DIFFUSION-KINETIC MECHANISM OF BONDING OF A POWDERED COATING TO THE BASE

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A theory of bonding of the surfaces of two different media (particles of powder and a base) during the plasma deposition process is constructed.

One of the most important problems of powder metallurgy is the construction of a theory of bonding of a powdered coating to the substrate. The problem as formulated by this author, and the ideas and calculations in [1, 2], enabled the analysis of the strength of bonding in a a number of particular cases. The construction of a phenomenological theory taking into account the contributions of the diffusion and reaction stages and their interaction in the general case, when the materials of the particle and of the substrate are different, led to the necessity of solving the independent problem of diffusion from a thin layer in two semi-infinite samples with different characteristics [3].

The problem is formulated as follows. Initially the boundary between the substrate and the particle, compressed as a result of deposition, contains a plane of vacancies. With time the vacancies (and the atoms adsorbed on the surface) interact with the surface atoms (molecules, complexes) of the particle and of the substrate. The particle is characterized by a surface density of atoms N_+, coefficient of diffusion of vacancies D_{v+}, and an average interatomic distance a_+. We shall denote the characteristics of the substrate by the index −. When a bond is formed a surface atom of, for example, the particle occupies the location of the vacancy in the vacancy layer (between the surface atoms of the substrate and the particle).

The reaction stage [1] terminates with the transition of the complex from the state 1 into the state 3 through the state 2 at the top of the potential barrier and in reverse transitions from 3 into 1. The difference of the free energies in the states 2 and 1 and 2 and 3 is equal to G_{21} and G_{23}, respectively. The diffusion stage consists of the fact that the diffusion of vacancies to one interactomic spacing means that an atom of, for example, the particle has been transferred into the vacancy layer and has formed a bond with the surface atoms of substrate. The number of bonds formed owing to the diffusion stage is determined by the number of diffused vacancies. Because of interaction of both stages the reaction and diffusion contributions do not add. The reaction stage depends in time on the diffusion. The effect of diffusion consists of the fact that it removes vacancies from the surface boundaries of the layers, reducing the number of reverse transitions. As a result N_1 vacancies (N_1 is the smaller of the surface densities of the atoms N_+ and N_-) are distributed not only on layers n = 0 (in the vacancy surface) and n = ±1 (in the surface monoatomic layers of the particle and substrate), but also in the volume.

Taking into account the contributions of the reaction and diffusion stages and their interaction, we shall write the equation for the rate of formation of bonds Γ accompanying the formation of a strong bond in the form

$$\frac{d\Gamma}{dt}=(N_1-\Gamma)\exp\left(-\frac{G_{21}}{RT_{\text{к}}}\right)f_1f_2f_4f_\Gamma\nu_D-\left(\Gamma-\sum_{n=2}^{\infty}\Gamma_{n_+}-\sum_{n=-2}^{-\infty}\Gamma_{n_-}\right)\exp\left(-\frac{G_{23}}{RT_{\text{к}}}\right)f_3f_5\nu_D-\frac{d\Gamma_0}{dt}; \tag{1}$$

$$f_\Gamma=\frac{N_+}{N_-}(N_+\geqslant N_-),\quad f_\Gamma=\frac{N_-}{N_+}(N_-\geqslant N_+), \tag{2}$$

where the first term on the right side corresponds to the reaction contribution of direct transitions, the second term corresponds to the reaction contribution of reverse transitions, and the third term corresponds to the diffusion contribution; f_1, f_2, f_3 are the correlation factors, taking into account the probability for breaking of the bonds in the particle in the substrate, and in the new phase (of the order of unity), f_4, f_5 are the probability for the transition out of the state 2 and into the state 3 and 1, equal to approximately 1/2; ν_D

