-2} Pa of He for W and Ir and about 10^{-2} Pa of Ne for Fe, Ni, Cu and Al.

When a thermal activation is considered for the evaporation process, activation energy of an n-fold-charged ion, Q_n , can be given by

$$Q_n = k \cdot \ln(\gamma_0/\gamma) \cdot T, \quad (1)$$

where k is the Boltzmann's constant, γ_0 the pre-exponential, γ the evaporation rate-constant and T temperature. The evaporation rate, J (layers/s), on a specified plane is related to γ by $J = n_{hr} \cdot \gamma$, where n_{hr} is the amount of materials at high risk of evaporation which is assumed to be of the order of 0.01 layers /3/. Since $J = 0.1$ layer/s, γ in the present case will be about 10/s. In the charge-exchange model, Q_n can be expressed by

$$Q_n = \Lambda + \Sigma I_n - n\phi + (1/2)(\alpha_a - \alpha_i)F^2 - neFx_c - n^2e^2/16\pi\epsilon_0x_c \quad (2)$$

where Λ is the binding energy of a surface atom, ΣI_n the total ionization energy, ϕ the work function, F the applied field, x_c the position at which the ionic potential curve intersects the atomic curve under F , α_a and α_i the effective polarizabilities for the atomic and ionic

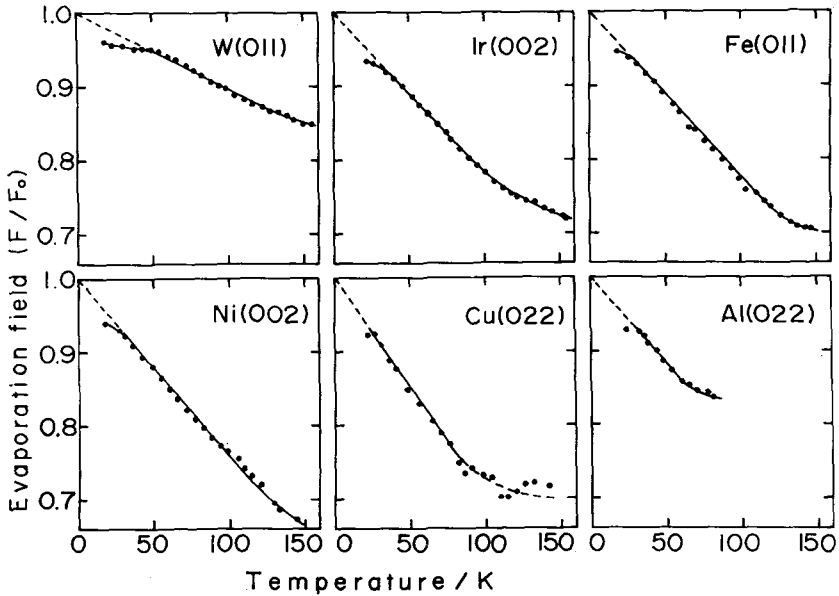


Fig. 1 - Temperature dependence of the applied field for the evaporation of atomic planes at 0.1 layer/s.

states, respectively and ϵ_0 the electric constant. In the model, one expects that x_c depends on F and we first examine the F dependence of x_c and discuss the atomic potential curve deduced from the dependence.

From the linear temperature dependence of F in Fig. 1, we assume $F = F_0 - \theta T$, where F_0 is the evaporation field for $Q_n = 0$, and $\theta \equiv -(\partial F / \partial T)_J$ which is constant. If γ_0 is constant, x_c is expressed as,

$$x_c = (2neF)^{-1} \left\{ [K_n - s(F_0 - F)] + \{ [K_n - s(F_0 - F)]^2 - n^3 e^3 / 4\pi\epsilon_0 \}^{1/2} \right\}, \quad (3)$$

