Composition Coating Formation on the Base of Intermetallide Phases Using Electron-Beam Treatment[1]

A.G. Knyazeva*, I.L. Pobol**

**ISPMS SB RAS, pr. Academicheskii, 2/1, Tomsk, 634021, Russia, (3822)286831, anna@ms.tsc.ru*
*** PhTI NANB, St. Kuprevicha, 10, Minsk, 220141, Byelorussia*

Abstract – Theoretical and experimental modeling have been carried out for direct deposition of Ni-Ti coating by method of self-propagating high-temperature synthesis (SHS) on the steel substrate using electron beam treatment.

1. Introduction

The powder metallurgy methods employments possess the special possibilities to obtain together with the concentrate energy beam the materials and their compositions with unique properties. That allows, particularly, creating the nano-structure compositions and forming from them the macro objects of different functionality. There is the possibility to change the material properties by fundamental way.

Electron-beam (EB) treatment allows to improve essentially the operational properties of details with metallizate coatings deposited using the traditional methods. Due to the electron-beam heating the structure change occur in the deposited layer and in the substrate; adhesion growths; at the same time, hardness and wearlessness of the coating increase. In the other hand, employment the electron beam action allows to deposit the layers without other additional energy souses (plasma, arc ones etc.). Simultaneous, it permits to lowers the cost of technology process and prime cost of the produces.

The possibilities are known for self-sustaining high temperature synthesis (SHS) to new material producing, including the protective coatings. SHS-fusing is one of variety of similar technologies. As a rule, obtained layers have low adhesion to the base and high porosity; their thickness is more some millimeters and could be weak controlled by technology parameters of deposition process.

The powder metal-ceramic materials have a great practical significance, because they obey high wearlessness in the various conditions of wearing. In the sintered state they are used widely as instrumental materials (extrusion nozzles, stamps etc.). But, such material deposition of 1 millimeters thickness is almost insuperable problem.

One should be expected the special properties of the composition from unalloyed steel with multi layer, deposited using EM-heating and representing the metallic matrix with inclusions of wearproof ceramic particles, for example, of metal-oxides. The advantage of similar composition compared to traditional sintered solid alloys consists in relatively low cost and in the possibility of thermal treatment of productions with the coating.

Intermetallic compound of titanium and nickel find the wide application in medicine and as protective coatings. SHS-methods is one of variant of Ni-Ti alloy production. In many characteristics (for example, corrosion stability) this material exceed titanium alloys and stainless steels. The properties of Ni-Ti – alloy depend essential on the way of intermetallide production. The repeated electric arc fusion of pure charge materials provides higher passivateness of the alloys then SHS from powders together with following double electric arc refining because the structure and chemical heterogeneities and higher admixture concentration remain in the materials obtaining by second methods.

Ni-Ti – alloys, obtained using SHS, contain many admixtures as in solution, as in the form of the phases Ti_4Ni_2O (C, N). That serves for dispersed hardening of similar alloys produced by the traditional methods of fusion with the following hot repartition. Pure, Ni-Ti absorbs the oxygen during following mechanical treatment with the purpose of obtaining of required form.

The publications devoted to the Ni-Ti – coating (and other intermetallide systems) formation on the steel substrate using the combined EB-SHS – method in vacuum are absent. The properties of the composite materials can be different essentially on the same obtained by known methods.

2. Mathematical modeling of the coatication using electron-beam heating

Let assume, that one – layer coating was preliminary deposited on the surface of the metal block of form of thin plate (fig. 1), that is, the specimen, the thickness of which is less then width and length ones. In the simplest formulation the problem on the

