Anna GIBAS
Jolanta GĄSIOREK*

DOI: https://doi.org/JoT2021_08

PERSPECTIVE OF SOL-GEL HYDROPHOBIC SILICA DEPOSITED USING LOW-PRESSURE COLD SPRAY AND ULTRASONIC ATOMIZING FOR AUTOMOTIVE COATINGS

Keywords: *sol-gel, low pressure cold spray, ultrasonic atomizing, coatings, silica, hydrophobic*

The automotive sector is under constant pressure to minimize fuel consumption and reduce pollution emissions while maintaining a declining tendency for weight and cost reduction. This makes the material selection process a major of engineering design considerations. In the paper, the main automotive requirements were formulated to analyze the potential of selected deposition (low pressure cold spray and ultrasonic atomizing) and material fabrication (sol-gel method) techniques for application in the automotive industry.

1. INTRODUCTION

The general trend in automotive engineering is and always will be more for less. The importance of material selection for product development is influenced by sought-after performance and operational characteristics. Most surfaces are designed to work in dry conditions, and for that reason, hydrophobic surfaces are widely studied among many different industries, including automotive. The hydrophobic potential in automotive is used to repel water and dust, making the coated surface self-cleaning. This feature may prevent the surface from fading or stains and facilitate abrasion resistance, UV resistance, while extending the service life of the coated component.

In the first place, the paper underlines the importance of material engineering in material selection for the automotive industry by displaying selected material engineering solutions for automotive industry requirements. The following chapter presents literature overview aimed at indication of material trends and the most common materials used in the automotive industry. A description of modern automotive

* Wroclaw University of Science and Technology

coatings, as well as future perspectives focusing on the potential of low-pressure cold spray (LPCS) and ultrasonic atomizing (UA) for coating deposition and sol-gel technique as a method for material fabrication, is also provided.

The paper constitutes a theoretical part to the master thesis of the first author [1]. The series of morphological, topographical, chemical, and thermal analyses of hydrophobic silica coatings deposited LPCS are presented in the previous papers [2–4]. The initial research of UA coatings concerning the etching time and technique, delay influence between substrate preparation and coating spraying, as well as the deposition sequence, all influencing the hydrophobicity of deposited coatings, are presented in [5].

2. MATERIAL SELECTION AND INDICES OF AUTOMOTIVE MATERIALS

The development of a new product is supposed to follow a specific routine (Fig. 1). Engineering design process including geometry, material, processes, and economic considerations [6] establishes product requirements. In terms of information flowchart, these requirements are defined as an input variable and can be treated as a starting point for introducing new ideas for materials or creating variants being outputs of the selection process [7]. The appropriate linkage between inputs and outputs is, however, ensured by proper selection process. This information processing relies on material selection based on available material databases. Alongside, the development of entirely new material is performed and introduced to the material bases, but this approach is more time-consuming [6, 7].

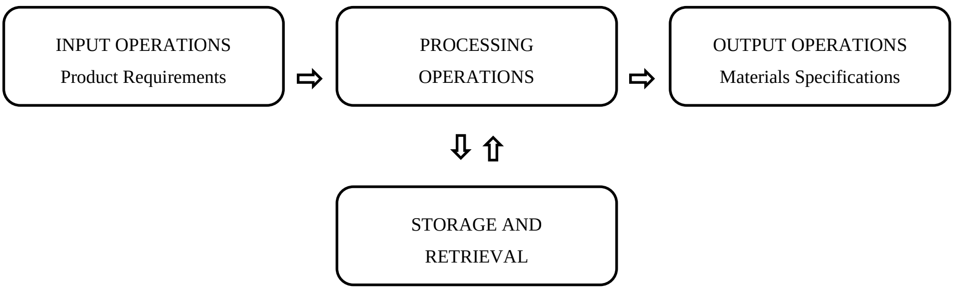

Fig. 1. Information processing routine for material selection, based on [7].

The growing importance of material selection can be summed up as: significance in design engineering and manufacturing in terms of final cost or cost of material, exploitation of available manufacturing technologies, providing adequate quality, consideration of aesthetics and possible failures; weighting material conservation and environmental protection in terms of limiting the quantities of utilized resources and environmental impact; facing technological advances in terms of familiarization and adopting new solutions and systems in materials technology [2].

2.1. FUNCTION: AUTOMOTIVE REQUIREMENTS

The emerging call for new technologies and solutions is one of the everlasting features of the automotive industry. Currently, minimization of the impact of vehicles on the environment is an industrial trend gaining high popularity [8]. Previously, environmental care was commonly undervalued, which has been gradually changing due to government legislation, independent agencies, and eco-friendly community actions. The other automotive requirements are resource constraint and cost reduction [8]. For that reason, the number of actions from the very first day of the concept till the last day of the vehicle life is still invariably aimed at reduction of environmental footprint at the least amount of resources and lowest possible price.

The comprehensive approach of automotive companies to the implementation of environmental, economic, and cost requirements may involve technical and organizational innovations improving the quality and reducing resource overuse, environmental impact, and overpaying. Exemplary actions to implement automotive requirements can be minimization of consumption [9] or elements' weight [10], closed-loop cycles [11], environmental management [12], prevention of pollution [13, 14], cost reduction (Tab. 1).

