FLUCTUATION METHOD OF CALCULATING THE ABSOLUTE VALUE OF THE BOND ENERGY IN THE CONTACT OF DIFFERENT MEDIA

G. A. Babushkin

UDC 539

The investigations [1, 2], on the basis of the notion and calculations by the author regarding the need to allow for reverse transitions in Eyring's theory [1] and the consideration of vacancy density in the contact of two media [2], presented a method of finding the relative bond strength $\varepsilon = \sigma/\sigma_0$ (σ_0 is the maximum possible bond strength, while σ is the value actually achieved during the time t_0 of effective interaction in the contact during decomposition) between two media in the case where the substrate and particles are made of the same material. The study [3] proposed a method of calculating the absolute value of bond strength in the special case of identical materials for the substrate and particles of a powder. In connection with the importance of creating a strong bond between the coating and the base in plasma deposition, it is of both scientific and practical interest to construct a theory of bonding of two media with different characteristics.

At the initial moment of formation of the contact, the absence of bonds between the surface atoms (complexes) of the two media (particles of powder and substrate) can be approximated by the existence of a plane of vacancies at the interface. The formation of bonds results from the migration of vacancies from the vacancy plane and the appearance of atoms of the particles or substrate in their place.

We will examine a vacancy plane at the moment of time $t = 0$ as one of the microstates of a system ν of quasiequilibrium vacancies corresponding to the temperature T_k of the contact (we will ignore the effect of three-dimensional vacancies present at the initial moment). We will assume that the state with the vacancy plane represents a significant fluctuation (greater than the mean), i.e., that the system is significantly nonequilibrium. The nonequilibrium vacancies (the vacancy plane) will tend to undergo a redistribution to reach an equilibrium state. After the effective time t_0 (when T_k can be approximately considered constant and relatively high), the system changes from the significantly nonequilibrium state to another state which is less nonequilibrium. We will distinguish certain small volumes $V_\pm$ corresponding to an equilibrium concentration of vacancies at T_k and containing a single contact plane (henceforth, + and – will characterize quantities pertaining to the particles and substrate). Considering that these volumes are in thermal contact with a thermostat, we can apply a Gibbs distribution [4] to the system of $N_\pm$ vacancies included in $V_\pm$.

Proceeding on the basis of thermodynamic considerations, we assume that the maximum possible bond strength σ_0 is equal to the difference between the free energy $G^{(1)}$ ($t = 0$) of the system of vacancies in the state with the vacancy plane and the free energy $G^{(2)}$ of all of the vacancy complexes included in V_+ and V_- in the state of complete equilibrium ($t \geqslant \tau$, τ is the relaxation time to establish complete equilibrium):

$$\sigma_0 \approx G^{(1)} - G^{(2)}, \quad G^{(2)} = G_+^{(2)} + G_-^{(2)}. \tag{1}$$

We calculate the equilibrium concentration $N^e_{nv_\pm}$ of n vacancies, i.e., the ratio of the equilibrium number $N_{n_\pm}$ of complexes consisting of n monovacancies to the number of components (atomic volumes) $N_{V_\pm}$ in a volume $V_\pm$. For this, we write the free energy of a volume $V_\pm$ with n vacancies of one type:

$$G^{(2)}_{n_\pm} = G^{(0)}_\pm + N_{n_\pm}\Delta G^f_{nv_\pm}, \quad \Delta G^f_{nv_\pm} = n\Delta G^f_{v_\pm} + \delta G^f_{nv_\pm}, \tag{2}$$

where $\Delta G^f_{nv_\pm}$ is the change in free energy connected with the formation of one n-th vacancy; $\delta G^f_{nv_\pm}$ is the change in free energy with the formation of an n-th complex of n monovacancies, with the superscript 0 pertaining to the defect-free state; $N_{n_\pm}$ is the quasiequilibrium number

---

Sverdlovsk. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 1, pp. 139-143, January-February, 1985. Original article submitted December 19, 1983.