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is the Debye frequency; T_c is the contact temperature; $\Gamma_n(t)$ is the number of vacancies at time t in a single monatomic layer n; and $\Gamma_0(t)$ is the number of vacancies in the vacancy plane at the time t. It can be shown [3] that in Eq. (1) $\Gamma_{n\pm}$ and Γ_0 are defined by the relations

$$\Gamma_{n_\pm}(t)=\frac{N_1\sqrt{D_{v_\pm}}}{\sqrt{D_{v_-}}+\sqrt{D_{v_+}}}\left[\Phi\left(\frac{a_\pm(2n+1)}{4\sqrt{D_{v_\pm}t}}\right)-\Phi\left(\frac{a_\pm(2n-1)}{4\sqrt{D_{v_\pm}t}}\right)\right],$$
$$\Gamma_0(t)=\frac{N_1}{\sqrt{D_{v_-}}+\sqrt{D_{v_+}}}\left[\sqrt{D_{v_+}}\Phi\left(\frac{a_+}{4\sqrt{D_{v_+}t}}\right)+\sqrt{D_{v_-}}\Phi\left(\frac{a_-}{4\sqrt{D_{v_-}t}}\right)\right] \tag{3}$$

($\Phi(z)$ is the probability integral [4], $n > 0$ for media with the index +, and $n < 0$ for the medium with the index —).

We shall write the solution of Eqs. (1) in the form [5]

$$\Gamma(t_0)=\exp(-kt_0)\left[\int_0^{t_0}N_1k_1\exp(kt)\,dt+\int_0^{0}k_2\sum_{n=2}^{\infty}\Gamma_{n_+}\exp(kt)\,dt+\right.$$
$$\left.\int_0^{t_0}k_2\sum_{n=-2}^{\infty}\Gamma_{n_-}\exp(kt)\,dt-\int_0^{t_0}\frac{d\Gamma_0(t)}{dt}\exp(kt)\,dt\right]; \tag{4}$$

$$k_1=f_1f_2f_4f_\Gamma\nu_D\exp\left(-\frac{G_{21}}{RT}\right)\simeq\frac{1}{2}f_\Gamma\nu_D\exp\left(-\frac{G_{21}}{RT_{\text{к}}}\right),\quad k_2=f_3f_5\nu_D\times$$
$$\exp\left(-\frac{G_{23}}{RT_{\text{к}}}\right)\simeq\frac{1}{2}\nu_D\exp\left(-\frac{G_{23}}{RT_{\text{к}}}\right),\quad k=k_1+k_2 \tag{5}$$

(t_0 is the effective interaction time in the contact).

Taking into account the fact that the relative strength of the bond $\varepsilon = \sigma/\sigma_0 = \Gamma(t_0)/N_1$ (σ_0 is the maximum possible bonding strength, σ is the real strength achieved at t_0) and also the relations (3)-(5), after quite cumbersome transformations, we obtain

$$\varepsilon=1-\frac{1}{\sqrt{D_{v_-}}+\sqrt{D_{v_+}}}\left[\sqrt{D_{v_+}}\Phi\left(\frac{a_+}{4\sqrt{D_{v_+}t_0}}\right)+\sqrt{D_{v_-}}\Phi\left(\frac{a_-}{4\sqrt{D_{v_-}t_0}}\right)\right]$$
$$-\frac{k_2}{\sqrt{D_{v_-}}+\sqrt{D_{v_+}}}\exp(-kt_0)\left[\sqrt{D_{v_+}}\int_0^{t_0}\Phi\left(\frac{3a_+}{4\sqrt{D_{v_+}t}}\right)\exp(kt)\,dt\right.$$
$$\left.+\sqrt{D_{v_-}}\int_0^{t_0}\Phi\left(\frac{3a_-}{4\sqrt{D_{v_-}t}}\right)\exp(kt)\,dt\right]+\frac{k}{\sqrt{D_{v_-}}+\sqrt{D_{v_+}}}\exp(-kt_0)$$
$$\times\left[\sqrt{D_{v_+}}\int_0^{t_0}\Phi\left(\frac{a_+}{4\sqrt{D_{v_+}t}}\right)\exp(kt)\,dt+\sqrt{D_{v_-}}\int_0^{t_0}\Phi\left(\frac{a_-}{4\sqrt{D_{v_-}t}}\right)\exp(kt)\,dt\right]. \tag{6}$$