2.2. TRANSLATION: MATERIAL ENGINEERING SOLUTIONS

Automotive engineering-imposed requirements are directly translated to the material engineering world (Tab. 1). The material selection process, however, is driven by different assumptions than automotive engineering ones. Weight reduction and environmental protection criteria are not of prior importance. Resource cost remains still the decisive feature, but it needs to be balanced with performance attributes, listing mechanical, tribological, chemical, and physical properties.

Tab. 1. Approach for adapting new materials in the automotive industry, based on [3].

Automotive Industry Requirements	Automotive Engineering Implementations	Material Engineering Alternatives
Resource Conservation	Minimization of Consumption	High-Performance Resources
	Minimization of Elements Weight	Low-Weight Resources
	Closed-Loop Cycles	Recyclables
Environmental Protection	Environmental Management	Eco-Friendly Treatments
	Pollution Prevention	Non-Toxic Resources
	Closed-Loop Cycles	Recyclables
Price Reduction	Cost Reduction of Development Stage	Low-Cost Resources
	Cost Reduction of Production Stage	Low-Price Solutions

In automotive engineering, material science has never been more strategic. The process of material selection influences not only the final cost of the vehicle, but also contributes to increasing safety, risk mitigation, weight reduction, public outreach support, and cutting vehicle emissions. Material engineering provides the competitive advantage of combining quality, emission goals, and legislation requirements with critical insight on the material characteristics (Tab. 1). This results in an optimized fuel economy, recyclability, economics, and specification of the material.

3. TECHNOLOGICAL ADVANCES AND POTENTIAL IN AUTOMOTIVE

Within the wide range of materials in the automotive sector, steel and aluminum continue to play a major role among vehicle components. Various types of steel (highly-plastic interstitial-free steels, bake-hardenable steels, dual-phase steels, transformation induced plasticity steels, complex phase steels, mart steels, austenitic steels (twinning induced plasticity steels), high-strength and super-plastic steels, nano-structured hot-rolled steel, advanced high-strength steels, ultra-high-strength steels [15]) are commonly employed due to their high strength, possibility of plastic forming, welding, and coloring, sufficient service life when proper anti-corrosion treatment applied, satisfactory cost. Besides, the small thickness of steel sheets translates into significant vehicle weight reduction.

Various types of aluminum (silumines with modifiers of the first type: titanium, vanadium and ultrafine particles of oxides, carbides, borides, and other non-metallic inclusions, and modifiers of the second type: lithium, sodium, potassium, rubidium, cesium, sulfur and phosphorus [15]) are mainly used due to their low weight [16].

Metals and alloys are susceptible to corrosion. NACE Corrosion Basis defines corrosion as "the deterioration of a material (usually a metal) because of a reaction with the environment". Corrosion is provoked primarily by the working environment and it affects the degradation rate of the material [17]. Additionally, mechanical wear (as a result of friction or fatigue) facilitates the corrosion rate. In steel, iron is oxidized, which leads to the production of rust [18]. Aluminum is corroding due to intermetallic compounds in the alloy structure [19].
A typical method for providing corrosion resistance is covering the susceptible surface with protective layers.

3.1. MODERN AUTOMOTIVE COATINGS – CURRENT STATE

Due to the multi-functionality of automotive coating, usually the sandwich structure is used where each layer performs a specific function. A modern automotive coating includes: pre-treatment for cleaning and protection or just the surface of a vehicle body; e-coat (electro-coating) for corrosion protection and prevention; sealer for leakproof, minimization of chipping, noise reduction; primer for finish quality improving basecoat adhesion and stone chip; basecoat for the cover tone; optional multicoat for additional visual effects (such as gloss or smoothness); and finally, clearcoat for color protection (weather resistance) and visual depth [20]. All the components of sandwich structures of coating are applied using specific techniques with a certain time-lag between them. This leads to elongating the service life of the coating and shields the vehicle from external forces (environmental conditions such as rain, snow, fog, heat, cold, humidity, UV radiation, pollution, or mechanical conditions such as scratching).
The external panels of the vehicle, such as fitting panels, roof, side panels, are the first example when listing the automotive coatings. Other areas for coating application are underbody, floor, wheel housings, rockers [20].

There are several issues pertinent to the currently used solutions for the fabrication of automotive coating. The automotive industry requirements (Tab. 1) are fulfilled as follows:

- resource conservation – a large amount of paint cannot be recovered (40-50%) [21], improper paint amount affects the surface finish (composition of paint, final geometry, and coating positioning are the target surface characteristics to be controlled), number of initial and finishing techniques increases energy consumption
- environmental protection – an increase in paint utilization leads to volatile organic compounds (VOC) emission, the remaining paint should be stored properly in order not to pollute the environment, good air-conditioning is

needed to protect the operator and the workplace, but the spraying is humidity- and temperature-dependent
- price reduction – large losses of paint and energy as well as waste collection and storage do not contribute to price lowering

3.2. LOW-PRESSURE COLD-SPRAY (LPCS) – PERSPECTIVE FOR COATING DEPOSITION

LPCS is extensively used in coating building or rapid manufacturing by spraying a powder [22–25]. The key importance distinguishing CS from other thermal spraying techniques is that the powder is not melted in the gas stream during its deposition. For that reason, the temperature of the gas stream is set as low as possible, which facilitates retaining the structure of the initial powder [26]. The mechanism is not the temperature, but the increasing kinetic energy. The powder particles hit the substrate when the critical velocity, different for each material, is exceeded. The acceleration of particles is obtained due to the introduction of feedstock powder particles to the gas stream. As particles reach the nozzle, their velocity is following the increasing velocity of the gas stream (**Błąd! Nie można odnaleźć źródła odwołania.**a). The gas stream velocity is connected with the construction of the converging-diverging nozzle itself [27]. In the converging part, the preheated gas is compressed, which leads to an increase of pressure and temperature with an instant decrease of velocity. In the throat, pressure and temperature reach their maximal values and the velocity begins to increase. In the diverging part, an expansion of the gas is observed, accompanied by a drop of pressure and temperature with an instant increase of velocity up to the sonic level. All of these enable the powder to reach a velocity of up to 700 m/s [24, 25].