0021-8944/85/2601-0128$09.50

of n vacancy complexes. It should be noted that $\Delta G^{f}_{nV_{\pm}}$ depends not only on n, but also on the configuration. The formation of vacancies requires a supply of energy, but in this case there is an increase in the configuration entropy $S_{nv\mathrm{conf}}$. Thus, at high temperatures the free energy (such as the thermodynamic potential G in relation to the variables p and T, where p is pressure) may be lower. The free energy minimum corresponds to the equilibrium concentration of vacancies. Minimizing $\Delta G^{(2)}_{n_{\pm}} = G^{(2)}_{n_{\pm}} - G^{(0)}_{\pm}$ with respect to $N_{n_{\pm}}$ with $N_{V_{\pm}}$ = const, T_k = const, $\Delta G^{f}_{nV_{\pm}}$ = const and with allowance for $N_{n_{\pm}} \ll N_{V_{\pm}}$, $\ln k! \approx k \ln k - k$ at $k \gg 1$, we obtain the following for the equilibrium concentration of n complexes of defects

$$N^{e}_{nv_{\pm}} = N_{n_{\pm}}/N_{V_{\pm}} \approx \exp\left(-\Delta S^{f}_{nv\mathrm{conf}_{\pm}}/R\right)\exp\left(-\Delta G^{f}_{nv_{\pm}}/RT_{\text{к}}\right); \tag{3}$$

$$N_{n_{\pm}} = N^{e}_{nv_{\pm}}N_{V_{\pm}} \approx N_{V_{\pm}}\exp\left(-\Delta S^{f}_{nv\mathrm{conf}_{\pm}}/R\right)\exp\left(-\Delta G^{f}_{nv_{\pm}}/RT_{\text{к}}\right). \tag{4}$$

The number $N_{n_{\pm}}$(4) of n complexes and their equilibrium concentration $N^{e}_{nv_{\pm}}$(3) are expressed through an as-yet undetermined quantity N_V. We should note that the number of vacancies ν in the vacancy plane included in V_+ and V_- is approximately equal to half the sum of the surface densities of the atoms (molecules) $[(|N_+| + |N_-|)/2]$ and corresponds to the equilibrium state for the contact temperature T_k. It can be shown [5] that the distribution of the particle vacancies obeys the following law as a function of the distance to the vacancy plane

$$c_{\pm}(x, t) = \frac{\nu}{\left(\sqrt{D_-} + \sqrt{D_+}\right)\sqrt{\pi t}}\exp\left(-\frac{x^2}{4D_{\pm}t}\right), \tag{5}$$

where D is the diffusion coefficient of the vacancies. Now we introduce the number $V_{\pm}$ of monovacancies (including in the complexes) in $V_{\pm}$. Finding the ratio of the flows of vacancies (including in the complexes) in $V_{\pm}$. Finding the ratio of the flows of vacancies in V_+ and V_- from (5) and considering that $\nu = \nu_+ + \nu_-$, from the relation $\nu_+/\nu_- \approx \sqrt{D_+}/\sqrt{D_-}$ we obtain

$$\nu_{\pm} \approx \nu\sqrt{D_{\pm}}/\left(\sqrt{D_+} + \sqrt{D_-}\right), \quad V_{\pm} \simeq \nu_{\pm}/N^{e}_{\pm}. \tag{6}$$

Normalizing on the condition $\sum_{n=1}^{\nu_{\pm}} N_{n_{\pm}}n = \nu_{\pm}$, we obtain

$$N_{n_{\pm}} \approx \nu_{\pm}Q^{-1}_{\pm}\exp\left(-\Delta S^{f}_{nv\mathrm{conf}_{\pm}}/R\right)\exp\left(-\Delta G^{f}_{nv_{\pm}}/RT_{\text{k}}\right); \tag{7}$$

$$N_{V_{\pm}} \simeq \nu_{\pm}Q^{-1}_{\pm}; \tag{8}$$

$$Q_{\pm} = \sum_{m=1}^{\nu_{\pm}} m\exp\left(-\Delta S^{f}_{mv\mathrm{conf}_{\pm}}/R\right)\exp\left(-\Delta G^{f}_{mv_{\pm}}/RT_{\text{k}}\right). \tag{9}$$