For very small t_0 (when $\varepsilon \lesssim 1/2$) the expression (6) assumes the form

$$\varepsilon=1-\left\{\frac{1}{\sqrt{D_{v_-}}+\sqrt{D_{v_+}}}\left[\sqrt{D_{v_+}}\,\Phi\left(\frac{a_+}{4\sqrt{D_{v_+}t_0}}\right)+\sqrt{D_{v_-}}\Phi\left(\frac{a_-}{4\sqrt{D_{v_-}t_0}}\right)\right]\right\}+\frac{k_1}{k}[1-\exp(-kt_0)],$$

where the first two terms correspond to the diffusion contribution are the third term corresponds to the reaction contribution.

In the limiting case ($D_{v+}t_0 \to 0$, $D_{v-}t_0 \to 0$) (purely reaction contribution) the expression (6), substituting (2) and (5), transforms into the expression (9) from [1], and when the particle and the substrate consist of the same material it transforms into (10) from [1]. In the case when the particle and substrate consist of the same materials (6) transforms into (4) from [2] in the limit $k \to 0$ (purely diffusion limit) and into (6) from [2] when $k \neq 0$, $D_{v\pm} \neq 0$ (in this case the first term on the right side of (6) from [2] should be replaced by $\exp(-kt_0)$).

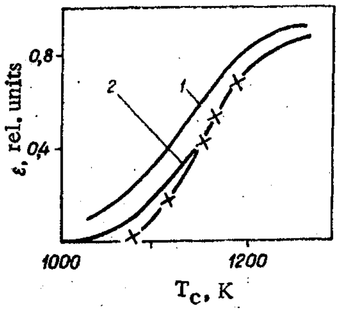

Fig. 1

Determining the relative strength ε from the relation (6) and knowing the maximum possible strength (the adhesion energy) of the bond σ_0 (see, for example, [6]),* from the relation $\varepsilon = \sigma/\sigma_0$ we find the actually attained (over the effective time t_0) bonding strength σ.

In order to compare with the experiment carried out in [8] with the deposition of Cu on Ag, we shall make some estimates. To construct the curve $\varepsilon(T_c)$ we shall take into account (5) and the following relations:

$$D_{v_\pm} = N_{v_\pm}^{-1} D_\pm \,[9], \quad D_{v_\pm} = D_{0v_\pm} \exp\left[-\left(\Delta H_v^m - \varkappa\alpha\right)/RT_c\right], \quad D_{v_\pm} = D_{0_\pm} \times \exp\left[-\left(u_{0_\pm} - \varkappa\alpha\right)/RT_c\right], \; D_0 = N_v^{-1}\gamma\nu_D\Delta^2\,[9], \quad N_v = = \exp\left(-\Delta H_v^f/RT_c\right)[9], \quad f_\Gamma = N_+/N_- = a_-^2/a_+^2, \quad \Delta_\pm = a_\pm/\sqrt{2}\,[9],$$
$$G_{21} \simeq \left(G_{21_-} + G_{21_+}\right)/2, \quad u_0 \sim E_s,$$