where $s \equiv k \cdot \ln(\gamma_0 / \gamma) / \theta$, $K_n = \Lambda + \Sigma I_n - n\phi + 1/2(\alpha_a - \alpha_i)F^2$ and F_0 is a smaller value of the solutions of an equation $(K_n)^2 = n^3 e^3 F / 4\pi\epsilon_0$. We take Ni for an example and consider the relation between x_c and $Q_n^{1/2}$ which is $s(F_0 - F)$, using the experimental value of s where $\gamma_0 \approx 10^{12}$ /s is assumed and θ is estimated by the experimental value of F at 78 K /4/. Values of Λ , ΣI_n and ϕ are those listed by Tsong /5/. In Fig. 2, $Q_n (= s(F_0 - F))$ is plotted against x_c for $n = 2$ and for various values of $\alpha (= (\alpha_a - \alpha_i) / 4\pi\epsilon_0)$. In the figure, each curve has been slightly shifted horizontally assuming that the potential minimum of the atomic curve is at a_0 , the atomic radius. Fig. 2 should directly reflect the atomic potential curve. Since $F(78K) = 32$ V/nm /4/, the expected value of F_0 should be about 40 V/nm from Fig. 1. If eq. (2) is solved for $Q_n = 0$, one can show that α should be somewhere between 1×10^{-3} and 2×10^{-3} nm³ for $F_0 = 40$ V/nm. Therefore the expected atomic potential curve deduced from the obtained temperature dependence of the field in Fig. 1 should lie between curves B and C. The dashed curve M is an atomic potential of a Ni atom on the Ni(002) plane calculated by Morse potential /6/. It is clear that curves based on eq. (3) with the experimental value of s do not agree with the expected potential curve M. Although the case for $n = 1$ was also calculated, no satisfactory agreement was obtained.

The disagreement shown above is mainly due to the observed large value

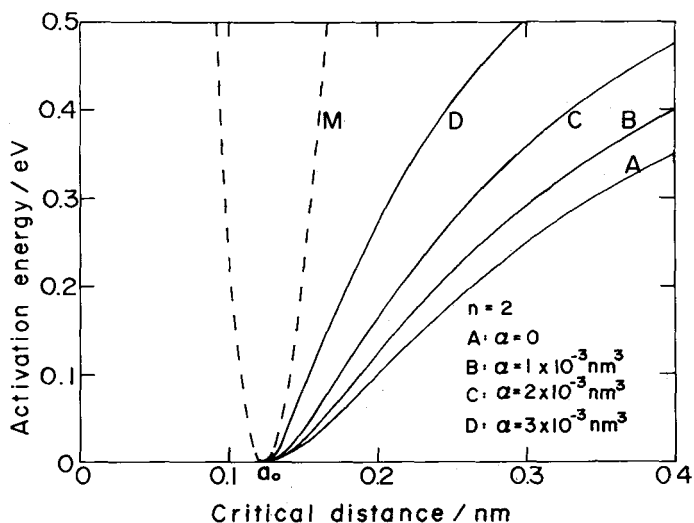


Fig. 2 - Relation between Q_n and x_C for Ni with $n = 2$ calculated by eq. (3). The dashed curve M is an atomic potential curve of a Ni atom on the Ni(002) plane calculated by assuming Morse potential. The potential minimum is placed at a_0 for comparison.

of θ which gives a large and quite unrealistic value of Q_n , when Q_n is estimated by

$$Q_n = (dQ_n/dF)(-\theta)T. \quad (4)$$

Since Q_n is proportional to T , (dQ_n/dF) should be constant. According to Forbes /7/, $x_C \approx a_0 F_0 / F$. Using this and from eq. (2), we have,

$$dQ_n/dF = -n^2 e^2 / 16 \pi \epsilon_0 a_0 F_0 + (\alpha_a - \alpha_i) F. \quad (5)$$