The most important element of the LPCS system is de Laval nozzle [23–25, 28]. The typical setup of LPCS is of small dimensions that favor portability. Additionally, a small number of elements makes LPCS easy in maintenance and operation.

The potential outreach of the cold-sprayed (CS) coatings in automotive may result from adding functionalities while deposition [22, 23] and the possibility of repair of damaged components [21, 29, 30].

The automotive industry requirements (Tab. 1) are fulfilled as follows:

- resource conservation – utilization of high-performance resources – the properties of feedstock powder determine the properties of final coating [23], they are retained in the course of spraying [26]; reduction of the amount of feedstock powder by utilization of nano- and submicron size feedstock powder which enables enhancement of properties; possibility of several different material systems (substrate and coating) including highly dissimilar materials or thermally sensitive materials [21, 30]; full recycling of the remaining feedstock powder [24].
- environmental protection – minimal energy consumption (minimal preparation of substrate and optional minimal preheating of the substrate) [24].

- price reduction – minimal surface preparation which lowers the price of the final product; obtaining cold-worked structure, high hardness, high density, heat and electric conductivity with retaining low residual stress without additional treatment [25]; remanufacturing of scraps [30]; guaranteeing simple, low maintenance design of spraying system; replacing expensive material with cheaper substrate covered with a functionalized coating to reduce the final price.

The disadvantages of the LPCS may be nozzle clogging as the result of electrizing of powder agglomerates. The second issue is the correlation of velocity and pressure which disables an unlimited increase of the velocity [25]. Additionally, even though new material systems are still being developed, not all combinations are possible using LPCS.

LPCS remains a tempting option in the automotive industry, as it enables improvement of functionality and repairments. Using cold spray for imparting functionalities makes possible the development or enhancing of macroscopic and microscopic features [21, 30]. In general, the structural layout and surface characteristics determine the properties of the material system. In most cases, mechanical, tribological, thermal properties, as well as corrosion resistance are selected in such a manner to minimize the surface exposition to the degradation of the working conditions [21]. The potential for repair application promotes the conservation of resources and energy for production and extends the service life of the elements and assemblies in a cost-effective manner [21, 30]. Possible repair solutions are being tested in military and aviation applications, which enables creating repair protocols providing repeatability and high quality (in terms of corrosion, tensile, compression/bearing, shear, fatigue, residual stress, impact, hydrogen embrittlement [30]) for future repairs. In the automotive industry, LPCS utilization is especially interesting when it comes to the repair of large or complex panels or precise elements such as engine block [30]. Additionally, cold spraying may be an alternative for the restoration of manufacturing scraps [30].

3.3. ULTRASONIC ATOMIZATION (UA) – PERSPECTIVE FOR COATING DEPOSITION

The innovation of UA lays in the deposition of ultrathin coatings due to the formation of small droplets of feedstock liquid. The key importance, distinguishing UA from other spray nozzle techniques, is that in UA pressureless low-velocity spray (0.08–0.13 m/s) is used [31]. This contributes to reduction of overspray which directly translates into material conservation. The mechanism of droplet creation lies in the conversion of electric energy into acoustic waves of high frequency, and then into mechanical energy [32]. At first, the vibration of the nozzle in the direction perpendicular to the surface of the nozzle leads to transforming vibration energy into standing waves. This particular type of wave is called a capillary wave; they form a rid pattern in the feedstock liquid sucked to the nozzle. With an increased amplitude of vibration, the wave amplitude increases respectively. At the critical amplitude, different for different liquids, the wave collapses, producing small droplets of liquid (typically of a range 18–85 μm [31]), which are ejected from the surface of the nozzle.

The most important part of the UA system is the ultrasonic spray nozzle [33]. Every nozzle has a specific resonant frequency determined mainly by its length [32]. The UA bases on liquid feed onto the vibrating surface of the nozzle, hence the feed rate influences the atomizing rate. To provide a wide variety of possible depositing material, the UA nozzle usually has a wide range of flow rates [31].

The ultrasonic atomization for the automotive industry is feasible for the deposition of thin coating which is consistent with the minimization of element weight by the application of high-performance resources (functionalization by thin layers). The automotive industry requirements (Tab. 1) are fulfilled as follows:

- resource conservation – limiting material consumption and overspray (high homogeneity, high precision); adjusting coating thickness via flow rate adjustment and choice of nozzle frequency; reducing material consumption via utilization of repeatable spray patterns for invariable results; optional providing corrosion-resistance depending on sprayed material; optional spraying of sandwich structures; possibility to reuse material portions remaining in the spraying system.
- environmental protection – reducing waste, so that overspray can be recovered and re-used; reducing VOC production.
- price reduction – guaranteeing simple, low-maintenance design of spraying system; any element of the spraying system can be replaced (nozzle, pump, lines, etc.) – the remaining components may still be used; replacing expensive material with cheaper substrate covered with a functionalized coating to reduce the final price.

