Technology of combined chemical-mechanical fabrication of durable coatings

V P Smolentsev¹, V V Ivanov², A I Portnykh¹

¹ Voronezh State Technical University, 14, Moskovsky Prospect, Voronezh, 394026, Russia
² Don State Technical University, 1, Gagarin Sq., Rostov-on-Don, Russia

E-mail: vsmolen@inbox.ru

Abstract. The article presents the scientific fundamentals of methodology for calculating the modes and structuring the technological processes of combined chemical-mechanical fabrication of durable coatings. It is shown that they are based on classical patterns, describing the processes of simultaneous chemical and mechanical impact. The paper demonstrates the possibility of structuring a technological process, taking into account the systematic approach to impact management and strengthening the reciprocal positive influence of each impact upon the combined process. The combined processes have been planned for fabricating the model types of chemical-mechanical coatings of durable products in machine construction. The planning methodology is underpinned by a scientific hypothesis of a single source of impact management through energy potential of process components themselves, or by means of external energy supply through mechanical impact. The control of it is fairly thoroughly studied in the case of pulsed external strikes of hard pellets, similar to processes of vibroimpact hardening, thoroughly studied and mastered in many scientific schools of Russia.

1. Introduction

The long experience of Russian scientific schools has clearly shown that wave processes, associated with the vibroimpact method of hardening treatment, make it possible to significantly enhance the technological parameters, obtained by consistent use of chemical and mechanical impacts. However, the fullest use of the potential of these impacts is possible only with their combination in an integrated way of treatment, which became known as a chemical-mechanical method [1-4]. The presented structuring methodology for such method of combined technological processes [5-7] helped to create the mechanism of increasing technological durability of products, which is demanded in industry and relevant for present-day domestic and foreign machine construction.

2. The stages of planning combined technological processes

The technological process of combined treatment [7-9] includes several planning stages, formed on the basis of energy levels of each impact [10-12].

Initially, (i.e. at the first stage) the minimal level of activation energy is set, which corresponds to the amount of energy, necessary for the chemical reaction to flow. Then, the required number of components, involved in the reaction, is specified:
\[ \Sigma^1_{i} K_1 \rightarrow \Sigma^1_{i} K_2 \]  

(1)

where \( \Sigma^1_{i} K_1 \) is the sum (i) of chemical components, involved in chemical reaction; \( \Sigma^1_{i} K_2 \) is the sum (j) of components after termination of the chemical reaction.

The energy parameters of the reaction (1) have the following form:

\[ U_a < U_{mg} \pm U_{xg} < U_{max} \pm U_{xg} \]  

(2)

In accordance with the formula of a chemical reaction, the energy values \( U_a \) and \( U_{xg} \) are calculated in (2), which is taken into account on the basis of reference materials for similar operations. If \( + U_{xg} \) is greater than \( U_a \), \( U_{mg} \) is adjusted. If value \( U_{xg} \) is negative, energy value \( U_{mg} \) of the mechanical component is altered.

Figure 1. Structuring technological processes for designing combined vibrowave chemical-mechanical coatings
Value $U_{xg}$ is determined by energy costs in rational technological modes of treatment. To ensure the specified operating properties of a product with coating under research, matching the level, reported by the customer and determined by the project developer, this parameter is set within the reached limits or possible modes are created (mainly, those of mechanical impact or combined process), on the basis of which, if necessary, the parameters of chemical impact are adjusted. The examples of such solutions are shown in [10-12].

The basis for creating the methodology of structuring the combined chemical-mechanical process is the level of technological parameters attained, which ensure the achievement of specified operating characteristics of a product, primarily, with respect to reliability, durability and trouble-free operation resource [11, 12].

The application of the proposed methodology makes it possible to restrict the zone of search for the optimal variant from the list of known impacts in a combined process, and scientifically substantiate the area of works for creating new methods with combination of chemical and mechanical impacts, most fully implementing the positive aspects of the combined process of obtaining highly durable coatings. Comparing the virtues of the types of planned combined processes is carried out on the basis of consolidated technical and economic parameters, validated by the experience in the use of similar technologies with consistent chemical and mechanical (particularly, vibration) impact.