Since this is supposed to be constant, we neglect the last term. It can be shown that this does not affect the following argument. Another possibility for the constant (dQ_n/dF) is to assume a constant x_C as,

$$dQ_n/dF = -n e x_C, \quad (5)$$

where the polarization term is again neglected. The activation energies at 78 K estimated by eq. (4) using eq. (5) and eq. (6) are 2.2 eV and 1.9 eV, respectively, for Ni with $n = 2$. For $n = 1$, they are 0.6 eV and 1.0 eV at 78 K. In eq. (6), it is assumed that $x_C = a_0$. These values are too large and quite unrealistic, since the expected Q_n at 78 K would be about 0.17 eV by eq. (1) for $\ln(\gamma_0/\gamma) \approx 25$. When Q_n is estimated similarly by eq. (4) for other metals shown in Fig. 1, large values are also obtained. Thus it is demonstrated here that the temperature dependence shown in Fig. 1 can not be described adequately by eq. (2) which is based on the charge-exchange model.

The obtained large Q_n is the result of a large value of $(dQ_n/dF)(-\theta)$ in eq. (4). Therefore we look for a process which gives a smaller value of $-(dQ_n/dF)$. It has been known that under applied field atoms move on the surface /8-11/. It was shown that the evaporation probability is higher at low-coordination sites /12/. We consider now that the short-range migration of atoms from a high to low coordination site is the rate-controlling. The controlling process would be the migration of about one atomic distance just before the evaporation. Since the evaporation of atomic planes, as in the present experiment, takes place at the edge of the plane, the possible rate-controlling migration paths would be those schematically shown in Fig. 3. Among the considered paths, there should be a predominant path from A to B site

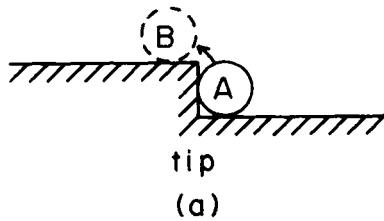
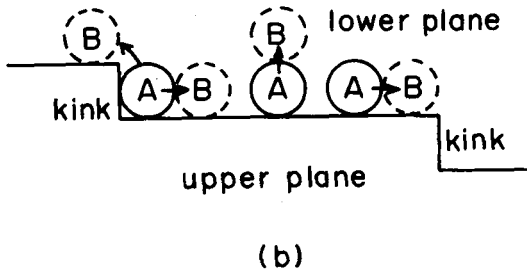


Fig. 3 - (a); Schematic cross-section of an atomic step on the tip surface.

(b); Plan view of a schematic atomic step with kinks on the tip surface. Initially no atoms are at B sites. All the paths are not necessarily the actual migration paths.



which determine the evaporation field. Consider the evaporations directly from the A site and from the B site. Field necessary to remove the atom from A, labelled F^A , would be higher than F^B from B site for the same evaporation rate. If the applied field on A site is between F^B and F^A and if it gives a sufficient rate of migration from A to B, the field-induced migration from A to B occurs and then the atom evaporates from B. Under applied field F , surface atoms experience a force $(\epsilon_0/2)F^2$ per unit area along the field direction. Because of a variation of local field, an atom at A may be moved towards B relative to more strongly bound surrounding atoms, and the work done by the applied field on the atom can be approximated by $\beta(\epsilon_0/2)F^2 \cdot \pi a_0^2 \cdot \delta$ where $\beta (\leq 1)$ is a geometrical factor and δ is the displacement of the atom. Therefore the activation energy will be given by

$$Q^M = (\Lambda_A - \Lambda_S) - \beta(\epsilon_0/2)F^2 \pi a_0^2 \delta, \quad (7)$$

