ADVANCED COATING PROCESSING TECHNOLOGIES FOR METALLURGICAL EQUIPMENT BASED ON THE ELECTRON-BEAM, PLASMA AND FUEL GAS SPRAYING TREATMENT


Institute of Strength Physics and Materials Science SB RAS, 634021, Akademicheskii av. 2/1, Tomsk, Russia

*) High-Current Electronics Institute SB RAS, 634055, Akademicheskii av. 2/3, Tomsk, Russia

Abstract
We have developed and enhanced a number of technologies to produce materials and coatings designed for improving the processing and operational characteristics of metallurgy equipment. The processes of coating deposition as well as physical properties of the obtained coatings are studied experimentally depending on the operating conditions, chemical composition of cathodes, modifying powders and methods of their processing. Interesting results are obtained, which can be used to solve practical problems of improving the operational characteristics of metallurgy equipment. We have developed and made a computer-aided power-supply and control system for vacuum equipment as well as measuring and control devices for typical vacuum systems. The software has been developed to calculate temperature fields as applied to electron-beam and ion-plasma treatment of variously shaped bodies in order to optimize the conditions of processing materials and coatings of various types and properties.

Introduction
In the last decade the researchers of the Institute of Strength Physics and Materials Science SB RAS (ISPMS SB RAS) have developed a wide range of technologies for producing nanostructured materials, particularly with the use of high-energy effects, such as electron-beam, plasma and gas-flame treatment. Some technologies are unique and have no prototypes worldwide. Much experience has been gained in the diagnostics of the produced materials and in developing mathematical models of treatment processes to synthesize algorithms of optimal processing equipment control. The present paper reviews some modern technologies developed at the Institute and findings concerning the improvement of operational characteristics of metallurgy equipment parts.

1. Vacuum electron-beam surfacing

1.1. Electron-beam technology of wear-resistant coating deposition
The researchers of ISPMS SB RAS have developed the technology and produced the equipment for the deposition of protective wear-resistant coatings on metal materials and articles, and for reclaiming worn-out machine parts. The technology can be applied to deposit the monolithic and gradient coating of strength 40\(^{\circ}\) 70 HRC on copper, steel, titanium, cast iron and alloys on their basis. The charge is prepared of commercial powders of hardeners (TiC, TiCN, TiB\(_2\)) and low alloys (R6Mo5, Cr20NMnAG20, Mn13, PG-US-25, PCr20Ni20). Before surfacing the charge is sintered in vacuum furnaces and granulated. The technology provides the coating adhesion strength comparable to the substrate strength. The advantages
of the developed technology are the high quality of coatings, absence of substrate shrinkage and warpage; the possibility to deposit thick coatings (up to 20 mm); high equipment performance (25 mm²/s at a thickness of 1 mm); the possibility to deposit monolithic coatings with the porosity of on the level of hard alloy (<0.5%); high efficiency (about 90%); the possibility to deposit materials with low mutual solubility and melting temperature.

The technology of electron-beam surfacing can be used for modifying the surface of blast furnace tuyeres (with a 2-fold increase in the service life of the tuyeres) and crystallizers of continuous steel casting machines (with a 2–3 fold increase in the number of heats without regrinding), for face sealing rolling mills (with a 7–9 fold increase in the rod volume without recovery), etc.

1.2. Surface layer hardening of steel cylinders in a relativistic electron beam

One of the ways to enhance the surface hardness of mill rollers is surface hardening of the rollers by a high-energy relativistic electron beam propagating in air. The electron energy in the beam is within the range of 1–1.6 MeV at a total power of 100 kW. The effective depth of electron penetration into the metal is 0.5–1 mm, which correlates with the required depth of the hardened layer. The efficiency of surface treatment amounts to 200 cm²/s. The treatment of the metal surface out of vacuum allows fast replacement of the processed parts and removes limitations on their size. The short-time thermal cycle eliminates the necessity to use coolants and provides a high hardness layer, which preserves the initial surface smoothness. The stability of the process, its high rate and small heat-affected zone ensure minimal shrinkage and warpage of the parts. The thermal surface treatment procedure can thus be final polishing. The required operational parameters necessary for the formation of homogeneous, uniformly hardened surface layer on a part are determined.

A special study was carried out for medium-carbon steel 45. This steel is a kind of the model material with no alloying elements but carbon. So, we can reveal the general mechanisms of electron beam treatment influence on the structure and hardness of the hardened zone. The study has made it possible to determine the major operational parameters; governing the parameters we may govern the hardened layer properties, such as thickness, hardness and grain size.

