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The algorithm of development safe methods for depositing metallic coatings by CVD-method of organometallic compounds

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Abstract. The CVD-method of organometallic compounds is a universal method of obtaining functional metal coatings on substrates of various chemical composition and configuration. The essence of the method is the evaporation (sublimation) of the organometallic compound in the reactor of the metallization unit and the deposition of metal on the substrate heated to the decomposition temperature of the initial reagent. This article presents the results of research work group of authors to create the algorithm of development safe methods for depositing metallic coatings by CVD-method. The increase of the industrial safety of metallization is achieved due to automation of the process, equipping the plant for the application of metal coatings with locking and alarm systems. The ecological nature of the CVD-method, in which extremely hazardous substances were used as initial reagents, was ensured by sealing equipment and conducting the process in a closed cycle with the possibility of re-use of the reagents. This eliminated the flow of pollutants into the environment and allowed the implementation of the principles of resource and energy conservation.

Keywords: chemical vapor deposition, organometallic compounds, safety, automation, resource saving.

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Introduction

The application of functional metal coatings is characterized by a complex negative impact on the environment, regardless of the method and apparatus design of the process. The implementation of technological processes, including restoration and hardening of machine parts, the creation of composite materials using the CVD method (Chemical Vapor Deposition, that means, “chemical gas-phase deposition”) come with the expenditure of natural resources (energy, water, etc.), are accompanied by

emissions of pollutants into the air (gaseous substances, aerosols of organometallic compounds, etc.), wastewater discharges of complex composition, forming at the stages of preparation of substrates for metallization (surfactants, metal cations) into water bodies, the formation of solid waste production and consumption (waste filters, packaging waste, etc.). This makes it necessary to apply a comprehensive and integrated approach in the search for mechanisms to ensure the required level of safety of relevant technological processes and production [1 - 3].

When developing technological processes and

introducing them into enterprises, it is necessary to justify the safety of all elements of the production system (feedstock, auxiliary materials, hardware design, marketable product) for human health and the environment [1, 2].

The purpose of this study is to create an algorithm for the development of environmentally friendly methods for applying metal coatings using the CVD method.

Experimental part

The preparation of a metal coating on the surface of a substrate can be carried out by various methods, such as galvanic deposition, diffusion metallization, gas-flame and plasma spraying, laser and gas-powder surfacing [4 - 6]. Recently, the CVD method has been of great interest, the use of which allows one to obtain high-quality coatings and films on substrates of various chemical compositions and configurations. As starting reagents, various groups of organometallic compounds (OMC) are used.

The essence of this method is as follows: the initial compound, converted by evaporation or sublimation into a gaseous state, enters the reaction chamber, where it is deposited on the surface of a substrate heated to the decomposition temperature of the reagent.

The main safety problems in the implementation of the CVD method in the production environment are associated with the potential risk of contamination of the air of the working area, atmospheric air and surface water bodies with toxic chemicals used as auxiliary and starting compounds,

as well as those formed as products of chemical gas-phase deposition of organometallic compounds.

The discussion of the results

Analysis and assessment of the safety level of the production cycle begins with the stage of preparatory operations for metallization, including the following main stages: washing, including interoperational and final, degreasing, activation, sensitization or chemical oxidation of the surfaces of substrates (parts, filler elements of composite materials).

Parts washing at the stage of preparatory operations is carried out in hot water ($t = 60 \dots 70 \text{ }^\circ\text{C}$) without adding reagents, which is accompanied by the formation of category I wastewater. The remaining stages are characterized by the use of reagents and the formation of wastewater of categories I, II, III and IV [1].

To quantify the degree of environmental danger of the components of technological solutions, it is necessary to determine the value of their environmental criterion, which is calculated as the ratio of the final concentration of each component of the solution in discharged waste water to its maximum permissible concentration in the water of the water body being exposed. Table 1 presents the results of the analysis and calculation of the degree of environmental danger of the solution components used in the preparatory stages of the technological processes of applying wear-resistant coatings and metallization of the elements of the reinforcing phase of composite materials by the CVD method of carbonyl organometallic compounds [1, 6 - 8].

