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(V mire nauchnykh otkrytiy)

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BORATING OF SOLID PARTICLES COMPOSITE MATERIALS

Bystrov V.A., Borisova T.N.

Found that under most conditions of surfacing of composite materials (CM) is the dissolution of solid particles in a matrix with segregation on the surface section of the degradation products of metal and carbon, which has a negative impact on the durability of CM. There are several ways to reduce the dissolution of solid particles in a matrix of CM, one of which is the application of protective coatings. In the papers [2–5] studied the effectiveness of nickel-based protective coatings deposited on solids by precipitation, which is a costly method. In quality of a covering it is offered to use alloys on the basis of iron, nickel, cobalt. However such sheeting doesn't lead to increase of wear resistance of CM as it is completely dissolved in the CM matrix at a high-temperature hard facing, significantly reducing its microhardness. Authors offered a way of drawing coverings by method of sedimentation of pine forest on firm particles that leads to increase of thermal stability and wear resistance of CM.

Keywords: *of boride a covering; a composite material; solid particles; thermal stability.*

Thermodynamic and kinetic compatibility of components of composite materials (CM) on the basis of TN 20

The majority of CM – representatives thermodynamic nonequilibrium systems for which existence of the developed network of internal limits of the section and gradients of chemical potentials of elements in a matrix and solid particles is characteristic. These gradients are a driving force of processes of interphase interaction, in particular mutual diffusion and chemical reactions. Interphase interaction in limited degree is necessary for receiving CM with optimum properties; however intensive interaction usually leads to deterio-

ration of physical-thermal properties, especially thermal stabilities and wear resistances of CM at high-temperature abrasive wear.

Chemical interaction can happen both when receiving CM, and at their high-temperature operation. Intensive interphase interaction – the main obstacle in a way of creation of heat resisting CM. In order that the CM possessed stable properties at the increased temperatures, its components have to be chemically compatible. The concept of chemical compatibility includes concepts of thermodynamic and kinetic compatibility.

Thermodynamic compatibility – ability of a matrix and solid particles to be in a condition of thermodynamic balance unlimited time at temperatures of receiving and operation. Thermodynamic the limited number of the CM consisting of components almost insoluble in each other in a wide interval of temperatures are compatible in isothermal conditions (for example, Cu – WC). The majority of CM consists of thermodynamic incompatible components for which of charts of a state it is possible to define only possible phase balance and an orientation of reactions. Kinetic compatibility – ability of the CM components to be in a condition of the metastable balance controlled by such factors as adsorption, diffusion speed, speed of chemical reaction, etc. Thermodynamically incompatible components of CM in certain temperature and time intervals can be compatible kinetically and pretty reliably operate at high temperature wear. Along with chemical it is important to provide mechanical compatibility of the CM components, i.e. the compliance of their elastic constants, coefficient of thermal expansion and indicators of plasticity allowing reaching durability of the communication necessary for effective transfer of tension through of the surface section a firm particle-matrix.

Influence of the surface section on strength and fracture mode of composite materials

Durability of the surface section can be as above, and matrix durabilities are lower. The part of CM properties is defined by durability of the surface section on breaking strength (transverse strength, compression strength, vis-

cosity of destruction), part – durability of limit of the surface section on shift (longitudinal durability at CM stretching; critical size of fraction of firm particles, etc.).

For CM of the third class distinguish three sites on graphics of dependence of durability of CM on thickness of a reactionary zone h_3 . On the first site of the expressed dependence σ_b from x_3 it isn't observed. Here thickness of a reactionary zone is small (on average 0,5–4 microns), concentration of tension in it is less, than the concentration of tension caused by defects of a firm particle. Critical value of thickness of a reactionary zone x'_{cr} , corresponding to the first site, pays off on a formula [7]:

$$x'_{cr} \approx [E_{el} / (10B\sigma_{vf})]^2 r', \quad (1)$$

where $B = 0,5-1,0$ – the coefficient depending on distribution of tension near crack top;

r' – curvature radius in crack top;

E_{el} – the module of elasticity of a firm particle.

At $x_3 \ll x'_{cr}$ cracks in a reactionary zone don't influence durability of solid particles and, in general, CM durability.

On the second site CM durability with increase in thickness of a reactionary zone decreases. Here $x_3 < x_{cr}$ and concentration of tension in a zone is higher than concentration of tension from own defects of solid particles. The average sizes of the reactionary zone for various CM corresponding to the second site make 0,5–10 microns. There is second critical thickness of a zone x''_{cr} which is estimated on a formula [7]:

$$x''_{cr} = [E_{el} / (10B\sigma_{str})]^2 r', \quad (2)$$

where E_{el} , σ_{str} – the module of elasticity and strength of products of reaction.