1.3. Pulsed electron beam treatment of materials

Electron sources used in surface treatment of materials should satisfy a number of specific requirements. In particular, the surface treatment area must be from unit to tens of square centimeters; current density inhomogeneity over the beam cross-section should not exceed 10% of the average value; the energy density in the treatment zone should vary with a wide range, etc. The electron sources with the grid plasma emitter designed at the High-Current Electronics Institute SB RAS meet the above requirements. Special studies have been performed to understand the formation mechanisms of the structural-phase state of the near-surface layers for structural steel 38CrNi3MoVN of composition Fe – 0.38 wt.% C – 1 wt.% Cr – 3 wt.% Ni – 0.8 wt.% Mo – 0.3 wt.% V (in the previously hardened state) processed by the pulsed low-energy electron beam of microsecond duration.

The studies have shown that the pulsed electron beam treatment causes melting of a steel layer ~25–30 µm thick in the irradiated area. The high-rate melting and crystallization are accompanied by a significant modification of hardness in the steel layer ~110–120 µm thick. The complex studies of the structure and phase composition as well as the measurements of nano- and microhardness of steel subjected to the pulsed electron beam treatment have revealed the formation of the gradient multi-layer structure. The maximum nanohardness values are attained in the near-surface layer recrystallized during high-rate cycling of steel with the transition through the point of polymorphous $\alpha \rightarrow \gamma \rightarrow \alpha$ martensitic transformation.
One of the reasons for the considerable increase in steel hardness is the formation of the nanosized morphologically uniform structure.

2. Ion-plasma synthesis of superhard coatings

2.1. The deposition of wear-resistant TiN-based coatings synthesized in low-pressure arc plasma

In plasma-assisted methods of TiN coating deposition plasma is generated and ionized in arc vacuum and gas non-self-maintained discharges. The arc discharges are preferred due to high ionization degree of both reactive gas and sprayed cathode material, which amounts to 80% for refractory metals, and due to high efficiency of chemical reactions going at a relatively low temperature of the condensation surface. The discharge separation allows in a wide range the control over the ionic components of the deposited coatings and, consequently, over the structure, stoichiometry, phase composition and service properties of the obtained coatings. The radiation treatment on the stage of coating deposition has a beneficial effect on growth kinetics, morphology and defect structure of the coatings. As a result, it can considerably change the operational characteristics of the coatings. To increase TiN coating adhesion we use the formation of the transition layer $\gamma$-Fe$_4$N by ion nitriding, along with plasma assistance by low-energy nitrogen ions. The peculiarity of the considered method is that the transition layer formation occurs together with coating spraying in one vacuum chamber.

The single cycle of complex (three-layer) coating formation in arc plasma consists of the following stages: specimen heating and cleaning by argon ions; surface nitriding in arc plasma with the hot cathode; and plasma assisted deposition of the TiN coating. After the treatment cycle the multi-phase three-layer structure with an in-depth gradient decrease of hardness is obtained. This causes an increase in the TiN coating adhesion and a significant increase in wear resistance of the obtained composition. The described technology is realized in a single technological cycle using the modified installation for vacuum-arc spraying NNV 6.6-I1.

2.2. Deposition of hard heat barrier coatings

At ISPMS SB RAS the equipment and technology of high-temperature plasma (up to 1600 °C) deposition of hard (microhardness of up to 40 GPa), dense (from 0.1 to 5 mm thick) ceramic (Cr$_2$N) coatings on critical machine parts is developed. The equipment enables the deposition of coatings with uniform structure. It is established experimentally that being introduced into the plasma jet nitrides decompose very rapidly; in so doing the heat from nitrogen atom recombination into a molecule is released and the total heat of the two-phase flow increases. This technology can be considered as a method of producing protective new metal-ceramic materials. In protective coating deposition, of special interest are systems Al$_2$O$_3$-CrN, Al$_2$O$_3$-Cr$_2$N and Al$_2$O$_3$-Mo$_2$N. The component contents in Al$_2$O$_3$-Me$_x$Ny coatings are found experimentally based on their quality after deposition and after the maximum hardness and wear resistance values are attained.

The metallographic analysis and tribological testing results have shown that coatings with chromium nitrides Cr$_2$N have the best combination of properties. It is revealed that with 30% of Cr$_2$N the coating is characterized by a smaller wear-in area and the lowest wear rates ($I_h = 0.4$) and friction coefficient ($K_f = 0.4$). Increased tribotechnical characteristics of Cr$_2$N-containing metal-ceramic coatings result from a more uniform structure, minimum porosity (up to 7%), the presence of a pronounced transition zone with smooth microhardness distribution between the substrate and coating and from the presence of NiCr$_2$O$_4$, NiAl$_2$O$_4$ spinels in the contact zone acting as a lubricant.
The technology is intended for wear-resistant coating deposition on critical parts and products of metallurgy, power and engineering industries, for example, to increase the service life of oxygen tuyere. It is demonstrated that the tuyere service life increases by a factor of 6 with a reduction of operating costs and decrease in the human factor effect on the coating quality.