We find the free energy of the body after the distribution of the vacancies over the volume (i.e., at $t > \tau$). Considering that $\nu_{\pm} \ll N_{V_{\pm}}$, $N_{n_{\pm}} \ll N_{V_{\pm}}$, we will consider an equibrium system of vacancies to be a mixture of ideal gases (monovacancy, and in general n-vacancy). Using the expression in [4] for the free energy of dilute solutions and considering the fluctuating part $G_{\mathrm{osc}_{\pm}}$ of the free energy (which becomes important at high temperatures) of a system of two and n-vacancy complexes, we obtain

$$G^{(2)}_{\pm} \simeq G^{(0)}_{\pm} + \sum_{n=1}^{\nu_{\pm}} N_{n_{\pm}}RT_{\text{к}}\ln\left(\frac{N_{n_{\pm}}}{e}e^{\alpha_{n_{\pm}}/RT_{\text{к}}}\right) + \sum_{n=1}^{\nu_{\pm}} G^{(2)}_{n\,\mathrm{conf}\pm}. \tag{10}$$

The expression for $G_{n\mathrm{osc}_{\pm}}$ depends on the number of vacancies in the complex and in accordance with [4] is determined by the expressions

$$\begin{gathered} G_{n\,\mathrm{osc}_{\pm}} = N_{n_{\pm}}RT_{\text{k}}\ln\left[1 - \exp\left(-\hbar\omega_{n_{\pm}}/RT_{\text{k}}\right)\right], \quad n = 2, \\ G_{n\,\mathrm{osc}_{\pm}} = N_{n_{\pm}}RT_{\text{k}}\sum_{\beta_{n_{\pm}}}\ln\left[1 - \exp\left(-\hbar\omega_{\beta_{n_{\pm}}}/RT_{\text{k}}\right)\right], \quad n \geqslant 3, \\ G^{(2)}_{\mathrm{osc}\,\pm} = \sum G^{(2)}_{n\,\mathrm{osc}\pm}, \end{gathered} \tag{11}$$

where the nonlinear complexes $\beta_{n_\pm} = 3n - 6$ and for linear complexes $\beta_{n_\pm} = 3n - 5$. In Eqs. (10) and (11) $\alpha_{n_\pm} = \alpha_{n_\pm}(p, T_k, N_{V_\pm})$ is a small change experienced by free energy with the introduction of a single n-th vacancy into $V_\pm$; ω_n and ω_{β_n} is the frequency of the normal oscillations of the complex. Differentiating $G_\pm^{(2)}$ (10) with respect to $N_{V_\pm}$ and $N_{n_\pm}$, we find the chemical potential of n-vacancy gases and the potential referred only to the volume $V_\pm$, without the $\nu_\pm$ vacancies we examined, in relation to $N_{n\pm}$:

$$\begin{gathered}\mu_\pm = \mu_\pm^{(0)} - RT_k \sum_{n=1}^{\nu_\pm} N_{n_\pm}/N_{V_\pm},\\ \mu_{n_\pm} = RT_k \ln\left(N_{n_\pm}/N_{V_\pm}\right) + RT_k \ln N_{V_\pm} + \alpha_{n_\pm}\end{gathered} \tag{12}$$

(for the sake of simplicity, the oscillatory part is not written). The free energy is written in the form

$$\begin{gathered}G^{(2)} = \left(N_{V_\pm} - \nu_\pm\right)\mu_\pm + \sum_{n=1}^{\nu_\pm} N_{n_\pm}\mu_{n_\pm} + G^{(2)}_{\text{osc}\pm} = G_\pm^{(0)} + G_\pm^{(0)\prime} +\\ + RT_k\left[-\left(N_{V_\pm} - \nu_\pm\right)\sum_{n=1}^{\nu_\pm} N_{n_\pm}/N_{V_\pm} + \sum_{n=1}^{\nu_\pm} N_{n_\pm}\left(\ln\frac{N_{n_\pm}}{N_{V_\pm}} + \frac{\alpha_{n_\pm}}{RT_k}\right)\right] + G^{(2)}_{\text{osc}\pm},\\ G^{(0)\prime} = RT_k \ln N_{V_\pm} \sum N_{n_\pm} = \text{const.}\end{gathered} \tag{13}$$