In limits $x''_{cr} \leq x_3 \leq x_{cr}$ durability of CM decreases with increase x_3 . Limit deformation ε_f before destruction of particles in CM is connected with x_3 dependence:

$$\varepsilon_f = (1/10B) (r' / x_3)^{1/2}. \quad (3)$$

The third site begins at values $x_3 > x''_{cr}$. Here durability of particles is equal to durability of products of reaction and doesn't depend on thickness of a reactionary zone.

Wetting of firm particles fusions of metals (alloy-bundle metals)

Wetting – one of the most important characteristics of interphase interaction in CM considered when planning their receiving by liquid-phase methods. Receiving CM by method of impregnation and ensuring strong communication between components possibly only provided that the liquid matrix moistens a surface of firm particles [9–11].

The increase in a surface of both a liquid and solid body is followed by work commission. The size in number equal to work of reversible isothermal formation of unit of a surface of a body is called as specific free superficial energy σ_{str} . Along with it in the analysis of processes of wetting the coefficient of a superficial tension (or simply superficial tension) characterizing the force of a superficial tension having per unit length a free surface and operating in the direction, perpendicular this line is used. The superficial tension is defined by a formula [7, 11]:

$$\sigma_{str} = P/\ell_s, \quad (4)$$

where P – is the force of surface tension;

ℓ_s – the length of the free surface, which has this power.

For liquids the specific free surface energy and coefficient of the interfacial tension coincide both on dimension, and on a numerical value (they are measured or in the newton's divided into meter, or in the joules divided into a square meter). For solid bodies of their value can significantly differ that is caused by anisotropy of crystals and existence of lattice imperfections. The free surface energy of metals strongly depends on availability of impurity. Small additives in molten metal of surface-active substances lead to falloff of size σ_{str} .

Liquid cohesive forces with a solid body are characterized by work of adhesion of W_a equal to work of their division according to the interface and Dyupre determined by the equation [4]:

$$W_a = \sigma_h + \sigma_l - \sigma_{h.l.} \quad (5)$$

At a rupture of the single liquid the work of formation of a new surface of W_k called by work of a cohesion is counted on a formula of [5] $W_k = 2\sigma_l$.

Work of adhesion is a measure of interaction of two phases on their demarcation, and work of cohesion characterizes binding forces in a phase. In system liquid – a solid body – gas liquid can moisten a surface of a solid body and spread on it or not moisten it. Wetting is characterized by a wetting angle Θ_c , formed by a liquid surface on a joint with a solid surface (counting of a corner Θ_c is made through a liquid phase). The size of work of adhesion pays off on T. Yunga equation:

$$W_a = \sigma_l (1 + \cos \Theta_c). \quad (6)$$

The condition of a spontaneous spreading of liquid on a smooth solid surface has an appearance $\sigma_l + \sigma_{h,l} - \sigma_h < 0$. At a stable equilibrium of system the wetting angle of wetting Θ_c is defined by $\cos \Theta_c$ equation $= (\sigma_h - \sigma_{h,l}) / \sigma_l$, or $\cos \Theta_c = (W_a - \sigma_l) / \sigma_l$, i.e. depends on properties of liquid (σ_l) and on intensity of interaction of liquid and a solid body. When $\Theta_c < 90$ degrees the liquid will soak the solid and $\Theta_c > 90$ deg-will not

In systems refractory connection – molten metal wetting happens mainly thanks to chemical interaction which is defined by establishment of chemical bonds between liquid and a solid surface. The physical interaction determined by dispersion and inductive forces plays an essential role when wetting in systems with a low surface energy (for example, when wetting solid bodies water, organic liquids), but when wetting by molten metals its role is negligible.

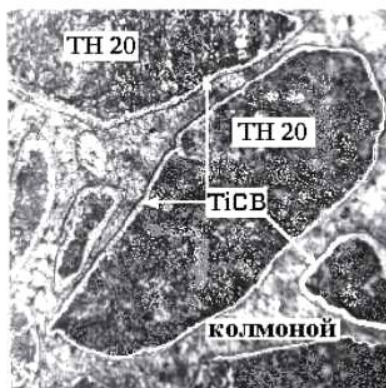
Borating of solid particles CM

Because pure titanium carbide, due to its high reactivity, the CM are not applicable in [1–3, 10–14] were used as wear-resistant solids CM sintered hard alloys based on titanium carbide type TN 20. When choosing alloy ligaments must take into account its interaction with particles in the process of surface welding. The anchoring strength of solids with a matrix providing high wear resistance of CM, preventing solids from an ejection and chunk-out from a matrix body at influence of grit, the solid particle of – a matrix is reached by regulation of processes of interaction on an interface. In case of partial dissolution of solids in a matrix on an interface it should not be