The disadvantages of the ultrasonic atomizing may be nozzle clogging as a result of setting inappropriate parameters of the process, properties of atomized fluid, which rheology is changed on the route of atomizing, or decomposition of the supply lines as a result of the chemical composition of the coating material.

Typical applications include windshields, headlamps, glazing, touch screens, sensor covers, exterior trim elements, interior elements such as internal console, dashboard elements, fabrics, textiles [33, 34]. The specific functions of the ultrasonic spray coatings may be an extended service life, UV-protection, enhanced abrasion, mechanical, thermal, and chemical resistance, improved weatherability [34]. Besides functionality, additional features comprise aesthetics (transparency, clarity, coloring) and easy-to-clean properties [33].

3.4. SOL-GEL METHOD – PERSPECTIVE FOR FEEDSTOCK MATERIAL FABRICATION

A sol-gel method is a bottom-up approach [35] that facilitates the fabrication of materials of certain properties or enhancement of certain features. The manufacturing of functionalized silica used in [1–5] can be described as follows. Sol-gel synthesis alkoxide precursor (typically being tetramethoxysilane or tetraethoxysilane) is subject to numerous hydrolysis and polycondensation processes. At first, sol is formed. On this step of the sol-gel process, substitution reactions in the solvent environment take place – the replacement of an alkoxy group (− OR, where R is an alkyl group) with a hydroxyl group (− OH), then, the creation of ≡ Si − OH bridges (via hydrolysis), and simultaneously ≡ Si − O – Si ≡ network (via condensation)). The progressive condensation and solvent evaporation lead to obtaining gel. At any stage, it is possible to introduce the functionalization, but the preferred option is to anchor the agent onto the surface of already formed construction, i.e. an extended network or separate particles suspended in the alcohol-water environment. The modification, as for the silica synthesis itself, bases on the hydrolysis and condensation between silica and functionalization agent that can be subjected to hydrolysis. The coupling proceeds by bonding functionalizing agent in the places of physically and chemically active residual silanol groups (≡ Si − OH). Silanol groups react with the agent and the oxygen bridges ≡ Si − O – Si ≡ are created, which provides covalent bonding of agent chains to silicon central atom. High level of homogeneity, as well as size and shape uniformity, are typical features of sol-gel synthesis products [35]. The parameters influencing the hydrolysis and condensation rates are type of precursor used, molar ratio of precursor to solvent, type and concentration of the solvent, polarity of the solvent, pH of the solution, temperature of synthesis [2, 3, 36, 37].

A quick overview of possible sol-gel products indicates the versatility of the method in terms of the form of the final product [35]. The general usefulness of modern sol-gel products is reflected in the available literature. It is possible to obtain dense films, fibers, powders, xerogels, aerogels, and dense coatings [35, 36]. Additionally, organic-inorganic material systems can be successfully produced [36, 37].

The sol-gel for the automotive industry may offer corrosion resistance, water repellence, wear resistance, self-cleaning, antibacterial, antifungal, (semi)conducting, antistatic, UV-protective, and other properties [17, 38, 39].

The automotive industry requirements (**Błąd! Nie można odnaleźć źródła odwołania.**) are fulfilled as follows:

- resource conservation – possible for functionalization in a large-scale process; ensuring a high level of homogeneity and purity on a molecular level; possibility of fabrication of high surface area materials; feasible for complex materials designed on a molecular level; suitable for thin (microns) high-quality films.
- environmental protection – possible to be carried out at room temperature or relatively low processing temperatures.
- price reduction – low-cost facilities; rather inexpensive substrates of the synthesis; during a single process, morphology, shape, textual properties can be controlled.

The disadvantages of sol-gel processing may be a relatively high price of precursors and long-lasting dehydration [40]. Sol-gel coatings may be, for instance, applied for automotive glass (mainly fluorine functionalized alkoxysilanes), metal panels, constructional elements, or display screens [38]. Exemplary coatings may exhibit different properties, such as photocatalytic, anti-reflective, self-cleaning, and hydrophobic properties [41–43].

4. ESSENCE OF HYDROPHOBICITY AND ITS IMPORTANCE FOR THE AUTOMOTIVE INDUSTRY

There are two main types of surface interaction with water: water repelling and water spreading out [44]. According to Young's equation, a hydrophobic surface is characterized by the water contact angle higher than 90°. The boundary between hydrophilic and hydrophobic states is called intrinsic wetting threshold (IWT). Sometimes, lower IWT of 65° is even suggested for the construction of superhydrophilic and superhydrophobic surfaces, which is connected with molecular interactions and nanometric size [45]. Surfaces exceeding the 150° threshold are called superhydrophobic.

The important role in water-repellency is played by two main features [17, 46]: free surface energy – generally, low surface energy facilitates higher hydrophobicity; hierarchical roughness – generally, high surface area favors higher hydrophobicity.

Free surface energy can be modified using chemical components that may react with physically and chemically active residual silanol groups (-OH) left after sol-gel synthesis [46]. These chemical compounds contain chemical elements characterized by high electronegativity [17, 47]. Functionalization of sol-gel products with the compound containing highly electronegative fluorine (F) reduces free surface energy, while increasing hydrophobic potential [48–50]. A good example is the application of 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FOTS), which is composed of a single long fluoroalkyl chain grafted to a central silicon atom [2]. During the functionalization of silica gels, these functionalizing chains replace -OH groups bonded with central silica atoms [51]. Additionally, the 3-dimensionality of functionalizing chains is a steric barrier for grafting other chains and never the whole structure to-be-functionalized, being extended network or separate particles, can be covered with FOTS chains [48, 51]. The side effect of functionalization is blocking some -OH groups in the silica structure [2].

