

THE SCIENTIFIC PRINCIPLES OF CHEMICAL TECHNOLOGY
OF HEAT-RESISTANT COATINGS

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Abstract

Some factors determining a choice of optimum conditions and kinetic problems of coating's formation, peculiarities of association and aggregation processes are considered.

In this report kinetic principles of formation of multicomponent coatings are considered on examples of dross-burned, plasma, reactionary and organosilicate compositions.

Key words: *coating, temperature-time parameters, formation, reactionary interfacial boundary, reactionary diffusion, interphase interaction, dross-burned coatings, summary kinetics, metal substrate and oxide melt, sol-gel technology, organosilicate composition, thermooxidative destruction, solid-phase reactions, structural transformations in the material, polyorganosiloxanes, dehydroxylation of layered hydrosilicates, association, aggregation., reactionary coatings*

1. INTRODUCTION

At creation of functional coatings one operates with three-dimensional system of coordinates «property of a coating – its structure – a method of application». «Property of a coating» is an initial point for a choice of a structure and a method of application. «The structure of a coating» defines conditions of its formation, and also physical and chemical interactions at formation. «The method of application» provides these interactions, the necessary phase structure and operational reliability of all composition. Thus, systematization of coatings can be based on two attributes – «property of a coating» and «a method of application», thus it is meant, that «the structure of a coating» is determined by the researcher in view of all factors.

We shall consider some factors determining a choice of optimum conditions of coating's formation.

2. OPTIMUM CONDITIONS OF COATING'S FORMATION

The first and the most essential factor is the choice of temperature-time parameters for coating's formation. On Fig. 1 the temperature-time schematic drawing, characteristic for the majority of methods of coating's application is resulted.

At the initial stage of coating's formation there is a warming up of substrates and components of a coating. On this segment the reactionary interfacial boundary is formed. In an interval of isothermal endurance there are basic chemical reactions and the coating formation, and also a coupling a coating with a substrate takes place. The third segment characterizes cooling of a composition. It is defined by a relaxation of diffusion stress and possible formation of crystal phases. The extent of each segment can be various for different functional coatings.

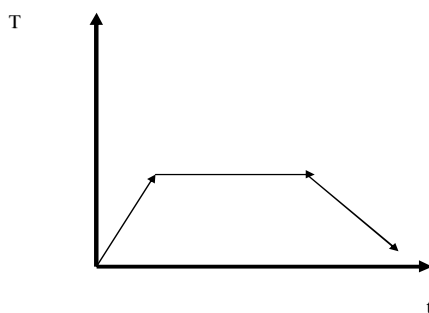


Fig. 1. Temperature-time parameters of coating's formation

3. KINETIC PROBLEMS OF COATING'S FORMATION

It is necessary to discuss kinetic problems of coating's formation from the point of reactionary diffusion view. Reactionary diffusion means that the rate of coating's formation is limited by a substance migration. In reactionary interphase boundary there are chemical transformations, but their rate is much higher, than the rate of a substance migration. We are going to consider all kinetic laws of interphase interactions only on the basis of interaction of two phases [1, 2].

In multicomponent system there are more than two interphase boundaries and fluxes of substances are also more, than two. For n -componential system will be n fluxes and $(n-1)$ from them will be independent.

The set of interphase boundaries leads to that the probability of this or that interphase interaction sometime appears rather great and the character of this interaction will work on all process kinetics. When the system, as a result of evolution, achieves a point of bifurcation, the fluctuation makes system to choose a branch of the further evolution of the system, and the transition through bifurcation is a probabilistic process. At the maximal reproduction of entropy it is impossible to trace a separate trajectory of the chemical system and to predict details of its development in time. Existence of instability should be considered as result of fluctuation which at first has been located in a small part of the system, and then it has been distributed and has led to a new macroscopical state.

Let's consider the kinetic features of coating's formation on concrete examples. For this purpose we will address to the dross-burned coatings which technology is based on preparation of wet or dry dross, its application on a surface and the further coating's formation at high temperature.

3.1 The dross-burned coatings

Generally coatings on the basis of glass, rendered on dross-burned technologies, represent a combination of several different on a chemical composite vitreous frits, and oxide or oxygen-free fillers. The combination of vitreous frits provides necessary for each coating continuity and coordination on physic mechanical properties with a substrate. Oxide or oxygen-free filler, as a rule, having high temperature of fusion, finally provides operational reliability of a coating. Dross is rendered on a metal (or any another) surface as a thin layer. Formation of a coating is carried out in an isothermal mode; if necessary the operation of dross application and formation of layers of a coating can be repeated several times. It is possible to settle out several kinetically significant reactions determining quality of dross-burned coatings:

- interactions between vitreous frits different on a chemical composite;

- interactions between frit and oxide or oxygen-free filler;
- interactions between components of a coating with metal.