---

[1] The work was supported by Russian Fond of Fundamental Investigation, grant number is 06-08-81006-Бел_а

coating formation when the exothermic chemical conversion goes during EB-treatment includes two – dimensional thermal conduction equation fro two – layer plate

$$[hc\rho + h_1 c_1 \rho_1]\frac{\partial T}{\partial t} = \left[\frac{\partial}{\partial x}\bar{\lambda}\frac{\partial T}{\partial x} + \frac{\partial}{\partial y}\bar{\lambda}\frac{\partial T}{\partial y}\right] -$$

$$-\alpha_{эф}(T - T_e) - \sigma\varepsilon_0 T^4 + q_e(x,y,t) + h_1\eta q_i(z,T), \quad (1)$$

where T is the temperature; $\bar{\lambda}=\lambda h+\lambda_1 h_1$; effective thermal conduction coefficient of the material with the coating follows from the equality $\lambda_{eff}=\bar{\lambda}/(h_1+h)$; c, ρ, λ, and are the heat capacity, density, thermal conductivity and thickness of the base (substrate); c_1, ρ_1, λ_1, и h_1 and are the heat capacity, density, thermal conductivity and thickness of the coating; T_e is the environment temperature. The equation (1) is obtained by integration of three-dimensional equation with taking into account the exchange condition on the plate surfaces. Hence, we neglect the temperature redistribution along the thickness of the coating and substrate, and elements redistribution in this direction also. In turn, the coating properties depend on the properties of all its components. If the coating is composite material, in which inert particles, made from material with high thermal conductivity, volume part η and properties ρ_p, c_p, λ_p, is contained, the coating properties can be presented in following manner:

$$c_1\rho_1 = c_p\rho_p\eta + c_m\rho_m(1-\eta),$$

$$\lambda_1 = \lambda_p\eta + \lambda_m(1-\eta)$$

or

$$\frac{1}{c_1\rho_1} = \frac{\eta}{c_p\rho_p} + \frac{(1-\eta)}{c_m\rho_m}, \quad \frac{1}{\lambda_1} = \frac{\eta}{\lambda_p} + \frac{(1-\eta)}{\lambda_m},$$

or using other formulae in dependence on composite structure, interface character etc. Index m relates to matrix or to the remaining material.

The rest of designations: $h_1\eta q_i$ is summary density of internal heat sources due to the volume chemical reactions in the coating (or rather, in the matrix, because the particles are inert); α_{eff} is the effective heat transfer coefficient from plate surfaces; t is the time, x, y are the space coordinates. The third item in (1) describes the heat losses due to thermal radiation with Stephan-Boltzmann; σ is Boltzmann constant; ε_0 is the blackness index.

Effective energy source moves along the surface the substrate with the coating in the direction OX with the rate V (Fig. 1). The energy in the source is distributed by the law

$$q(x,y,t) = \begin{cases} q_0 \exp(-(x-Vt)^2/a^2), & y \le b; \\ 0, & y > b, \end{cases} \quad (2)$$

where q_0 is the maximal capacity density of the source; a is its effective radius; the value b is proportional to the scanning thickness. Such source corresponds to saw tooth oscillations of scanning electron beam.

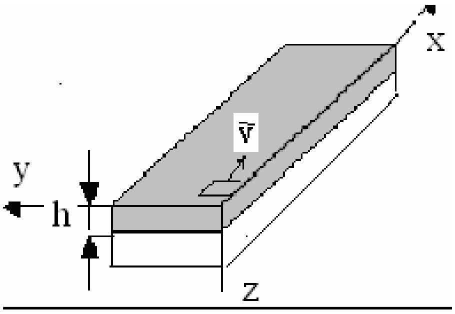

Fig. 1. EB-treatment scheme for specimen with preliminary deposited coating

Using state diagram, one can write the chemical reaction system, which leads to the different compound formation in the matrix of the composite coating of non-stoichiometric composition, and formulate on the base of the active mass law the kinetic equation system. All kinetic constants relating to kinetic equations are calculated on the base of thermodynamic properties containing in the literature, or known from the experiment.