where ϰ is a structure-sensitive coefficient; α is the stress in the contact; u_0 is a quantity of the order of the binding energy [10, 11]; N_V is the atomic fraction of vacancies; γ is a geometric factor; ΔH_V^f, ΔH_V^m are the enthalpy of formation and displacement of the vacancy; and E_s is the binding energy of the lattice. Setting $t_0 \cong 10^{-6}$ sec [8], $G_{21} = 1.59 \cdot 10^5$ kJ/mole, $G_{23} = 1.69 \cdot 10^5$ kJ/kmole [8], $a_- = 4.10 \cdot 10^{-10}$ m, $a_+ = 3.62 \cdot 10^{-10}$ m [12], $\nu_D \sim 10^{13}$ sec^{-1}, R = 8.31 kJ/(deg·kmole), γ= 1/6 [9], $\Delta H_{V-}^f = 1.06 \cdot 10^5$ kJ/kmole, $\Delta H_{V+}^f = 1.13 \cdot 10^5$ kJ/kmole [9], $u_{0-} = 2.87 \cdot 10^5$ kJ/kmole, $u_{0+} = 3.37 \cdot 10^5$ kJ/kmole, $\varkappa\alpha \sim 2.5 \cdot 10^4$ kJ/kmole [8], and using the tables of the possibility integral [13], from the relation (6) we find the quantity $\varepsilon(T_c)$ presented in Fig. 1 (× are the experimental results of [8], curve 1 represents the calculation based on [8], and curve 2 represents the calculation employing (6)).

It is evident from Fig. 1 that Eq. (6) describes the experimental curve significantly better than does [8]. For very high T_c the curve calculated employing (6) and the experimental curve practically coincide.

The relation (6), which was first derived in this work, is of scientific and practical interest and predicts the selection of materials for creating a strong bond between the powdered coating and the substrate in terms of the coefficients of diffusion, the parameters and binding energy of the lattice of the powder and of the substrate materials, and the effective interaction time in the contact. The formula (6) contains diffusion and reaction contributions (taking into account reverse transitions) and their interaction.

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SELF-SUSTAINING DETONATION IN LIQUIDS WITH BUBBLES OF EXPLOSIVE GAS

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Compression waves in liquids with gas bubbles cause the most significant change in such basic parameters of the medium as bubble size and volumetric gas content β_0. When a bubble is compressed by a shock wave, the temperature of the gas in the bubble increases and may be high enough for ignition of the reactants. Compression ignition of liquid explosives when cavitation bubbles are collapsed near the walls of a tube has been widely studied and described, for example, in [1, 2]. It was experimentally confirmed in [3, 4] that it is possible for a single bubble of an explosive gas to undergo shock ignition in a nonreactive liquid. The ignition of systems of the oxidant bubble — liquid fuel type was observed in [5, 6].

In [7], the term "bubble detonation" was used for the process of the shock-wave ignition of a chain of vertical bubbles of explosive gas in a liquid over a length of 0.7 m. It is premature to introduce such a term since it has not been shown that an ignition wave can propagate independently via bubbles over a greater length without additional action by the initiating shock wave. Also, it follows from [8] that the process observed in this case was not self-sustaining — the wave attenuated as it propagated (pressure and velocity decreases). There has been almost no study of shock-wave phenomena and ignition conditions in reactive gas—liquid systems with gas bubbles uniformly distributed in the volume (systems of the nonreactive liquid—explosive gas and liquid fuel—gaseous oxidant types). The features of processes accompanying shock-wave motion have been explained only recently [5, 6]. The same is true of the experimental observation of a self-sustaining detonation wave [5, 9].

It is most worth noting that the amount of heat given off per unit mass in these systems as a result of the reaction is several orders smaller than, for example, in liquid and gaseous explosives, i.e., the Hugoniot and detonation curves nearly coincide. In light of this, the existence of a detonation wave in a bubble system [5, 9] is an important matter.

Here we have the goal of explaining the properties and conditions of excitation of detonation in relation to the value of β_0 and the physicochemical composition of the bubble medium.

The experiments were conducted on the unit shown in Fig. 1. The vertical shock tube, 35 mm in diameter, consisted of an initiation section 1 separated from a working section 2 by a breakaway membrane 3, two optical sections 4 and 5 with 8 × 240 mm organic glass windows, and a bubble generator 6. Piezoelectric transducers 7-13 were placed flush against the inside surface of the tube. The natural frequency of the transducers was about 300 kHz, while the diameter of the piezoelectric ceramic was 2 mm. The optical input 14 of a photomultiplier (FÉU-31) was located opposite either transducer 12 or 11.

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