It is natural that the certain reaction is not the criterion of process kinetics and it calls for accurate investigation. Summary kinetics of the processes proceeding at interaction of a metal substrate and oxide melt of the frit can be described only qualitatively, for example, on the basis of concentration changes of metal in oxide melt.

3.2 Liquor methods of coating's formation

Liquor methods of coating's formation, including sol-gel technology, also mean preliminary preparation of solutions. For formation of multicomponent coatings on the base of sol-gel process the same (in many respects) interphase interactions, as for coatings on the basis of a glass, will be characteristic.

3.3 Organosilicate coatings

Organosilicate (OS) composition represent suspensions of finely dispersed layered silicates and inorganic or organic pigments in solutions of organosilicon and (or) organic oligomers with different special modifiers (curing agents, plasticizers, etc.). In the case of OS coatings, it is common practice to distinguish two operating modes. (1) At temperatures below the destruction temperature of the organosilicon film former, the coating operates as paint and varnish coating with wide interval of working temperatures. (2) At temperatures above the destruction temperature, the coating operates as a high-temperature inorganic coating that is formed through the interaction of products of thermooxidative destruction of polyorganosiloxanes with mineral components, solid-phase reactions, and structural transformations in the material [3, 4, 5].

Let's consider only the high-temperature processes proceeding in OS coatings, for example transformations in the system polydimethylphenylsiloxane – muscovite – chrysotile asbestos – low-alkaline aluminum-boron-silicate glass – V_2O_5 / BaO_2 – ZrO_2 – toluene.

The main directions of interphase interactions at OS coatings during heating are destruction and structurization of polyorganosiloxanes, dehydroxylation of layered hydrosilicates, formation of amorphous reactive silica, occurrence of a circuit metastable (that is why active) states, formation of new high-temperature steady crystal phases.

At rather low temperatures, at curing under heat-treatment of OS coatings besides the reaction of homocondensation of polyorganosiloxane's OH-groups, resulting in their sewing, acid-base interactions between functional groups of film former and oxide fillers and glass can take place.

First attributes of degradation of coatings are observed already at 500°C. After heat-treatment at 900°C the coating undergoes essential changes: color changes, thermal resorption of the coating occurs– its thickness decreases, there is an expressed roughness and heterogeneity of a surface, but the coating carries out the electro insulating function, and adhesive contact to a substrate is kept.

At research by X-ray diffraction method of powders of coatings of the given series of structures, heat-treated at different temperatures, reorganization of crystal lattices of asbestos and mica is observed. In a sample, heat-treated at 600°C – disappearance of barium peroxides lines, reduction of V_2O_5 line's intensity and occurrence of barium *meta*-vanadate lines are marked. In a sample, heat-treated at 800°C, reflexes of barium *meta*- and *ortho*-vanadates are evidently visible. Initial aluminum-boron-silicate glass is Roentgen amorphous and for it the wide dim strip in an 2θ interval of 10–60° is characteristic. At heat-treatment at 800°C there are new crystal phases of structure: $BaMg_3Al_2Si_2O_{10}(OH)_2$ and potassium-magnesium-boron-silicate-hydroxide $KMg_3BSi_3O_{10}(OH)_2$ and potassium aluminosilicate $K_4Al_2Si_2O_9$. Thus the glass content in system decreases, the glass of the given

structure slows down the processes of organosilicon polymer destruction due to shielding of silanol groups by formation of coordinative bonds, thus in system the intermolecular interactions increase, mobility of separate sites decreases, the structure is ordered. As a result the generation of low-molecular organosilicon cycles decreases the volume of destruction in system polyorganosiloxane – silicate is reduced. More over introduction of glass into a composition leads to change in interphase interaction's kinetics due to the reduction of amount of O_2 mobile carriers in siliceous-oxygen coating matrix. Delay of transformation process of chrysotile asbestos to forsterite and silica, apparently, is caused by linkage of generated MgO in new alumo- and boron-silicate phases. The important role in activation of these processes belongs to BaO_2 and V_2O_5 , forming at temperatures above $600^\circ C$ new chemical compounds – barium *meta*- and *ortho*-vanadates, and at $800^\circ C$ and above – new vitreous phases. At presence of BaO_2 processes of structural reorganization of all coating's components go more intensively.

Interaction of components of a coating with a substrate submits to the same laws, as in two previous cases.

3.4 The association and aggregation processes

One more remark is necessary to make, considering dross-burned, liquor and organosilicate coatings. For these coatings a characteristic first stage is the preparation of an initial composite. All initial compositions represent suspensions of firm particles in the liquid medium. Be it a dross (combination of frits, fillers, binders in water), a sol-gel system, tyxotropic properties of which raise in with time or an OS composite (combination of silicate and oxide fillers in a solution of organosilicon polymer in toluene). Therefore, eventually beforehand prepared compositions "grow old", that is association and aggregation processes take place in them.