Figure 1 shows the workflow for designing model combined vibrowave chemical-mechanical coatings.

3. Structuring technological processes for designing model chemical-mechanical durable coatings [1, 2].

**Vibrational chemical-mechanical solid-lubricant coating**

The process of coating formation, presented in figure 2, provides the opportunity to evaluate the technological interrelations, that occur in the enclosed volume of a vibroimpact chamber.

The formation procedure can be presented in stages, using the example of solid-lubricant molybdenum disulphide coating.

Stage 1. **Mechanical contact and adsorption of MoS$_2$ particles.** It helps to calculate or assign the modes of mechanical and chemical processes, as to cause plastic and elastic-plastic deformation in the contact zone at the moment of applying the external force of ball collision with the surface of the processed material. At the same time, the adsorption of powder particles on the metal surface occurs in the zone where the deposited molybdenum disulphide contacts the workpiece.

Stage 2. **The activation of the metal surface layer** is implemented as a result of plastic deformation and increase in the density of dislocations, the destruction of oxide films, the formation of juvenile surface zones and the enlargement of the contact area for such chemical reactions to proceed. It is required to calculate or assign the technological modes, compatible with those selected at the first stage of calculation.

Stage 3. **The formation of the boundary layer.** This stage requires the substantiation of energy, directed at MoS$_2$ crystallite grinding, the destruction of chemical oxide metal coatings in microrelief cavities by mechanical action of the working medium, the infiltration of powder particles and their adsorption to the surface layer of the activated metal.

Stage 4. **The formation of the lubricant layer, where the previously adopted technological modes are specified,** with account of the energy costs for compaction of particles of the deposited coating, crystallite grinding, their reciprocal chemical and diffusional adhesion, and the formation of the composite lubricant layer.

Stage 5. **The formation of the surface layer of the coating.** As a result of sliding and implementation of internal and external energy of the combined process, the particles of the working medium are oriented relative to the surface processed, the powder particles are laid parallel to the friction surface as reference planes, and the final coating profile is formed.

The technology of obtaining the vibrational chemical-mechanical zinc coating [3;4].
The stages of vibrational chemical-mechanical zinc coating formation, which determine the procedure for calculating the modes, as well as modelling the technological process and its features, can be represented as follows:

Stage 1. *The chemical-mechanical contact of workpieces with the working medium*. Under the influence of external energy, caused by the impact of solid bodies at the moment of applying the mechanical load, following the ball collision with the surface of the material processed, the film destruction occurs in the contact zone, which provides the possibility for the flow of chemical reactions and, when designing the modes, the energy parameters are evaluated by the mechanical component of the combined process.

Stage 2. *Activation and cleaning of the surface layer of the metal*, which occurs from mechanical impact of the working medium (for example, balls). In this case, the density of dislocations and active centres can increase, with simultaneous activation of ions and molecules in the (Zn++, Zn) solution, which must be taken into account when assigning the modes of chemical transformations of the surface layer.

As a result of the dynamic action and mixing of the working medium, the fresh solution is supplied and the waste is withdrawn. The greasy dirt is removed from the metal surface together with waste solution, thus combining the cleaning processes and improving the surface layer quality, which also requires the energy costs and must be considered in calculating the modes of combined processes for specific parts.

Stage 3. *The modes of coating formation*, where the areas of the metal surface with high activity adsorb Zn++ ions, which, when discharged, are deposited in the form of zinc coating. This determines the energy costs of the chemical component, and must be taken into consideration when structuring the technological process.

Stage 4. *The modes of setting the given density of combined coating*. Under the conditions of vibrowave impact and activation of galvanizing process components, the formation and growth of zinc coating occurs, involving chemical and mechanical components, for which it is required to design the modes and the technological process, and take account of the energy for constant inflow of fresh solution (suspension) of zinc powder to the metal surface. It provides the concentration balance, which determines the speed of coating formation. The intensive motion of the working medium causes the hardening of zinc powder.

Stage 5. *The modes for obtaining the required parameters of surface layers of vibrowave chemical-mechanical zinc coatings*. Under the influence of vibration impact and the increase in the coating thickness, the growth intensity and operational performance are declining. In this case, the associated processes can occur. In particular, the zinc particles, having weak adhesion to the base coating, are crumpled and deformed. Also, part of the coating and small bumps are removed, which can modify the roughness of the processed surface and increase its gloss.