Finding the expression for the chemical potentials $\mu_\pm$, μ_ν at t = 0

$$\mu_\pm = \mu_\pm^{(0)} - \frac{RT_k}{N_{V_\pm}}, \quad \mu_\nu = \alpha_\nu, \tag{14}$$

we then write the free energy $G^{(1)}$

$$\begin{gathered}G^{(1)} = G_+^{(0)} + G_-^{(0)} + \alpha_\nu + G^{(0)\prime\prime} + G^{(1)}_{\text{osc}} \quad G_\pm^{(0)\prime\prime} = -\left(N_{V_\pm} - \nu_\pm\right) RT_k/N_{V_\pm} = \text{const},\\ G^{(1)}_{\text{osc}} = RT_k \sum_{\beta_\nu}^{3\nu-5} \ln\left[1 - \exp\left(-\hbar\omega_{\beta_\nu}/RT_k\right)\right].\end{gathered} \tag{15}$$

Inserting (13) and (15) into (1), we obtain the following for the maximum bond energy

$$\begin{gathered}\sigma_0 = \{G_+^{(0)\prime\prime} + G_-^{(0)\prime\prime} - G_+^{(0)\prime} - G_-^{(0)\prime}\} + \left\{\alpha_\nu - RT_k\left[\sum_{n=1}^{\nu_+} N_{n_+}\left(\ln\frac{N_{n_+}}{N_{V_+}} + \frac{\alpha_{n_+}}{RT_k}\right)\right.\right.\\ \left.\left. + \sum_{n=1}^{\nu_-} N_{n_-}\left(\ln\frac{N_{n_-}}{N_{V_-}} + \frac{\alpha_{n_-}}{RT_k}\right) - \left(N_{V_+} - \nu_+\right)\sum_{n=1}^{\nu_+}\frac{N_{n_+}}{N_{V_+}} - \left(N_{V_-} - \nu_-\right)\sum_{n=1}^{\nu_-}\frac{N_{n_-}}{N_{V_-}}\right]\right\} + \{G^{(1)}_{\text{osc}+} + G^{(1)}_{\text{osc}-} - G^{(2)}_{\text{osc}+} - G^{(2)}_{\text{osc}-}\},\end{gathered} \tag{16}$$

where the expression in the first bracket is a constant (for example, with T_k, p = const), $G_\pm^{(0)\prime\prime}$, $G_\pm^{(0)\prime}$, $N_{n_\pm}$, $N_{V_\pm}$, $G^{(2)}_{\text{osc}\pm}$, $G^{(1)}_{\text{osc}\pm}$ are determined by Eqs. (15), (13), (7), (8), (11), (15), while $\alpha_{n_\pm}$ can be taken equal to the energy of formation of the n-th vacancy, i.e., $\alpha_{n_\pm} = \Delta G^f_{n_\pm}/N_A$ (N_A is Avogadro's number).

Equation (16), found for the maximum bond strength, is of general physical interest in problems of bond energy. Let us use this result to find the bond strength σ (through the bond strength σ_0) attained in the deposition of a powdered coating on a substrate.

Multiplying the relative bond strength ε (see [1, 2], for example) (in view of its complexity, the diffusive-kinetic mechanism of bonding of a powdered coating with a substrate for different substrate and particle materials will be examined in a later article) by σ_0, we find the actual strength

$$\sigma = \varepsilon\sigma_0. \tag{17}$$

Let us point out yet one other method of calculating the actual bond strength σ without allowing for the relative strength ε. We will examine the fluctuation of the free energy of the vacancy system we examined, ignoring fluctuations in the number of particles $N_{n_\pm}$:

$$\Delta G(t) = G(t) - G(\tau) = G(t) - G^{(2)},$$

$$G(t) = G_+(t) + G_-(t), \quad G^{(2)} = G_+^{(2)} + G_-^{(2)}. \tag{18}$$

Obviously, $\langle \Delta G \rangle = 0$, $\langle (\Delta G)^2 \rangle \neq 0$. Let the quantity $\Delta G(t)$ at the moment of time t have a value greater than the mean fluctuation, i.e., $\Delta G(t) > \langle (\Delta G)^2 \rangle^{1/2}$. Then there is a correlation between the values of $\Delta G(t)$ at different moments of time $t < \tau$, i.e., the value of $\Delta G(t)$ at the moment t affects the value of $\Delta G(t')$ at another moment of time t'. As a characteristic of the time correlation we introduce the mean value of the product $\langle \Delta G(t) \Delta G(t') \rangle$. It should be noted that the state of the volume $V_+ + V_-$ at the moment $t = 0$ with the vacancy plane can be considered a state of incomplete equilibrium, in which $\Delta G(0) \gg \langle (\Delta G(t))^2 \rangle^{1/2}$.