When it comes to wetting, Robert N. Wenzel, 1936, recognized that behavior of water droplet on smooth and rough surfaces is different [52]. Cassie-Baxter, 1944, found out that the asperities of roughness may create special pockets for air entrapping [53, 54]. A combination of both – a highly rough surface that is filled with air-pockets – facilitates the enhancement of **multi-level roughness**. Each level of roughness may contribute to an increase in specific wetting behavior. To put it simply, the microscale roughness forms micro pockets which prevent water penetration into the asperities of the surface. The nanoscale roughness also entraps air in nanopockets, but this prevents mainly water condensation [53, 55–57]. Therefore, nano-level can excessively promote superwettability.

In that sense, grafting, fluoroalkyl chains may be employed not only for decreasing surface energy but also for enhancement of surface roughness [51]. Unfortunately, the hierarchical structure is very fragile and may irreversibly transform into a homogenous solid-liquid interface [57]. This means that the usage of FOTS for functionalization and the development of hierarchical structure may make the fabricated surface more prone to mechanical wear and tear [46]. However, both surface energy and surface roughness may facilitate surface wettability [51]. When a surface is hydrophobic, adding multi-roughness may promote it to a superhydrophobic state. However, this phenomenon is double-sided [45]. A hydrophilic surface may become superhydrophilic when hierarchical roughness is provided.

The hydrophobic potential in automotive is desirable, as hydrophobic surfaces tend to repel water. Very often, dust can be easily removed together with water, making the surface easy-to-clean or self-cleaning [58–63]. Usually, water repellency relates to a decrease of wear on metal surfaces which helps in maintaining corrosion resistance [59, 60, 63, 64]. The coating may act as an interlayer reducing interaction with corrosive substance [59, 60, 64–66]. This makes the surface less prone to fading or stains and also enhances abrasion resistance and UV resistance, all prolonging the service life of the surface.

5. SUMMARY

The growing significance of material selection, especially in the automotive industry, relates to a direct influence of material properties on designed or manufactured components and assemblies. In this context, the 3 major automotive requirements are minimization of resource exploitation, environmental impact, and final cost. Exemplary actions for implementing these requirements can be easily translated into material engineering solutions. In that sense, material engineering may offer development of entirely new materials and methods or improvement of already existing tools.

A tempting alternative to tailor properties of steel or aluminum substrates may be the deposition of functional coatings. The most typical protective and aesthetic coating in automotive includes painting. Additionally, the importance of application of hydrophobic surfaces should be emphasized as a method to reduce the wear of the coatings and their degradation.

ACKNOWLEDGEMENT

The paper bases on a master thesis [1]. The work was carried out in the Department of Mechanics, Materials and Biomedical Engineering at Wroclaw University of Science and Technology, Poland. The work has been concluded under the supervision of dr hab. Agnieszka Baszczuk, WUST professor.

LITERATURE

[1] GIBAS A., BASZCZUK A., GĄSIOREK J., *Fabrication and Examination of Sol Gel Hydrophobic Coatings Deposited Using Low Pressure Cold Spray and Ultrasonic Atomizing,* Wroclaw University of Science and Technology, 2020

[2] GIBAS A., BASZCZUK A., JASIORSKI M., WINNICKI M., *Prospects of Low-Pressure Cold Spray for Superhydrophobic Coatings. Coatings,* 2019, 9 (12), 829; DOI:10.3390/coatings9120829

[3] GIBAS A., GNYCH M., *Tlenkowe Materiały Proszkowe Otrzymywane Metodą Zol-Żel Jako Atrakcyjny Substrat Do Nanoszenia Powłok Techniką Niskociśnieniowego Natryskiwania Na Zimno.*, Nowoczesne technologie XXI w. – przegląd, trendy i badania. Tom 1; DANIELEWSKA A., MACIĄG M., Eds.; Wydawnictwo Naukowe TYGIEL sp. Z o.o.: Lublin, 2019; pp 118–137

[4] GIBAS A., BASZCZUK A., JASIORSKI M., WINNICKI M., *Hydrophobic Coatings by Low Pressure Cold Spray,* International Sol-Gel Conference. Next generation: book of abstracts, St. Petersburg, 2019, 405

[5] GIBAS A., GĄSIOREK J., *Ultrasonic Atomizing as a Feasible Method of Sol-Gel Coatings Fabrication*, 7th ISGS Online Summer School: "Hybrid Materials: cutting-edge applications", 2020

[6] ASHBY M. F., *Materials Selection in Mechanical Design,* Lecture Notes in Mechanical Engineering; 2014, Vol. 16, pp 145–153; DOI:10.1007/978-3-319-05203-8_21

[7] ODUORI M. F., PH D., *Materials Selection in Engineering Design and Manufacturing – Concept of an Information Processing Approach,* Assoc. Profr. Dep. Mech. Manuf. Eng. Univ. Nairobi, P.O. Box 30197, Nairobi, KENYA, 2016, No. January 2001, 1–14

[8] WILHELM M., *Materials Used in Automobile Manufacture - Current State and Perspectives.* J. PHYS. IV Colloq., 1993, *03* (7); DOI:10.1051/jp4:1993703f