where Λ_A and Λ_S are the zero-field binding energies at A and the saddle point on the reaction path between A and B sites, respectively. Among various paths in Fig. 3, the rate-controlling path should have a value of $(\Lambda_A - \Lambda_S)$ which results in a reasonably value of Q^M in eq.(7). Considering that $Q^M = 0$ at $F = F_0$, $(\Lambda_A - \Lambda_S)$ for the rate-controlling migration would be $\beta(\epsilon_0/2)F_0^2 \pi a_0^2 \delta$. This is about 1.8 eV for W(011) and 0.5 eV for Ni(002) if $\beta \approx 1$ and $\delta \approx 2a_0$ are assumed. We estimate Q^M by (dQ^M/dF) and by observed θ , using eq. (4). The distance from the A site to the saddle position, δ , may decrease with field because the saddle position approaches the site A when the applied field is increased. As it has been discussed earlier, the observed constant θ indicates a linear relation between Q^M and F . Therefore we assume in eq. (7) that $\delta \approx \delta_0 f_0 / F$ in the present field range where δ_0 and f_0 can be regarded as the typical values of δ and the corresponding field. For a rough estimate of (dQ^M/dF) , we also assume $\delta_0 \approx 2a_0$ and this gives,

$$dQ^M/dF \approx -\beta \pi \epsilon_0 a_0^3 f_0. \quad (8)$$

The values of $-(dQ^M/dF)$ estimated by eq. (8) are much smaller than those obtained by eq. (5) or eq. (6) as we have expected. The activation energies estimated from eq. (8) and by the observed θ at 78 K are about 0.1 eV for all the metals examined except Ir for which it is

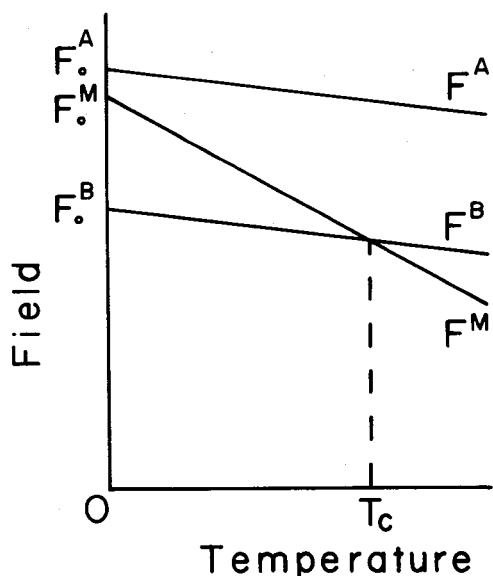


Fig. 4 - Fields for three evaporation processes. F^A and F^B are the fields necessary for the direct field evaporation of atoms from A and B sites in Fig. 3, respectively. F^M is the applied field for the field induced migration of an atom from A to B site.

about 0.2 eV. Here we assumed $\beta \approx 1$. Thus the observed temperature dependence of the evaporation field can be explained more favorably by considering the migration-controlled field evaporation.

In Fig. 4, hypothetical temperature dependences of the applied fields for three processes are compared schematically. Below T_c , the short-range migration is the rate controlling and above T_c , F^B is higher than F^M and the evaporation directly from B becomes the rate-controlling. Thus as long as $F^A > F^M$, migration of atoms is always involved in the evaporation process in the whole temperature range regardless of the rate-controlling process. If F^A and F^M cross at a very low temperature, or if $F^M_0 > F^A_0$, we expect a smaller temperature dependence due to the direct field evaporation from A site below this temperature. At a very low temperature, however, a thermal activation may not be effective and it is not certain at present if the observed smaller temperature dependence below about 30 K shown in Fig. 1 is due to this crossing of F^A and F^M curves.

It must be pointed out here that recently Forbes et al./13/ analyzed the field evaporation of Rh and indicated that the charge-exchange model can describe the evaporation behavior. Further studies seem necessary to clarify the discrepancy and to obtain a true picture of the field evaporation behavior.

The author would like to express his sincere thanks to professor O. Nishikawa for encouragement and discussions and to Mr. R. Uemori and Mr. H. Kita for experimental assistance. He is particularly grateful to Dr. R. G. Forbes for the critical and valuable comments and useful suggestions on this subject.

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