It seems that if the size of the particles which are included in a composition, prepared for a coating application, is known, its viscosity is also known, and it is possible to define the rate of stratifying (sedimentation). On Einstein's – Stocks or Frenkel equations the coefficient of diffusion in ideal system is inversely proportional viscosity $D = f(1/\eta)$. Using the fixed size of particles and medium viscosity it is possible to calculate the coefficient of diffusion and to estimate rate of stratifying as $x/t^{0.5} = 2\sqrt{D}$. However, the consideration of pseudo-binary system «a solution of branched polydimethylphenylsiloxane (PDMPHS) in toluene – a solution of linear polydimethylsiloxane (PDMS) rubber in toluene» shows significant deviations from additivity (ideality), Fig. 2.

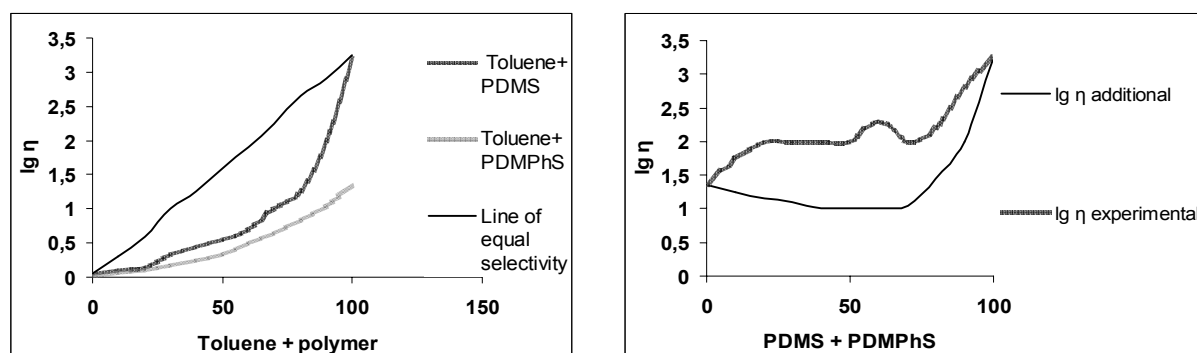


Fig. 2: Dependence of viscosity on structure for binary (at the left) and pseudo-binary systems

Let's enter into a consideration the parameter of mixing energy (ΔW_{mix}), generally represents the dependence of mixing enthalpies from structure:

$$\Delta H_{mix} = \frac{c_i \cdot c_j}{c_i + c_j} \cdot \Delta W_{mix}$$

The value of mixing energy shows a difference between bond's energies in initial components and energy of interpartial interaction in a mix of components:

$$\Delta W_{mix} = \epsilon_{ij} \cdot \frac{\epsilon_{ii} + \epsilon_{jj}}{2}$$

The dependence of $\lg \eta$ as function of structure resulted on Figure 2 can be treated as change of viscosity of system due to interpartial interaction, and the deviation from ideality can be connected to the value of mixing energy:

$$\Delta \ln \eta = \frac{\beta \cdot \Delta W_{mix}}{RT}$$

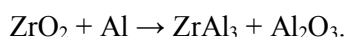
If in binary systems interpartial interaction renders the great influence on viscosity of a solution, in pseudo-binary systems the dependence of viscosity on structure is far from ideality. It is difficult to predict the system's behavior; bifurcation processes can accelerate or slow down sedimentation.

3.5 Degradation of ZrO_2 coatings

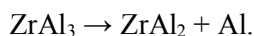
Let's consider the processes proceeding at the destruction of the zirconium dioxide coating, spreaded on turbine vanes.

A turbine vane represents a steel complex form set. Basic elements of substrate are Fe, Cr and Ni. On this substrate it is necessary to spread zirconium dioxide. The difference in coefficients of linear thermal expansion of steel and zirconium dioxide considerably exceeds allowable 10 %; therefore on steel vane the sub-layer is rendered. The sub-layer represents an aluminum matrix with Cr and Ni additives. These metals are entered in a substrate with the purpose of eliminating the diffusion fluxes of chromium and nickel from a substrate in a sub-layer matrix. ZrO_2 stabilized by Y_2O_3 is rendered on the sub-layer by a plasma-chemical method. Such coatings are short-lived, subjected to sulphuric acid corrosion and can be efficient only during limited time, especially at the increased temperatures.