3. Gas-flame spraying of powder compositions

When reconditioning and hardening the parts of metallurgical equipment use is made of surface spraying with fusion of powders on the basis of self-fluxing nickel alloys of type PG-12Ni-02. The coating together with the hardened part is a composite material. It is known that owing to a strong difference in the nature of coating and substrate materials during the composition formation residual tensile stress may arise in coatings, which greatly impairs the strength characteristics of the composition. To eliminate these phenomena and to increase the adhesion strength, a combined method of ultrasonic treatment of the composition at coating fusion has been proposed at ISPMS SB RAS. Spraying with subsequent fusion is carried out with a burner GN-2.

In the experimental study powder PG-12N-02 was sprayed on specimens of steel 20. Ultrasonic vibrations were applied to an end of a cylindrical specimen using an installation UZG-2-4M. The metallographic and durometric investigation as well as the micro X-ray spectrum analysis have shown that due to ultrasonic treatment the coating structure becomes more disperse and uniform, which improves the strength properties of the coating. On the “coating – substrate” interface there is an expansion of the diffusion zone that smooths an abrupt change of physico-mechanical properties. The local in-flows of the coating material into the substrate along the austenitic grain boundaries bring about an increase in adhesion and in strength properties of the “coating – substrate” composition.

4. Experimental technology of obtaining nanocomposite containing coatings

The researchers of ISPMS SB RAS have developed compositions for the deposition of protective nickel and copper-based coatings on crystallizers of continuous steel casting to increase their service life. The main idea of the proposed approach is to increase heat and wear resistance of nickel-based coatings due to the injection of nanosized titanium diboride particles into the fused charge. Commercial nickel-based powders are suggested to use as the matrix material. This will allow us to diminish considerably the manufacturing cost of Ni-based powder nanocomposites and exclude the copper ingress from the crystallizer surface during steel casting.

As initial powders we use self-fluxing composition Ni–Cr–B–Si conventionally applied in gas thermal spraying (industrial designation PG-10Ni-01 or PGSR4) as well as nichrome powder applied in sublayer deposition (industrial designation PCr20Ni80). Nanosized titanium diboride particles in the nickel matrix have been synthesized at the Institute of Solid State Chemistry and Mechanochemistry SB RAS. At ISPMS SB RAS we have developed the deposition mode for the nanocomposite powder coating on the copper substrate by electron beam surfacing. Fusion was performed using an installation ELU-5. For this purpose the installation is supplied with the system of electron beam sweep and powder feeder. Fusion was performed at the accelerating voltage 26 kV and beam current from 80 to 150 mA, the electron beam was swept into a line 5 mm long perpendicular to the direction of displacement (rotation) of the fused article. Powder was fed into the molten metal pool formed by the electron beam. The deposited layer 1–2 mm in thickness was formed on the face of a copper billet 100 mm in diameter and 60 mm in height. Powders PCr20Ni80 and PG-10Ni-01 as well as their mixtures were used as the matrix of titanium diboride coatings.
The conducted investigations allow us to conclude that the 10 mass% TiB₂ content in the powder mixture for sintering (fusion) of composites (coatings) is optimal. A decrease in TiB₂ content results in a decrease in strength properties and less uniform distribution of reinforcing particles. Whereas an increase in TiB₂ content determines a higher strength at a considerable increase in brittleness.

5. Obtaining of composite cathodes

In the majority of cases nitride coatings represent the nanocomposite, namely, the mixture of at least two phases that can have the amorphous structure. Nanocomposites TiN/BN, TiN/TiB, TiN/TiB₂, and TiN/Si₃N₄ have the highest hardness (HV > 50 GPa). To obtain a multicomponent composite cathode with the structure homogeneous in the chemical and phase composition powder metallurgy methods are most promising. These methods consist in preparing powder mixtures with the required chemical composition of disperse metal and nonmetal powders, compacting “raw” billets of a definite form and size from these mixtures and subsequent sintering, namely, heating and holding at high temperature. During high-temperature isothermal holding there occur the diffusive atom redistribution and formation of solid solutions and/or intermediate compounds in accordance with the equilibrium phase diagram. Simultaneously powder compacts shrink, i.e. their porosity decreases and mechanical strength increases.

At ISPMS SB RAS the structure formation at sintering of titanium and copper powder mixtures is investigated to develop operating modes of obtaining composite cathodes. Two compositions have been chosen for the study: Ti–12 at.% Cu and Ti–30 at.% Cu. The first composition is close to the maximum concentration of the solid β-Ti-based solution; in the range of sintering temperatures 950 – 1100 °C it is in a one-phase region. At lower sintering temperatures this composition passes into the two-phase region α-Ti – Ti₂Cu. The second composition corresponds to the two-phase region α-Ti – Ti₂Cu in the whole range of sintering temperatures up to 1005 °C. At similar equilibrium phase composition below 950 °C the content of the solid α-Ti-based solution and intermetallide Ti₂Cu in alloys of the above-mentioned compositions differs greatly.