[9] ŁUCZAK M., MAŁYS Ł., *Współczesne Koncepcje i Trendy w Branży Motoryzacyjnej*; Poznań, 2016

[10] TURNER J. W. G., POPPLEWELL A., PATEL R., JOHNSON T. R., DARNTON N. J., RICHARDSON S., BREDDA S. W., TUDOR R. J., BITHELL C. I., JACKSON R., et al. *Ultra Boost for Economy: Extending the Limits of Extreme Engine Downsizing,* SAE Int. J. ENGINES, 2014, *7* (1), 387–417; DOI:10.4271/2014-01-1185

[11] Environmental Protection Agency, *Delivering Change – Preventing And Recycling Waste, 2002*

[12] https://www.idis2.com (accessed: 10.01.2020)

[13] Council of the European Union. Council Directive 91/689/EEC of 12 December 1991 on Hazardous Waste

[14] KONSTANDOPOULOS A. G., KOSTOGLOU M., BEATRICE C., DI BLASIO G., IMREN A., DENBRATT I., *Impact of Combination of EGR, SCR, and DPF Technologies for the Low-Emission Rail Diesel Engines,* Emiss. Control Sci. Technol., 2015, 1 (3), 213–225; DOI:10.1007/s40825-015-0020-0

[15] HOVORUN T. P., BERLADIR K. V., PERERVA V. I., RUDENKO S. G., MARTYNOV A. I., *Modern Materials for Automotive Industry,* J. Eng. Sci., 2017, *4* (2), f8–f18; DOI:10.21272/jes.2017.4(2).f8

[16] STALEY J. T., LEGE D. J., *Advances in Aluminium Alloy Products for Structural Applications in Transportation*, Le J. Phys. IV, 1993, 03 (C7), C7-179-C7-190; DOI:10.1051/jp4:1993728

[17] KRZAK J., SZCZUREK A., BABIARCZUK B., GĄSIOREK J., BORAK B., *Sol–Gel Surface Functionalization Regardless of Form and Type of Substrate*, 2020, DOI:10.1016/b978-0-12-821381-0.00005-3

[18] ZHAO Y., JIN W., *Steel Corrosion in Concrete*, Steel Corrosion-Induced Concrete Cracking, Elsevier, 2016, pp 19–29; DOI:10.1016/B978-0-12-809197-5.00002-5

[19] Boag A., Hughes A. E., Wilson N. C., Torpy A., Macrae C. M., Glenn A. M., Muster T. H., How Complex Is the Microstructure of AA2024-T3? *Corros. Sci.*, 2009, *51* (8), 1565–1568; DOI:10.1016/j.corsci.2009.05.001

[20] AKAFUAH N. K., POOZESH S., SALAIMEH A., PATRICK G., LAWLER K., SAITO K., *Evolution of the Automotive Body Coating Process-A Review. Coatings*, 2016, *6* (2), DOI:10.3390/coatings6020024

[21] MAEV R. G., LESHCHYNSKY V., *Low-Pressure Cold Spray (LPCS)*, Cold-Spray Coatings; Springer International Publishing: Cham, 2018, 95–142, DOI:10.1007/978-3-319-67183-3_4

[22] ASSADI H., SCHMIDT T., RICHTER H., KLIEMANN J.-O., BINDER K., GÄRTNER F., KLASSEN T., KREYE H., *On Parameter Selection in Cold Spraying*, J. Therm. Spray Technol., 2011, 20 (6), 1161–1176; DOI:10.1007/s11666-011-9662-9

[23] MORIDI A., HASSANI-GANGARAJ S. M., GUAGLIANO M., DAO M., *Cold Spray Coating: Review of Material Systems and Future Perspectives*, Surf. Eng., 2014, *36* (6), 369–395, DOI:10.1179/1743294414Y.0000000270

[24] PAPYRIN A., *Cold Spray Technology*. *Adv. Mater. Process.*, 2001, *159* (9), 49–51

[25] MAŁACHOWSKA A., WINNICKI M., AMBROZIAK A., *Prospects of Low Pressure Cold Spray*, Przegląd Spaw., 2012, 84 (10), 2–6

[26] YIN S., CHEN C., SUO X., LUPOI R., *Cold-Sprayed Metal Coatings with Nanostructure*, Adv. Mater. Sci. Eng., 2018; DOI:10.1155/2018/2804576

[27] WINNICKI M., *Właściwości Powłok Cynowych i Miedzianych Naniesionych Na Podłoże Aluminiowe Metodą Niskociśnieniowego Natryskiwania Na Zimno,* Wroclaw University of Science and Technology, 2015

[28] YAMADA M., KANDORI Y., SATO K., FUKUMOTO M., *Fabrication of Titanium Dioxide Photocatalyst Coatings by Cold Spray*, J. Solid Mech. Mater. Eng., 2009, *3* (2), 210–216; DOI:10.1299/jmmp.3.210

[29] ASTARITA A., COTICELLI F., PRISCO U., *Repairing of an Engine Block through the Cold Gas Dynamic Spray Technology*. *Mater. Res.*, 2016, *19* (6), 1226–1231; DOI:10.1590/1980-5373-MR-2016-0109

[30] RAOELISON R. N., VERDY C., LIAO H., *Cold Gas Dynamic Spray Additive Manufacturing Today: Deposit Possibilities, Technological Solutions and Viable Applications*. *Mater. Des.*, 2017, *133* (July), 266–287; DOI:10.1016/j.matdes.2017.07.067