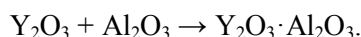
The chemical processes proceeding at operation of coatings, can be submitted by the following reactions: zirconium dioxide reacts with aluminum, forming zirconium trialuminid:



Zirconium trialuminid is formed very quickly and its concentration decreases in time due to the reaction of disproportion:



Relative concentration of aluminum oxide grows due to reduction of zirconium dioxide; it takes out yttrium oxide from ZrO_2 structure, forming aluminum-yttrium garnet:



From the chemical point of view set of above mentioned chemical interactions means that aluminum actively takes oxygen from zirconium oxide and forces out yttrium oxide from a lattice, thus worsening physic mechanical properties of coatings.

3.5.1 On the subject of the rate of coating's degradation

It is impossible to describe this process with in consideration of only diffusion fluxes using the kinetic equation such as Avrami – Erofeev equation. Even if to postulate, that the rate of all processes in the given system will be determined by diffusion fluxes of oxygen the independent fluxes of other components also will play an essential role [6].

The flux of oxygen ions will be the sum of fluxes and gradients of moving forces of all system's components:

$$J_o = \sum L_{oj} X_{oj}.$$

Cross Onsager coefficients as a first approximation can be treated as

$$L_{oo} = D_o^* c_o / RT \text{ and } L_{oj} = D_j c_j / RT,$$

and a gradient of moving forces as $\partial c / \partial x$. Then the flux of oxygen ions can be written as:

$$J_o = -D_o^* \partial c_o / \partial x = c_o D_o^* / c_j (1 + \partial \ln \gamma_o / \partial \ln c_j) \partial c_o / \partial x.$$

Let's assume, that a measure of process rate in the given system will be some effective coefficient of reactionary diffusion D_{ij}^* , designed on change of oxygen concentration at formation and operation of coatings. It will be defined by kinetic and thermodynamic parameters of all system:

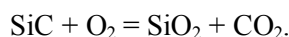
$$D_j^* = c_o D_o^* / c_j (1 + \partial \ln \gamma_o / \partial \ln c_j).$$

Thus, having calculated some effective coefficient of summary process in the given system it is possible to speak about the rate of degradation of coatings.

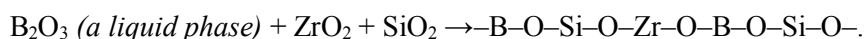
We shall pass now to reactionary coatings.

3.6 Reactionary coatings

For protection of carbon or porous materials the vitreous matrixes received by oxidation of some refractory intermetallides are frequently used [7]. At oxidation of the composition consisting, for example, from $ZrB_2 - MoSi_2$ or $ZrB_2 - SiC$ the following reactions proceed $ZrB_2 + O_2 \rightarrow ZrO_2 + B_2O_3$ (a liquid phase) or



Zirconium and silicium oxides are dissolved in fusible boron oxide, forming a uniform polymeric matrix of a coating:



The oxides dissolved in melt can interact with each other, forming for example crystal silicates of zirconium.

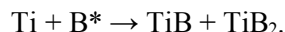
In this case the morphology of a surface is very interesting: at 1400°C there is oxidation of $ZrB_2 - MoSi_2$ system and formation of crystal structure of a coating. The further warming up of a composition leads to a formation of glass-crystal coating with fractal structure. The chemical aspects of coating's formation can be described also from the point of view of non-equilibrium processes thermodynamics or in the terms of formal kinetics.

One more version of reactionary coatings is temperature-resistant intermetal phases on a metal's surface. Preliminary carefully dehydrated borate melt has been taken as medium of reaction. Inorganic

reducer – aluminum, boron carbide and others have been brought into this melt in amount of 3 – 5 wt. %. In sodium tetraborate melt the reaction proceeds according to chemical kinetics as:

Sodium tetraborate + Al $\rightarrow$ B* + sodium aluminate.

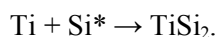
As a result of the reaction the boron in some active condition (B*) which reacts with metal according diffusion kinetics, in this case with the titan, is formed. According to the structural diagram the titanium monoboride and diboride are formed:



Kinetics of boride phase's formation is completely limited by diffusion in metal. At processing on air during 0.5÷8 hours reactionary coating with the minimal porosity (less than 3 %) is formed. Thickness of reactionary layer changes at investigated times and temperatures of processing from 5 up to 30 microns. At heating up to 600°C oxidation of boride phases proceeds slowly enough, formed thus melt on the basis of boric anhydride serves as a barrier on a way of access of oxygen to a metal surface.

Similarly it is possible to form a coating on the basis of silicides on a metal surface:

Sodium Silicate + Al $\rightarrow$ Si* + sodium aluminate



Similar results are received at processing in silicate and boron-silicate melts however in these cases the much greater number of intermetallic phases is formed.

4. CONCLUSIONS

In summary it is necessary to note, that considered chemical and diffusion processes at formation and operation of coatings are characterized with insufficient studies of processes at high temperatures. Fluctuation changes of quantitative and qualitative structure of reacting components can change the direction of process essentially.

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