To ascertain the qualitative regularities one can restrict the modeling by the simplest approximation. We assume that the coating has stoichiometric composition and the reagent turns during the heating in the product (stoichiometric compound) completely. That allows to describe the reaction by summary

$$A_s \rightarrow B_s. \quad (3)$$

The thermal – physical properties change due to the reaction is not taken into consideration. The change of the reaction product part or the conversion degree z obeys the equation

$$\frac{\partial z}{\partial t} = k_0\varphi_1(z)\varphi_2(T), \quad (4)$$

where $\varphi_1(z)$ is the kinetic function, $\varphi_2=(T)=\exp(-E/RT)$, k_0 is the preexponential factor E is the activation energy of the summary chemical reaction, R is the universal gas constant. The value of activation energy E is determined by the limiting stage of the chemical reaction (with deficit component); the kinetic function $\varphi_1(z)$ can have various view and reflects the reaction mechanism in the micro level (it form effect essentially on the result). Than

$$q_i = \eta Q_0 k_0 \varphi_1(z)\varphi_2(T).$$

Following boundary and initial conditions

$$x = 0, h_x: \ \lambda\frac{\partial T}{\partial x} = 0; \quad y = 0, h_y: \ \lambda\frac{\partial T}{\partial y} = 0, \quad (5)$$

$$t = 0: \quad T(x,y,0) = T_0; \quad z(x,y,0) = 0. \quad (6)$$

close the equation system.

We take into account in the model, that the heat capacities change essentially hear by the vicinity of melting temperatures of substances, that the formulae

$$(c\rho) = (c\rho)_{eff} + L_{ph}\rho_s\delta(T - T_{ph}),$$
$$(c_m\rho_m) = (c_m\rho_m)_{eff} + L_{ph,m}\rho_{s,m}\delta(T - T_{ph,m}), \qquad (7)$$

reflect, where

$$(c\rho)_{eff} = \begin{cases} c_s\rho_s, \ T < T_{ph}; \\ c_L\rho_L, \ T \geq T_{ph}, \end{cases}$$

$$(c_m\rho_m)_{eff} = \begin{cases} c_{s,m}\rho_{s,m}, \ T < T_{ph,m}; \\ c_{L,m}\rho_{L,m}, \ T \geq T_{ph,m}, \end{cases}$$

δ is Dirac delta- function; L_{ph}, $L_{ph,m}$ are the heats of the melting (crystallization); L_{ph}, $L_{ph,m1}$ – melting (crystallization) temperatures for the substrate and for the matrix of the coating; index L relates to liquid phase; S relates to solid phase. (In the real calculations, the Dirac delta-function δ is changed by the delta – shape function, satisfying to the normalization condition.

Subject to relation of energetic parameters characterizing the external source, exothermic chemical reaction and the substance melting, the coating formation regimes can be various. That was demonstrated, for example in [1], with the help of the simplest (one – dimensional) variant of model described above. The various regimes have been detected in two-dimensional model also: "heating" regime, when the reaction did not go; the control regime or step-by-step conversion in the wake of external source; conversion regime with wide reaction zone along all volume; self sustaining regime realized after external source unhooking.

The regimes detected theoretically are observed experimentally also.

The matrix and substrate melting effects essentially on the conversion regimes, on the reaction zone structure, characterizing by the temperature and conversion degree distributions. When the melting is taken into consideration, the plateau appears on the temperature curves relating to the phase transition. During the melting, due to the heat absorption the reaction is hampered, that leads to the appearance of the non-monotone concentration profiles.

The mathematical model of the coating formation process using the solid – phase synthesis could be added principally by the detailed reaction scheme, porosity evolution and by the formation of stress field of various physical natures.

3. Experimental results

To carry out the experimental investigations the EB-plant is used on the base of power-generating unit ELA-15 (Selmi, Sumy, accelerating voltage 60 kV; beam power – to 15 kVt). The powders are taken in various proportions: Ni – (40–60) mass. % Ti. The mixtures are intermingled, pressed with the help of the hand-power press in the form of plates and placed on the substrate made from steel-3.

SHS-process is carried out by locally initiation of the reaction on the system surface during EB-energy impulse with the following combustion reaction front formation and the reaction propagation along the initial substance. When the heating was very intensive with quick heat insertion, the synthesis goes in the form of thermal explosion. In this case, the reaction initiation, synthesis and particles ejection happen practically simultaneously.