The formation of vibration chemical-mechanical oxide coating [1-3]

The analysis of the mechanism of creating a durable hydroxide film, which was implemented in the medium of polymer balls, reveals the stages in the formation of vibrowave chemical-mechanical oxide coating, which govern the calculation of modes and structuring of the technological process.

Stage 1. *Selection and calculation of the modes*. At the first stage of the technological process structuring, the mechanical contact of parts with the working medium is taken into consideration. At the time when the load is applied, due to the collision of balls with the surface of the material processed, the elastic-plastic deformation occurs, and the oxide film is removed at the micro-/nanolevel in the contact zone. Ions and molecules of the oxidizing solution are adsorbed on the metal surface, requiring the external energy costs, which must be considered in calculating the technological modes.

Stage 2. *The calculation of modes, providing the compensation for the costs of activation and cleaning of the metal surface layer*. It must be taken into consideration that surface activation results from destruction of the natural oxide film, the growing density of dislocations and the formation of
active centres of juvenile surface areas. Simultaneously, the ions in the \( \text{Na}^+, \text{SiF}_6^{2-}, \text{H}^+, \text{OH}^-, \text{CrO}_4^{2-} \) solution are activated, along with their adsorption on the metal surface and contact with greasy dirt and oxides. The modes are adjusted, namely, the parameters of the working medium displacement during the supply of fresh oxidizing solution to the metal surface, and the withdrawal of the waste one, impaired after the reaction. Together with waste solution, oxides, greasy dirt and the products of chemical reaction are removed from the metal surface, which requires the external energy costs.

Therefore, the modes are calculated and the stage of the technological process is planned, combining the cleaning from dirt and oxides with preparation of the surface for oxidation with improved quality and durability of the surface layer.

Stage 3 includes the calculation of energy costs and modes of hydroxide film formation. It must be considered that surface areas of the processed metal with high activity adsorb the hydroxyl ion, and interact with it to form aluminium hydroxide by the reaction

\[
2\text{Al}^3+ + 6\text{OH}^- \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2\uparrow. \quad (3)
\]

This reaction flows with the emission of hydrogen, the removal of which is facilitated by the vibrating medium. Along with formation of aluminium hydroxide, side reactions can proceed in the solution. The interaction of \( \text{SiF}_6^{2-}, \text{OH}^-, \text{uCrO}_4^{2-} \) anions with soluble aluminium can result in formation of insoluble compounds of the \( \text{Al}_x(\text{SiF}_6)_3, \text{Cr(OH)}, \text{Al(CrO}_4)_3, \text{Al}_2\text{Cr}_2\text{O}_7 \) type, as well as more complex ones, having the ion \( \text{Al(H}_2\text{O)}_6^{3+} \), contained in the acidic medium of hexaquaaluminum.

Stage 4. The calculation of technological modes of obtaining the assigned thickness of the oxide film. The purpose of this stage is to ensure the desired quality (including service life) of the surface layer, where the impact of mechanical force and chemical activation of all components of the oxidation process results in formation and growth of the oxide film.

When calculating the modes, it should be remembered that the oxide film, formed on the surface, grows larger due to shrinking of the metal itself, which can modify the workpiece dimensions and violate its accuracy. The controlled continuous inflow of fresh solution to the metal surface through the pores in the oxide film supports its growth. At the same time, the new surface relief is formed, which determines its quality and involves the loosening of coating under the vibration impact.

Stage 5. The calculation of modes, providing the specified technological parameters of the product at the final stage of surface layer formation of the vibrowave chemical-mechanical oxide coating. At the last stage of coating formation, the internal energy of working solution activity is insufficient to overcome the distance from the oxide film surface to its base, therefore, there is a need in its external supply, which must be taken into account when structuring the technological process.