formed the new phases inclined to embrittlement, and thickness of the transition zone has to be minimum. Completely it is not possible to avoid interaction practically, however suggest to regulate this process in two paths: selection of the CM components insoluble or it is admissible soluble in each other; drawing a protective (barrier) covering on solids [2–3]. The first path brings a number of serious restrictions, especially regarding receiving rather wear-resistant and refractory matrix. The second path is represented to more fruitful as the put barrier coating protects a solid particle from an overheat and oxidation and serves as a barrier at interaction with superheated molten metal, promotes a doping of a matrix and improves wettability of solids a linking alloy [1–3].

As such barrier coating formation of a boride layer on a surface of the baked solids as a result of diffusion of pine forest in solids can serve. The favorable distribution of residual tension is established at low temperatures, in particular, at an electroslag hard facing not – the melted electrode on a fusion mixture layer when temperature of a matrix of CM does not exceed $T_{\text{melting}}^{\text{matrixes}} + 100 \div 150$ of $^{\circ}\text{C}$ [2].

Education and body height of borides on the diffusion mechanism happens on regularities of jet diffusion [2, 8] which idiosyncrasy is abruptness change of concentration of pine forest on thickness of a diffusion layer. On a surface at excess of solubility limit of pine forest in titanium there is a phase TiCBr with formation of the new interface representing carboboride the titan. TH20 CM microstructure + 55Cr16Ni75Si3Br3 (PG-SR3 – kolmonoy), the received electroslag hard facing on a fusion mixture layer is given in figure 1 (a linking alloy kolmonoy contains 3,2% Br). At endurance concentration of pine forest on a surface strives for the limiting values which decide by surface equilibrium conditions on the saturated environment, and structures of TiCBr and δ - of a solid solution on pine forest on a demarcation in isothermal conditions remain invariable. In these conditions intensity of body height of boride on a demarcation is defined by diffusion rate of pine forest in its lattice, diffusion rate of pine forest in α -solid solution and the surface concentration.



x 120

Figure 1. The CM microstructure with the besieged pine forest on a surface of solids diffusing from a linking alloy of the kolmonoy

At the diffusion and crystallization mechanism of formation of a borating layer creation of the conditions of formation of a liquid crystal state at a phase ratio providing preservation of a form of a detail and roughness of the processed surfaces is necessary and, the quantity of a liquid phase usually does not exceed 30% [7–9]. Can be a solid phase or not – the melted sites of a matrix solid solution, or solid components of CM. Temperature and concentration living conditions of this equilibrium are defined by composition of CM fusion mixture and the applied gumboil. Usually for exercise of borating a linking alloy, for example 55Cr16Ni75Si3Br3 is entered into composition of CM fusion mixture boron-containing, or to structure of gumboil are added the drill ($\text{Na}_2\text{Br}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and fumarole acid (H_3BrO_3). Introduction to composition of fusion mixture of a powder wire for receiving CM on the basis of TN 20 or addition in structure of gumboil of boron-containing elements (drills and fumarole acid) leads to formation of carboboride on a surface of solids that is shown in figure 2. On a surface of carbides not poisoned strip of a borating layer with the raised microhardness is legible observed that favorably affects wear resistance at a high-temperature gas-attrition of $\text{H}\mu(\text{Ti}_2\text{Br})\text{C} = 28,9 \text{ GPA}$ [2–3].

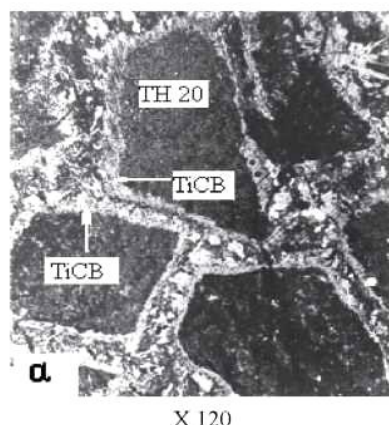


Figure 2. Microstructure of borating layer with the way electroslag hard facing with additives in slag borax and boric acid

The formed structure of a borating layer represents separate inclusions of borides of various dispersion, the distributed in rather weak solid solution. On solids, for example, the baked carbides of a titanium borating is carried out by replacement of atoms of carbon, with formation of boride of a titanium ($TiBr$), or formation of not stoichiometric composition of a carboboride of a titanium (TiC_xBr) figure 2.