Initiation temperature effects on the reaction rate and on the combustion temperature, phase composition and grain sizes that allows varying the structure of obtained coating wide-ranging. The combustion temperature and rate evaluate with SGS initiation temperature growth.

The part of SHS experiments of was organized without preheating of steel specimens. Other part of experiments includes the preheating of the base to various temperatures. Thereto electron beam with power equal to one in working conditions (0,5 kW), has been defocused and directed to surface of steel specimen. When the temperature achieves the necessary value (the control is carried out with the help of thermocouples), the pressed Ni-Ti specimen has been heated from them, and the beam has been focused to the 5 millimeters that was enough to the SHS initiation.

After combustion wave passing, the synthesized material in the Ni-Ti specimen with non-heated base has large structure heterogeneity; is noted by adhesion absence to the base additionally to the presence of big branched pores.

When the experiment was carried out according to second variant, the sintered layer was formed on the base surface and had porosity (50–55) % typical for materials obtained by SHS and good adhesion to steel. One can consider that the presence of branched porosity could be positive factor for details of some types, for example, if it is planned the following saturation of porous layer by fusible metal or alloy.

To coating homogenization, porosity removal and mechanical properties improvement the electron beam fusion of specimens is realized after SH-synthesis. It was carried out using various specific beam power and beam velocity along the surface. In this case, the base was melted in the depth about 1 mm, the layer of base and doped materials intermixing; the transient zone formation between the coating and substrate (Fig. 2).

The pronounced interface with stick-slip change of microhardness from 8 GPa to 2 GPa appear between the coating and base after SHS. EB-fusing forms the transient zone, microhardness is reduced step-by-step from 9 GPa near by the surface to 2 GPa near by the base. The cohesion strength of the coating with the base evaluates from 12–15 after SHS to 129–125 MPa after steel fusing.

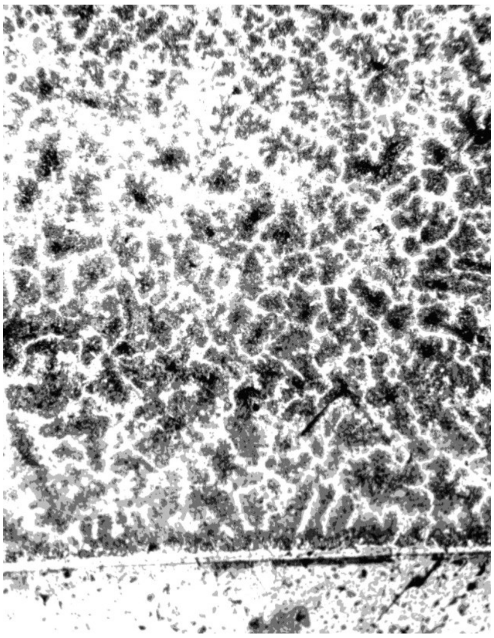

Fig. 2. Ni-Ti – coating cross-section on the steel-3 base (lower part) after SHS and EB-treatment, ×500

It was established that the initial powder consumption is low; their economy in employed EB-method is provided for exact batching and surfacing of local regions of details. In comparison with the gas-thermal technologies, the powder material powder absents practically; the overdimension of produce for mechanical treatment diminishes. At the same time, the productivity of the layer deposition process is not lower then it takes a place during arc, gas-thermal and plasma coating sputtering.

4. Conclusion

The experimental and theoretical modeling of the Ni-Ti coating deposition by combined EB-SHS – method. The using of such method allows constructing the composition materials with the coatings, the porosity and field-performance data of which could by vary in broad limits due to the initial material parameters and regime of the process organization.

References

[1] Knyazeva A.G., Pobol I.L., Gordienko A.I., *in Proc. 7th Intern. Conf. on Modification of Materials with Particle Beams and Plasma Flows*, 2004. – pp. 178–182.