[31] NII S., *Ultrasonic Atomization*, Handb. Ultrason. Sonochemistry, 2015, 1–19, DOI:10.1007/978-981-287-470-2_7-1

[32] GOGATE P. R., *The Use of Ultrasonic Atomization for Encapsulation and Other Processes in Food and Pharmaceutical Manufacturing.* in Power Ultrasonics; Elsevier, 2015, 911–935; DOI:10.1016/B978-1-78242-028-6.00030-2

[33] https://www.sono-tek.com/industry/glass-industrial/automotive/ (accessed: 12.05.2020)

[34] http://hardcoats.ru/en/ (accessed:14.05 2020)

[35] AROLE V. M., MUNDE S. V., *Fabrication of Nanomaterials by Top-down and Bottom-up Approaches - an Overview*, Jaastmaterial Sci. (Special Issue), 2014, *1* (2), 89–93

[36] CUSHING B. L., KOLESNICHENKO V. L., O'CONNOR C. J., *Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles.* Chem. Rev., 2004, 104 (9), 3893–3946, DOI:10.1021/cr030027b

[37] SMAGIEŁ D., *Synthesis and Mechanical Tests of sio2-Based Coatings Applied by Atomizing the Hydrolyzate at Frequencies above 50khz with High Selectivity of Particle Size*, Wroclaw University of Science and Technology, 2018

[38] https://straitsresearch.com/press-release/automotive-sector-to-drive-growth-of-sol-gel-coatings-market (accessed:25.05 2021)

[39] NARULA C. K., *Sol-Gel Processed Materials in the Automotive Industry*. ACS Symp. Ser., 1999, *727*, 144–156; DOI:10.1021/bk-1999-0727.ch011

[40] ULLATTIL S. G., PERIYAT P., *Sol-Gel Synthesis of Titanium Dioxide,* Sol-Gel Materials for Energy, Environment and Electronic Applications; 2017, 271–283, DOI:10.1007/978-3-319-50144-4_9

[41] FRANCIOSO L., PRESICCE D. S., TAURINO A. M., RELLA R., SICILIANO P., FICARELLA A., *Automotive Application of Sol–Gel* tio2 Thin Film-Based Sensor for Lambda Measurement. Sensors Actuators B Chem., 2003, *95* (1–3), 66–72; DOI:10.1016/S0925-4005(03)00405-2

[42] ÇAMURLU H., KESMEZ Ö., BURUNKAYA E., KIRAZ N., YEŞIL Z., ASILTÜRK M., ARPAÇ E., *Sol-Gel Thin Films with Anti-Reflective and Self-Cleaning Properties*, Chem. Pap., 2012, *66* (5); DOI:10.2478/s11696-012-0144-4

[43] WU Y., SHEN Y., TAO J., HE Z., XIE Y., CHEN H., JIN M., HOU W., *Facile Spraying Fabrication of Highly Flexible and Mechanically Robust Superhydrophobic* F-sio 2 @PDMS Coatings for Self-Cleaning and Drag-Reduction Applications. *New J. Chem.*, 2018, *42* (22), 18208–18216; DOI:10.1039/c8nj04275f

[44] CHIENG B. W., IBRAHIM N. A., DAUD N. A., TALIB Z. A., *Functionalization of Graphene Oxide via Gamma-Ray Irradiation for Hydrophobic Materials*; Elsevier Inc., 2018, DOI:10.1016/B978-0-12-815757-2.00008-5

[45] SI Y., DONG Z., JIANG L., *Bioinspired Designs of Superhydrophobic and Superhydrophilic Materials*, *ACS Cent. Sci.*, 2018, *4* (9), 1102–1112, DOI:10.1021/acscentsci.8b00504

[46] GĄSIOREK J., *Physicochemical and Mechanical Characterization of Protective Coatings Type "Easy-to-Clean", Obtained by the Sol-Gel Method on Metallic Substrates*, Wroclaw University of Science and Technology, 2014

[47] https://igcseandialchemistry.com/electronegativity-and-bond-polarity/ (accessed: 04.07 2020)

[48] LI L., LI B., DONG J., ZHANG J., Roles of Silanes and Silicones in Forming Superhydrophobic and Superoleophobic Materials, *J. Mater. Chem. A*, 2016, 4 (36), 13677–13725, DOI:10.1039/c6ta05441b

[49] RAVI K., SULEN W. L., BERNARD C., ICHIKAWA Y., OGAWA K., *Fabrication of Micro-/Nano-Structured Super-Hydrophobic Fluorinated Polymer Coatings by Cold-Spray*. *Surf. Coatings Technol.*, 2019, *373* (May), 17–24, DOI:10.1016/j.surfcoat.2019.05.078

[50] LOCK SULEN W., RAVI K., BERNARD C., ICHIKAWA Y., OGAWA K., *Deposition Mechanism Analysis of Cold-Sprayed Fluoropolymer Coatings and Its Wettability Evaluation. J. Therm. Spray Technol.*, 2020, DOI:10.1007/s11666-020-01059-w

[51] CALABRESE L., KHASKHOUSSI A., PATANE S., PROVERBIO E., *Assessment of Super-Hydrophobic Textured Coatings on AA6082 Aluminum Alloy. Coatings*, 2019, *9* (6), 352; DOI:10.3390/coatings9060352

[52] WENZEL R. N., *RESISTANCE OF SOLID SURFACES TO WETTING BY WATER*. *Ind. Eng. Chem.*, 1936, *28* (8), 988–994; DOI:10.1021/ie50320a024