Sintered composite cathodes with the composition Ti–12 at.% Cu and Ti–30 at. % Cu are used for the vacuum arc evaporation and deposition of ion-plasma nitride coatings. The coating is synthesized using evaporators with the arc current 50–100 A and a plasmotron PINK providing nitrogen plasma with the concentration 10⁹-10¹⁰ sm⁻³ in the spraying area. It is shown that to obtain the homogeneous time-stable structure and high hardness of deposited coatings the sprayed cathode should have the following: i) the disperse structure with components one order smaller than the cathode spot; ii) the minimum content of low-melting phases inducing an increased drop-formation in arc erosion; iii) metals forming stable nitrides (Ti, Al, Zr, etc.) and those not forming nitrides (Cu, Ni, etc.).

6. Measuring equipment and automation

The developed technologies of coating formation are realized in special equipment including sensors, measuring devices, power supplies, vacuum equipment of various types, etc.

To set and keep the required operating conditions the type and parameters of a sensor to measure physical quantity that appear as operational parameters are of importance. In the developed vacuum equipment applied for electron-beam and ion-plasma treatment the following types of vacuum sensors are used:

- active thermocouple vacuum sensors ATV-2, ATV-4 (pressure range from 100 Pa to 1,3*10⁻¹ Pa);
- active thermoelectric vacuum sensors ATV-6-3H (from 10⁵ Pa to 10⁻¹ Pa);
- active ionization vacuum sensors АIV-10-2, АIV-2, АIV-51 (from 100 Pa to $10^{-5}$ Pa);
- active magnetron vacuum sensors AMV-32 (from 1 Pa to $10^{-7}$ Pa).

These sensors have a digital output and are applied for measuring air or non-corrosive gas pressure in the moderate and high vacuum zones using a special controller of active sensors or in a measuring complex with the interface RS-485.

It is obvious that high technologies can be effectively applied only in the case of high-level automation of all technological equipment. There is a need for a high level of standardization and unification of all components and blocks, their interchangeability, which provides the high safety and maintainability of the equipment at its relatively low price. For the automated control and power supply of the vacuum electron-beam and ion-plasma equipment used for the treatment and modification of the material surface and machine parts the computer-aided power-supply and control system (PSCS) for the vacuum equipment has been developed at ISPMS SB RAS. Blocks of this system provide the full automation of all elements of the vacuum beam complex. The high-level control of the developed system is performed by a computer. A distinctive feature of the system in comparison with the existing analogs is the cellular structure with the replaceability of its components. PSCS is used for the control of electron-beam and ion-plasma power complexes that are applied in research and development as well as in metallurgy and mechanical engineering. We have produced and tested an experimental model of PSCS using an installation of electron-beam powder metallurgy ELU-5.

7. Simulation of heat processes at electron beam treatment of materials

Modification of material surfaces using electron beams and plasma flows is conventionally referred to high-temperature technologies, along with welding and cutting using high-energy sources. Mathematical modeling of such process usually reduces to heat-conductivity problems in variously shaped regions with effective mobile external heat sources and with the temperature dependence of thermophysical properties. At present there is a need for the development of a complex approach to the modeling of coating deposition and surface treatment, which would combine both conventional methods of modeling of high-temperature technological processes and methods that allow distinguishing special features inherent to various external influences and materials with various structures. It must be emphasized that the correct modeling of thermophysical processes provides a basis for the modeling of non-equilibrium structural, phase and chemical transformations occurring in treated materials.

We have posed problems on the heat treatment of variously shaped bodies and developed the computer software for their numerical solution. As the input information we use data for thermophysical properties and composition of materials and their coatings, information on geometrical characteristics of treated objects, parameters of external influences and operating modes. The calculation results are temperature fields at different time moments, size and form of the melt pool and heat affected zone. Using them we can obtain, in the first approximation, information on the post-treated surface structure on the basis of the existing atlases for the majority of structural materials and steels.

Conclusion

As the conducted investigations show, the developed technologies have allowed us to obtain coatings with unique physical properties. In particular, we have obtained composite coatings with the defect-free cast structure characterized by high hardness and abrasive wear-resistance ($K_{\text{res}} = 10$). On the basis of the experimental investigations we set requirements for the chemical composition and operating conditions of the formation of composite sprayed cathodes of products. Besides, we have found the regularities for the depth dependence of nanohardness at the pulsed electron-beam treatment of steel and determined operating modes
of the vacuum-arc plasma assisted deposition of TiN coatings at which the nanostructure is formed in the coating and the coating wear resistance increases. As industrial tests show, protective coatings deposited on tuyere arches allow an approximately 3-4-fold increase in the service life of air tuyeres.