Such structures call the pseudo-eutectic unlike the eutectic structures received at an alloyage of a layer or at flash-off of composition electrodeposited coatings [8]. They have as a smaller brittleness, than the nitrated layers, and higher microhardness that favorably affects wear resistance at a high-temperature attrition. Besides, the formed barrier coating from a borating layer on a surface of solids interferes with further dissolution of solids in CM matrix as prevents interdiffusion and migration of a fluid melt of a matrix in solids (see fig. 2) [8, 14].

Thus, apparently from the provided review of works, formation of a diffusion boride layer and its property in many respects depend on structure of the applied fluid – alloy environment. Thus the greatest interest is represented by structures of melts which can be at the same time not only the sating en-

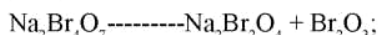
vironment but also heating for example a slag bathtub with boron-containing ingredients. The saved-up experimental material [2, 6–9, 10] allows to formulate requirements to such environment:

- the high sating ability at the surface strengthening;
- a chemical neutrality to the heated composition alloy;
- lack of oxidation and decarburization of a surface of solids;
- minimum interaction with the melted slag at CM EShN;
- the smoothly varying change of viscosity with change of temperature;
- ensuring good wettability of solids with a linking alloy and the filled-in metal when receiving the reinforced mold pieces [8];
- the thermal expansion coefficient of material of a covering has to provide minimum residual and thermal microstresses on interaction border a solid particle – a matrix [13];
- profitability of the used environments of borating and ecological purity.

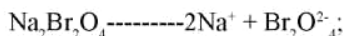
To the majority of the listed requirements satisfy the synthetic AN-SHT1 and AN-SHT2 slags developed in IES of E.O. Patton under the leadership of E.I. Frumin [14]. Intervals of operating temperatures of slags 900÷1100 of °C, viscosity in these temperature bands did not exceed 8 P. Slags well moisten a surface of the baked hard-facing alloys, on a surface completely there is no the oxidized and decarbonized layer, when processing impoverishment of the surface layers of solids alloying metals does not happen these slags.

The carried-out analysis of references [11–19] and the conducted laboratory researches allow the most probable to consider the following mechanism of formation of saturated atoms of pine forest at an electrolysis drills:

1. Thermal dissociation



2. The electrolytic dissociation of monoborate



3. Selection of sodium on the cathode



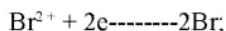
4. The category of boron-containing anions on the anode



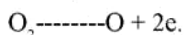
5. Interaction of metal sodium with a melt



6. Restitution on the cathode of suboxides of pine forest



7. The category of anions of oxygen on the anode



Thus, sodium and thermal restitution of oxide of pine forest in a slag bath-tub at EShN of CM happens according to the mass action law only in case of borating at high values of a current density when in of cathode space there is an excess amount of sodium.

Deserves attentions and other scheme of borating offered in work [8] during which process of borating proceeds in three main stages:

1. Formation of saturated atoms of pine forest on the processed surface. The generation rate of atoms depends on physical and chemical properties and structure of the environment, nature of interaction of structural complexes among themselves in a melt and with a saturable surface, etc.
2. Adsorption of the formed atoms a surface of solids, i.e. formation of strong interatomic communications (ionic, the covalent, metal and molecular) with a surface of carbides. The bonding decides by nature of interaction of pine forest on metals in the formed phase.
3. Boron diffusion into solid particles with the formation of boronized layer. Speed of formation of a layer at the first stage is defined by a pine forest diffusion coefficient in a solid solution, and at formation of borides – a diffusion coefficient.

Conclusion

Thus, formation of a boronized layer on a surface of carbides is led to increase in a microhardness of a demarcation by a solid particle – a matrix to $29 \div 32$ of GPA, to increase of anchoring strength to 780 MPA, owing to improvement of a wetting power of the pine forest possessing self-fluxing

properties. Improvement of these properties led to increase of wear resistance of the CM working at high-temperature types of a wear [2, 10–13].

The developed CM has transverse strength above ($\sigma_{\text{bend}} = 1,5 \div 1,6$ of GPA), and the variation factor on durability is lower ($W = 4,3 \div 6,2$), than known CM at identical quantity of solids and a linking alloy, at preservation of high hardness of a carbonitrid of a titanium with the protective coating ($87,2 \div 91,3$ HRA). Technical and economic effectiveness of new surfacing's material is caused by two factors:

1. Increase of stability of CM properties leads to the considerable decrease in percent of marriage when receiving solids.

2. Increase of anchoring strength of solids with a matrix allows to use composition of surfacing material during the work in a rigider external environment with shock loads [2, 3, 6].

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