4. The application of chemical and mechanical coatings in machine construction

Figure 2 shows the workpieces with oxide coating.
Figure 2. The workpieces with the oxide film, obtained by vibrowave chemical-mechanical oxide coating

The treatment of workpieces was carried out in the following modes; in accordance with the proposed technology, the workpieces were subject to cleaning and transferred to the vibration chamber, where the polyethylene balls of 3 mm were used as a working medium, together with the oxidizing solution containing 2.5 g of sodium silicofluoride and 3.5 g of chromic anhydride per 1 liter of water. The vibration processing and oxidation were conducted in the developed modes: the amplitude of vibration is 2 mm, the frequency of vibration is 25 Hz, the duration of treatment is 20 minutes. The high-quality coating of 4-5 µm in thickness has been obtained.

Solid lubrication coatings (vibrowave chemical-mechanical solid coatings, mainly made from molybdenum disulphide) were applied to the friction nodes. As shown in fig. 3, stable high-quality vibrowave chemical-mechanical solid coatings can be obtained within the process time of 50-60 minutes.

Figure 3. The dependence between the density of vibrowave chemical-mechanical solid coating and the deposition time. MoS₂ coating on steel 45. The annealed (1) and hardened (2) samples

In this case, the modes of vibrowave chemical-mechanical solid coating have the following parameters: chamber travel speed – 0.2 – 1.3 m/sec; temperature in the processing zone is 293 – 420 K; processing time - 50- 60 minutes.

Figure 4 shows the workpiece with a multi-layer coating, i.e. the vibrowave chemical-mechanical oxide coating and subsequent painting with a layer of about 0.3 mm in density.
Figure 4. A workpiece after multi-layer coating

The corrosion and coating adhesion tests of a workpiece have shown that in all operating conditions, the coatings produce the results significantly exceeding those previously achieved.

5. Conclusion
The integrated process of automated modelling of technological processes has been developed, taking into account the operating conditions for specific types of chemical-mechanical durable combined coatings, which made it possible to work out new methods of processing and obtaining the vibrowave chemical solid coatings, confirm the positive results of using new coatings [1-4], make fuller use of available information material, and accelerate the structuring of processes for new types of durable coatings up to 4-5 times.

References:
[1] Babichev A P et al. 2012 Vibrational mechanical chemistry in processes of finishing hardening treatment and coating of machine parts (Rostov-on-Don: The Publishing Centre of DSTU, 204)
[2] Ivanov V V 2009 Technological possibilities for combined vibrational mechanical-chemical coating deposition The issues of vibration technology: Inter-University collection of scientific papers (Rostov-on-Don: DSTU) pp 151-156
[3] Ivanov V V and Tsurkan O V 2010 The formation of the Al(OH)3 oxide film in conditions of vibrational processing with the use of polymer working mediums Vibrations in engineering and technologies 1(57) 94-97
[4] Babichev I A et al. 2010 Physical-technical fundamentals of vibration mechanical-chemical coatings The issues of vibration technology (Inter-University collection of scientific papers) (Rostov-on-Don: DSTU) pp 20-24
[5] Safonov S V 2015 The criterial system of planning and using technological processes for improving the operational characteristics of the surface layer The Bulletin of Voronezh State Technical University 11(3) 4-10
[6] Smolentsev E V 2005 The structuring of electrical and combined processing methods (Moscow: Mashinostroenie)
[7] Kuzovkin A V 2001 The combined processing by a loose electrode (Voronezh: The Publishing House of Voronezh State University)
[8] Smolentsev E V 2005 The design of electrical and combined methods of processing (Moscow: Mashinostroenie)
[9] Smolentsev V P 1983 Electrophysical and electrochemical methods of material processing
(Vol 1) (Moscow: Vyschaya Shkola)

[10] Smolentsev V P, Safonov S V, Smolentsev E V and Fedonin O N 2016 Magnetic pulse cleaning of products IOP Publishing Ltd *IOP Conference Series: Materials Science and Engineering* **124**

[11] Smolentsev V P, Safonov S V, Smolentsev E V and Fedonin O N 2016 Stampless fabrication of sheet bars using disposable templates *IOP Conference Series: Materials Science and Engineering* **124**

[12] Smolentsev V P, Safonov S V, Zolotarev V V 2016 Processing of Channels in Heat Engine Filters *Procedia Engineering* **150** 1124-1130