[53] CASSIE A. B. D., BAXTER S., *Wettability of Porous Surfaces*. *Trans. Faraday Soc.*, 1944, *40*, 546; DOI:10.1039/tf9444000546

[54] CASSIE A. B. D., *Contact Angles. Discuss. Faraday Soc.*, 1948, *3*, 11; DOI:10.1039/df9480300011

[55] FLEMING R. A., ZOU M., *Silica Nanoparticle-Based Films on Titanium Substrates with Long-Term Superhydrophilic and Superhydrophobic Stability. Appl. Surf. Sci.*, 2013, *280*, 820–827; DOI:10.1016/j.apsusc.2013.05.068

[56] MICHAEL N., BHUSHAN B., *Hierarchical Roughness Makes Superhydrophobic States Stable*. *Microelectron. Eng.*, 2007, *84* (3), 382–386, DOI:10.1016/j.mee.2006.10.054

[57] NOSONOVSKY M., BHUSHAN B., *Hierarchical Roughness Optimization for Biomimetic Superhydrophobic Surfaces. Ultramicroscopy,* 2007, *107* (10–11), 969–979, DOI:10.1016/j.ultramic.2007.04.011

[58] DENG X., MAMMEN L., ZHAO Y., LELLIG P., MÜLLEN K., LI C., BUTT H. J., VOLLMER D., *Transparent, Thermally Stable and Mechanically Robust Superhydrophobic Surfaces Made from Porous Silica Capsules. Adv. Mater.*, 2011, *23* (26), 2962–2965; DOI:10.1002/adma.201100410

[59] WANG N., XIONG D., DENG Y., SHI Y., WANG K., *Mechanically Robust Superhydrophobic Steel Surface with Anti-Icing, UV-Durability, and Corrosion Resistance Properties. ACS Appl. Mater. Interfaces*, 2015, *7* (11), 6260–6272; DOI:10.1021/acsami.5b00558

[60] LATTHE S. S., SUDHAGAR P., DEVADOSS A., KUMAR A. M., LIU S., TERASHIMA C., NAKATA K., FUJISHIMA A. A., *Mechanically Bendable Superhydrophobic Steel Surface with Self-Cleaning and Corrosion-Resistant Properties*. *J. Mater. Chem. A*, 2015, *3* (27), 14263–14271, DOI:10.1039/C5TA02604K

[61] BARTHLOTT W., NEINHUIS C., *Purity of the Sacred Lotus, or Escape from Contamination in Biological Surfaces. Planta,* 1997, *202* (1), 1–8, DOI:10.1007/s004250050096

[62] LU H., ZHENG Y., YIN W., TAO D., PESIKA N., MENG Y., TIAN Y., *Propulsion Principles of Water Striders in Sculling Forward through Shadow Method*. *J. Bionic Eng.*, 2018, *15* (3), 516–525; DOI:10.1007/s42235-018-0042-8

[63] ZHENG S., LI C., FU Q., XIANG T., HU W., WANG J., DING S., LIU P., CHEN Z., *Fabrication of a Micro-Nanostructured Superhydrophobic Aluminum Surface with Excellent Corrosion Resistance and Anti-Icing Performance*. *RSC Adv.*, 2016, *6* (83), 79389–79400, DOI:10.1039/C6RA13447E

[64] HASSANI-GANGARAJ S. M., MORIDI A., GUAGLIANO M., *Critical Review of Corrosion Protection by Cold Spray Coatings*. *Surf. Eng.*, 2015, *31* (11), 803–815, DOI:10.1179/1743294415Y.0000000018

[65] ZHANG D., WANG L., QIAN H., LI X., *Superhydrophobic Surfaces for Corrosion Protection: A Review of Recent Progresses and Future Directions. J. Coatings Technol. Res.*, 2016, *13* (1), 11–29; DOI:10.1007/s11998-015-9744-6

[66] GĄSIOREK J., SZCZUREK A., BABIARCZUK B., KALETA J., JONES W., KRZAK J., *Functionalizable Sol-Gel Silica Coatings for Corrosion Mitigation. Materials (Basel).*, 2018, 11 (2), 197; DOI:10.3390/ma11020197

PERSPEKTYWA WYTWARZANIA ZOL-ŻELOWYCH POWŁOK HYDROFOBOWYCH NANOSZONYCH Z UŻYCIEM NISKOCIŚNIENIOWEGO NATRYSKIWANIA NA ZIMNO I ATOMIZOWANIA ULTRADŹWIĘKOWEGO DLA BRANŻY MOTORYZACYJNEJ

Słowa kluczowe: *zol-żel, natryskiwanie niskociśnieniowe na zimno, atomizowanie ultradźwiękowe, powłoki, krzemionka, właściwości hydrofobowe*

Sektor motoryzacyjny znajduje się pod ciągłą presją, aby minimalizować zużycie paliwa i redukować emisję zanieczyszczeń przy jednoczesnym utrzymaniu dotychczasowego tempa redukcji masy i kosztów. To sprawia, że dobór materiału jest szczególnie ważny podczas procesu projektowania wybranego elementu. W artykule sformułowano główne wymagania branży automotive do analizy potencjału wybranych technik osadzania (niskociśnieniowego natryskiwania na zimno i atomizacji ultradźwiękowej) oraz wytwarzania materiału (metoda zol-żel) do zastosowań jako powłoki ochronne w przemyśle samochodowym.