Table 1 The degree of environmental hazard of the components of the solution at the stage of preparatory metallization operations CVD-method

Solution components	Name of the technological operation in which the components are used	Maximum permissible concentration, mg/dm ³	Danger Class	Ecological criterion of the solution component
OP-7	Chemical degreasing of a metallized surface, including glass and carbon fibers	0,3	3	$1,7 \cdot 10^4$
OP-10		0,5	4	$1,2 \cdot 10^4$
Cr ³⁺	Liquid phase oxidation of a metallized surface, including glass and carbon fibers	0,07	3	$0,4 \cdot 10^6$
Mn ²⁺		0,01	4	$0,5 \cdot 10^6$
Sn ²⁺ (SnCl ₂)	Metallic surface activation	0,112 (in terms of tin)	4	$0,3 \cdot 10^6$
Pd ²⁺		-	-	$0,03 \cdot 10^6$
Cl ⁻	Sensitization of a metallized surface	300,0	4	$1,4 \cdot 10^3$
SO ₄ ²⁻	Carbon nanomaterial purification oxidation	100,0	-	$0,9 \cdot 10^4$

According to table 1, the greatest environmental danger is wastewater formed at the stages of liquid-phase oxidation and activation of the metallized surface, which suggests the need for organizing and implementing complex multi-stage wastewater treatment at this production site.

CVD metallization is carried out in sealed reaction chambers. The release of harmful (polluting) substances into the atmosphere can occur in several cases:

1. Hazardous to the environment and human health substances are formed in the form of products of incomplete combustion of the MOC when non-compliance (violation) of the technological conditions of the process (temperature and pressure in the reaction chamber, pumping speed of reagent vapors, concentration of OMC vapors, volumetric gas velocity, the presence of additives to vapors OMC and others) and can enter the atmosphere when using installations that are not equipped with an afterburner.

2. Toxic compounds can enter the air of the working zone during depressurization of the reaction chamber during operation of faulty equipment.

This case can be attributed to the category of emergency situations at the facility, which determines the need for an accident risk analysis procedure, which includes identifying the conditions for the occurrence and development of a dangerous situation and assessing the risk of accidents at the metallization site of the enterprise.

For the CVD method, the essence of which is the evaporation (sublimation) of an organometallic compound and the deposition of metal on a substrate heated to the decomposition temperature of OMC (from 70 to 650 °C), it is rational to apply the hazard and operability analysis method [5].

The main metallization risks are associated with the initial reagents for the CVD process. In the practice of modern plants, when choosing initial OMC, preference is given to carbonyl, cyclopentadienyl and diketone compounds of transition metals, which is determined by their high volatility and ease of thermal dissociation at relatively low temperatures. Moreover, many OMCs are classified as highly toxic compounds (for example, nickel tetracarbonyl, iron pentacarbonyl), which imposes serious requirements on ensuring the safety of the technological processes in which they are used [3].

At the stage of experimental research, when the search for optimal temperature and speed conditions of metallization is carried out and the process is carried out unidirectionally, the installation for applying metal coatings should be equipped with an afterburner in which, under the influence of high temperatures, unreacted compounds are completely

decomposed to safe products. This will reduce the risk of returning to the reaction chamber of non-volatile compounds (products of incomplete thermal decomposition of the starting reagents) and eliminate the likelihood of their release into the environment.

In other cases, metallization is carried out in optimal technological conditions in a closed circuit: unreacted compounds (not more than 5%) are returned to the reaction chamber, where re-decomposition of the vapor-gas mixture occurs in subsequent intervals of the working cycle [4, 5].

In order to ensure environmental safety requirements and minimize the risk of accidental emission of harmful substances formed in the event of a change in technological process conditions, it is necessary to ensure the possibility of placing metallization plants in fume hoods, as well as equip the CVD coating plants with aerosol (dust) emission purification devices.

It is recommended to use filters of various designs to clean the exhaust air from potentially dangerous reaction products of the CVD process.

The composition of the forming aerosol includes particles of metal oxides and carbides, atomic carbon; particle size less than 1 micron. In this case, the efficiency of the dust collection will be significantly affected by the electric charge of the particles: the presence of unlike charges on the particles increases the filtration efficiency. This effect is weaker with increased moisture content (up to 70%) and high gas and dust flow velocities (up to 6 m / min) [1, 3].

