Inorganic and Organosilicate Coatings

Editor-in-Chief
M M SHUL'TS

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General Aspects of the Formation of Coatings

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Theoretical Criteria of Adhesion of Coatings to Metals

A.A. Appen

The article examines five theoretical criteria of contact activity of metals and adhesion of coatings to metals: thermodynamic, energy, electrochemical, electron-structural, electrostatic. It is proved that these criteria are not mutually contradictory and allow an examination of the phenomena taking place at metalcoating interphase boundary in all its aspects.

Adhesion of coatings to metals is related to the contact activity of the metals. Phenomena of interphase reaction at the boundaries between the metals and the solid coatings and liquid metals of different types are interpreted at present on the basis of at least five points of view. The theoretical criteria of adhesion and contact activity of metals are given below:

I. Gibbs free energies $\Delta G^{\circ}_{T,s}$ of reactions taking place in two-dimensional monoatomic boundary layer (thermodynamic criterion);

II. Mean energies of single bonds Me–O, Me′–Me″, and others, or in first approximation mean energies required to convert the corresponding compounds into atoms (U_{at}) (energy criterion);

III. Normal electrode potentials of metals φ°_{Me} at metal-melt boundary (electrochemical criterion);

IV. Degree of incompleteness of electron orbits of atoms and statistical weight of atoms having stable electron configurations (SWASC) (electron-structural criterion);

V. Discharge potential and charge density on metal-dielectric boundaries (electrostatic criterion).

Thermodynamic Criterion. During chemical reaction of a coating with the substrate, chemical bonds appear and new chemical compounds are formed. It is considered that the process of adhesion is related to the free energies of formation of the corresponding compounds. The more negative the free energy of formation of compounds ΔG°_{form} in monolayer, the greater is the work of adhesion. For example, on a metal-oxide boundary new Me–O

bonds are formed. Therefore, adhesion of molten oxide (silicate) to metals must increase in proportion to the increase in free energies of formation of corresponding oxides, i.e. affinity of metals to oxygen.

The affinity of metals to oxygen is generally found by assuming the combination of one mole of O_2 to metal. In this case, general reaction of formation of oxides for all electro-positive elements of any valency has the form

$$4/n\mathrm{Me} + \mathrm{O_2} = 4/mn\mathrm{Me}_m\mathrm{O}_{mn/2}, \tag{1}$$

where m—number of atoms of Me in a molecule of oxide; n—valency of the element.

Yttrium, thorium, graphite, uranium, scandium, alkaline earth and rare earth elements, titanium, zirconium, aluminum, and lithium are distinguished by their high affinity to oxygen. During casting of ferrous or nonferrous high melting metals, they act as deoxidizing agents (reducing agents), and in air, in a finely divided state, they possess pyrophoric properties.

Vanadium, tantalum, niobium, molybdenum, tungsten, chromium, manganese, zinc, sodium, and iron possess somewhat less, but nevertheless high, affinity to oxygen. Copper, nickel, cobalt, lead, tin, cadmium, bismuth, and antimony have less affinity to oxygen.

Precious metals are distinguished by their least affinity to oxygen. For their oxides, $\Delta G^\circ_T > 0$, i.e. at high temperatures, they decompose.

Eremenko [1] and Naidich [2] made an attempt to develop quantitative theory of adhesion and to find out a theoretical measure of adhesion, particularly, on the molten metal-solid oxide boundary. According to them an exchange reaction

$$\mathrm{Me'O} + \mathrm{Me''} = \mathrm{Me''O} + \mathrm{Me'}, \tag{2}$$

takes place on the surface of molten metal Me″ at the contact with solid oxide Me′O, and a decrease in the specific surface free energy $\Delta G^\circ_{T,s}$ of the system as a result of this reaction serves a measure of the adhesion. Consequently, $W_{sc} = -\Delta G^\circ_{T,s}$. They made an approximate calculation of value $\Delta G^\circ_{T,s}$ for the case when the reaction is limited to monoatomic surface layer. At temperature T, the value $\Delta G^\circ_{T,s}$ of reaction is equal to

$$\Delta G^\circ_{T,s} = \Delta G^\circ_T \mathrm{Me''O} - \Delta G^\circ_T \mathrm{Me'O}. \tag{3}$$

Similar calculations were carried out by Zhuravlev [3].

In calculations the number of moles (gram-atoms) of reacting substances contained in unit surface were taken into account. Finally, it was concluded that the work of adhesion W_{se}, determined according to Young's equation from wetting data, is near to $\Delta G^\circ_{T,s}$ of the corresponding reactions.

In accordance with equation (3), experience shows that with silicate glasses and oxides, the oxidizable metals adhere well but precious metals adhere poorly [4]. Metallic films Be, Al, Cr, Mg, Zr, Ti, W, Mo have good

adhesion and are not peeled from a glass substrate; adhesion of films Ni, Cu, Sn, Cd, In is weaker; films of Pt, Au, Ag, Rh are easily removed. To increase the adhesion strength of the latter, heat is necessary.