Due to the long relaxation time, the process of formation of a bond after the effective time t_0 ($t_0 \ll \tau$) while we are examining will be considered quasistationary, as will the energy fluctuation. In this case, the time t_0 has the meaning of the relaxation time to establish incomplete equilibrium. The rate of change in $\Delta G(t)$ in relation to t depends on the value of $\Delta G(t)$ [4]:

$$d\Delta G(t)/dt = -\lambda \Delta G(t) \tag{19}$$

in the case of large fluctuations, but it permits limiting ourselves to the linear term in the expansion of $d\Delta G(t)/dt$ in powers of $\Delta G(t)$. In (19), λ is the inverse of the relaxation time. Integration of (19) yields

$$\langle \Delta G(t) \Delta G(t') \rangle = \langle (\Delta G(t))^2 \rangle \exp(-\lambda |t - t'|). \tag{20}$$

Having used (20), we write the bond energy at the moment of time t in the form

$$\sigma = G(0) - G(\tau) - \Delta G(t) = G^{(1)} - G^{(2)} - \langle (\Delta G(t))^2 \rangle^{1/2}. \tag{21}$$

Since the relaxation is a stochastic process, then the time t_0 of bond formation can be broken down into s intervals. Then $\Delta G(t_0)$ is represented in the form

$$\langle (G(t_0))^2 \rangle = \langle (G(0))^2 \rangle \exp\left(-\frac{t_0}{s} \sum_{r=0}^{s-1} \lambda_r \right), \tag{22}$$

where $1/\lambda_r$ has the meaning of the relaxation time for establishing incomplete equilibrium in the interval $t_{r+1} - t_r$. At $t_0 \ll \tau$ we can approximately set $\lambda_r = \lambda$. Then (22) will have the form

$$\langle (G(t_0))^2 \rangle \approx \langle (G(0))^2 \rangle e^{-t_0 \lambda} = (G^{(1)})^2 e^{-t_0 \lambda}. \tag{23}$$

Considering that the process of transition to the equilibrium state is connected with the migration of vacancies, we can evaluate τ from the relation [6]

$$L \approx b\sqrt{D\tau}, \tag{24}$$

where D is the diffusion coefficient of the vacancies (D is equal to the lesser of D_+ and D_-); L is the characteristic diffusion path; b is a coefficient on the order of 1. Considering that at $t = 0$ there are ν vacancies in the vacancy plane in $V_+ + V_-$, from (24) and (7), (8) we find

$$\lambda \sim d\nu' b^2 D \left[\sum_{n=1}^{\nu'} n \exp\left[-\left(T_\mathrm{k} \Delta S'^{f}_{n\,\mathrm{conf}} + \Delta G'^{f}_{nv} \right) / RT_\mathrm{k} \right] \right]^2, \quad d = 1\,\mathrm{m}^{-2}, \tag{25}$$

where the prime above ν, S, and G means that in place of ν', S', and G' it is necessary to take ν_+, S_+, and G_+ if $D = D_+$, and conversely.

Insertion of (1), (16), (25), and (23) into (21) leads to an expression for the bond energy in the contact of two different media — in particular, in the contact of particles of a powder coating and a substrate and between the particles of a sintered powder.

We can be assured of a high level of accuracy in the theory when we limit ourselves to mono- and bivacancies while ignoring (11). Expressions which are very simple and convenient for applications are obtained. We will use only a monovacancy approximation as an illustration (the extension to the case of mono- and bivacancies is not difficult). Considering (2) and (6) and the relations $\nu_\pm = N_{1\pm} \ll N_{V\pm}$, $N_{1+} + N_{1-} = \nu \simeq 1/|a|^2$ (a is the atomic spacing) and noting that the number of ruptured bonds in the ν vacancies is one-third the number in the ν monovacancies and that the entropy factor can be ignored in metals, we obtain the following for the maximum possible bond energy σ_0