To implement the CVD method in the conditions of production of a unique high-tech commodity product, it is recommended to equip the metallization plants with fine filters, which are designed to capture predominantly submicron particles from the exhaust gases with a low input concentration (less than 1 mg / m³) and a filtration rate of less than 10 cm / sec. These filters cannot be regenerated. The degree of dust collection reaches 99% [1, 8].

Conclusions

Thus, in order to reduce the degree of negative impact on the environment, to ensure the safety of metallization processes using the CVD method, a comprehensive analysis and assessment of the process safety level with the justification of organizational, managerial, technical and design solutions for its optimization is recommended. For the CVD method, it is relevant:

- ✓ introduction of low-waste and resource-saving technologies,
- ✓ organization of local wastewater treatment systems;
- ✓ reduction of pollutants hazardous to the environment and human health into the

✓ air.

Among technological and technical approaches to optimizing production, the main attention should be paid to the following:

- ✓ the use of high-performance technologies in the lines, allowing to obtain high-quality coatings in the optimal high-speed mode of metalization;
- ✓ introduction to the line of devices of operational information on the status of the implementation of individual stages of technological processes;
- ✓ mechanization and automation of manual and labor-intensive processes;
- ✓ computerization and robotization of

technological processes.

Management approaches include the implementation of environmental and energy management systems or the use of their tools (auditing, environmental and energy efficiency programs).

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Металл органикалық қосылыстардың CVD-әдісімен металл жабындарын жағудың қауіпсіз әдістерін әзірлеу алгоритмі

Козырева Л. В., Фадеев О. В., Юдин А. О.

Түйіндеме. Металл органикалық қосылыстардың CVD-әдісі химиялық құрамы мен конфигурациялары әртүрлі төсеніштерде функционалды металл жабындарын алудың әмбебап әдісі болып табылады. Тәсілдің мәні – металдау қондырғысының реакторында металл органикалық қосылыстардың булануы (сублимациясы) және бастапқы реагенттің ыдырау температурасына дейін қыздырылған төсеніште металды тұндыру. Мақалада CVD-әдісімен металл жабындарын жағудың қауіпсіз әдістерін әзірлеу алгоритмін жасау бойынша авторлардың ғылыми-зерттеу жұмыстарының нәтижелері келтірілген. Металдандырудың өнеркәсіптік қауіпсіздігін арттыруға – үрдісті автоматтандыру, металл жабындарды жалатуға арналған қондырғыны бұғаттау және сигнал беру жүйелерімен жабдықтау есебінен қол жеткізіледі. Бастапқы реагенттер ретінде аса қауіпті заттар пайдаланылатын CVD-әдістің экологиялық жабықты герметизациялаумен және үрдісті тұйық циклде жүргізу арқылы реагенттерді қайта пайдалану мүмкіндігімен қамтамасыз етіледі. Бұл қоршаған ортаға ластаушы заттардың түсуін болдырмайды және ресурс - және энергия үнемдеу қағидаттарын іске асыруға мүмкіндік береді. **Түйінді сөздер:** Химиялық газфазалық тұндыру, металл органикалық қосылыстар, қауіпсіздік, автоматтандыру, қор (ресурс) үнемдеу.

Алгоритм разработки безопасных способов нанесения металлических покрытий CVD-методом металлоорганических соединений

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Аннотация. CVD-метод металлоорганических соединений является универсальным методом получения функциональных металлических покрытий на подложках различного химического состава и конфигурации. Сущность способа заключается в испарении (сублимации) металлоорганического соединения в реакторе установки металлизации и осаждении металла на подложку, нагретую до температуры разложения исходного реагента. В статье представлены результаты научно-исследовательской работы авторов по созданию алгоритма

разработки безопасных способов нанесения металлических покрытий CVD-методом. Повышение промышленной безопасности металлизации достигается за счет автоматизации процесса, оснащения установки для нанесения металлических покрытий системами блокировки и сигнализации. Экологичность CVD-метода, в котором в качестве исходных реагентов используются особо опасные вещества, обеспечивается герметизацией оборудования и проведением процесса в замкнутом цикле с возможностью повторного использования реагентов. Это исключит поступление загрязняющих веществ в окружающую среду и позволит реализовать принципы ресурсо- и энергосбережения.

Ключевые слова: химическое газофазное осаждение, металлоорганические соединения, безопасность, автоматизация, ресурсосбережение.

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