Energy Criterion. Adhesion is caused by the force of attraction of atoms located in different phases. Consequently, the work involved in the separation of atoms or, in other words, the work (energy) involved in the breaking up of interatomic bonds per unit interfacial area serves as a direct measure of adhesion.

The work expended in breaking the atoms of a single phase body is the work of cohesion. The work for breaking the chemical bond is often called the energy of interatomic chemical interaction or, simply, binding energy. It is determined by the work required to convert the substance into an atomic state. The work of cohesion W_c of a simple substance can be considered as the product of the number of atoms located in the cleavage plane $(N_0\rho/M)^{2/3}$ and the average energy required to break half of the bonds pertaining to one atom $U_{at}/2N_0$, i.e.

$$W_c = \frac{U_{at}\rho^{2/3}}{2N_0^{1/3}M^{2/3}},$$

where U_{at}—energy required to convert 1 g-atom of the substance into atomic state; N_0—Avogadro number; ρ—density; M—atomic weight.

Taking, for example, for aluminum $U_{at} = 77.3$ and for titanium $U_{at} = 112$ kCal/g-atom*, we get

$$W_{c\,Al} = 3250 \text{ and } W_{c\,Ti} = 4530 \text{ ergs/cm}^2.$$

These values are one-and-one-half times greater than the work of cohesion of metals, i.e. twice the values of the surface tension of aluminum and titanium at melting points. Taking into account the differences in temperature and the state of aggregation, such a difference is quite natural.

For a theoretical evaluation of adhesion, such an approach is conceivable in principle, but is actually complex [5].

On the boundary of molten oxide or silicate melt with solid metal, chemical bonds of type Me_s'–O–Me_l'' must appear as a result of initial stage of chemical reaction. Adhesion of oxide coatings to metal must directly depend on the energy U_i required to break the chemical bonds Me_s'–O or Me_s''–O. This basic reasoning does not change when the oxygen atom combines with two or many atoms of the metal. Namely, U_i characterizes the strength of the chemical bonds.

A theoretical measure of the adhesion of metal to the oxide of the same metal and vice-versa, in simplest interpretation, is approximately expressed as the product of average energy U_i of single bond Me_s–O and the number of bonds $\sum$ per unit interphase area:

*Values U_{at} are taken as equal to heats of sublimation at $T = 0$.

$$W_a = U_i \sum.$$

Number of bonds appearing at time t, is caused by the kinetics of the process of reaction of the coating with the given substrate and is obviously a complex and still unknown function of many parameters. Unlike the simplest method of calculation of cohesion, it is not possible to determine the number of bonds $\sum$ appearing under the given conditions and at a given time on the boundary of two different phases.

Without solving the problem quantitatively, we can make certain qualitative statements. The work of adhesion of oxide coatings to metals, in first approximation, must be proportional to the energy required to convert the oxides formed at the interphase into an atomic state, i.e. $W_a \approx U_{at}$. Average values of U_{at} of solid oxides can be calculated according to equation

$$U_{at} = -1/m\Delta H^0_{[Me_mO_n]} + L^0_{[Me]} + n/2mD_{(O_2)}.$$

Here $D_{(O_2)}$—dissociation energy of oxygen molecule; $L^0_{[Me]}$—heat of sublimation of metal; $\Delta H^0_{[Me_mO_n]}$—enthalpy of formation of oxide [6].

Electrochemical Criterion. At the interphase boundary, electrical double layers are always formed in which the different charges are distributed unevenly. This results in the appearance of a potential difference. A potential difference between two metals is equal to the difference in the work functions of electrons of the two metals. The surface of that metal is charged positive in which the work function is smaller. Alkali metals are distinguished by their small values of work function and the precious metals by their high work function. The work function also characterizes the metal-semiconductor interphase boundary. Potential difference at metal-silicate melt interphase depends on the ion work function of the metal in the liquid-metal, i.e. on the chemical nature, physical state, and temperature of metal and the melt.

On the whole, the properties of the interphase must be examined as a result of interaction of two factors—electron and ion.

A large number of investigations are devoted to the study of electrical double layers at the boundaries liquid metal—solid oxide, liquid metal—liquid oxide, silicate melt—solid metal. The parameters of the electrical double layer that can be measured experimentally are: potential difference φ at the boundaries of the phases; electrical charge of unit surface (electrical charge density q), capacitance of double layer C. Potential difference generally varies in the range 0–2 V, charge density—in the range 0–200^{-6} coulomb/cm^2, capacitance—in the range 0–600 μF/cm^2.

Depending upon the nature of the substance in contact with the metal, the metallic surface may have either positive or negative charge. In oxide melts, the surfaces of metals and alloys are generally charged positively. This is accompanied by oxidation of the surface and transfer of metal ions into