$$\sigma_0 \approx \alpha_v - \alpha_{1_+}\nu_{1_+} - \alpha_{1_-}\nu_{1_-} \simeq \delta H^f_{v\nu_+}/N_A + \delta H^f_{v\nu_-}/N_A \simeq \frac{2}{3}\,\Delta H^f_{v_+}\nu_+/N_A +$$
$$+\frac{2}{3}\,\Delta H^f_{v_-}\nu_-/N_A = \frac{2}{3}\,\frac{1}{|a|^2}\,\frac{1}{N_A}\left(\frac{\sqrt{D_+}}{\sqrt{D_+}+\sqrt{D_-}}\,\Delta H^f_{v_+} + \frac{\sqrt{D_-}}{\sqrt{D_+}+\sqrt{D_-}}\,\Delta H^f_{v_-}\right).$$

Here, ΔH_V^f and ΔH_V^m are, respectively, the enthalpy of formation and the displacements of the vacancies, $\Delta H_V^m \sim \Delta H_V^f \sim E/2$ (E is the diffusion activation energy).

As an example, let us evaluate the maximum possible bond energy on the boundary of Fe(+) and Cr(–) (such as in the deposition of Cr on Fe, between Fe and Cr particles in a consolidated powdered material, between Fe and Cr phases in an alloy, etc.). Considering that $D = D_0 \exp(-\Delta H_V^m/RT_k)$ and assuming $D_{0+} = 1.8\cdot10^{-5}$ m²/sec, $D_{0-} = 1.5\cdot10^{-8}$ m²/sec, $E_+ = 2.71\cdot10^5$ kJ/kmole, $E_- = 2.21\cdot10^5$ kJ/kmole [6], $a \simeq a_+ \simeq a_- \sim 2.5\cdot10^{-10}$ m [7], $\Delta H_V^f/E \stackrel{>}{\sim} 0.65$ (for a bcc lattice) [6], $T_k \stackrel{>}{\sim} 900$°K [8], we find $\sigma_0 \stackrel{>}{\sim} 3.13$ J/m². This agrees satisfactorily with the value 4.34 J/m² obtained in [9] by a completely different method. Similarly, an estimate the bond energy attained during the time of effective interaction in a contact $t_0 \sim 10^{-5}$ sec [8] in plasma deposition [from Eq. (21)] gives a value $\sigma \sim 1.5$ J/m², which also roughly agrees with the bond strength found experimentally.

LITERATURE CITED

1. G. A. Babushkin, V. Ya. Bulanov, et al., "Reactive contribution to the relative bond strength of a powdered coating with a substrate," Zh. Tekh. Fiz., 52, No. 1 (1982).
2. G. A. Babushkin, V. Ya. Bulanov, and L. V. Solov'ev, "Diffusive-kinetic mechanism of bonding of a powder coating with a substrate," Zh. Tekh. Fiz., 53, No. 3 (1983); Diffusive-kinetic mechanism of bonding of a powder coating with a substrate (general and limiting relations)," in: Theoretical Investigations and Practical Application of Wear-Resistant Plasma Coatings [in Russian], Ural Science Center, Academy of Sciences of the USSR, Sverdlovsk (1984).
3. G. A. Babushkin, "Fluctuation method of calculating the absolute value of the bond energy of two media," Materials of an All-Union Scientific Conference "Investigation and Development of Theoretical Problems in the Area of Powder Metallurgy and Protective Coatings," Minsk (1984).
4. L. D. Landau and E. M. Lifshitz, Statistical Physics [Russian translation], Nauka, Moscow (1964).
5. G. A. Babushkin, "Diffusion from a thin layer in two semiinfinite specimens with different characteristics," Inzh.-Fiz. Zh., 47, No. 2 (1984).
6. B. S. Bokshtein, Diffusion in Metals [in Russian], Metallurgiya, Moscow (1978).
7. R. Truell, J. Ellbaum, and E. Cheek, Ultrasonic Methods in Solid-State Physics [Russian translation], Mir, Moscow (1972).
8. V. V. Kudimov, Plasma Coatings [in Russian], Nauka, Moscow (1977).
9. A. I. Gubanov, "Theory of bonding of two crystals in a composite," Mekh. Kompozitn. Mater., No. 4 (1979).