Advanced corrosion resistant cylinder-bore coatings

B Schilder1,*, A Garling1, U Mayer1, R Grabs1 and T Lampke2

1 Process Development, Mercedes-Benz AG, 70546 Stuttgart, Germany
2 Institute of Materials Science and Engineering, Chemnitz University of Technology, 09125 Chemnitz, Germany

*e-mail: bernd.schilder@daimler.com

Abstract. This paper presents a novel approach to enhance the corrosion resistance of cylinder-bore coatings for internal combustion engines by changing surface characteristics and microstructures of the coating and utilizing alternative materials. The approach of this study refers to the knowledge of the complex gas-flow conditions during the internal-diameter coating of cylinder-bores using a twin-wire arc-spray process. Selective influencing of the gas flow enables the preparation of sample coatings with inhomogeneous and more homogeneous microstructures and surfaces. The various coatings were exposed to corrosive environments using the Kesternich testing method and an alternating immersion test. Significant improvements in corrosion resistance have been demonstrated by up to 50 % through altering the microstructure of the coating and almost 100 % by additional changing the spraying material. The study reveals an increased protection of cylinder-bore coatings against corrosive attacks through a homogeneous microstructure prepared in oxygen-poor coating conditions.

1. Introduction

In 2019, the European Union tightened the regulation for average CO₂ emissions for new car fleets by 15 % in 2025 and by 37.5 % in 2030 based on the average fleet target of 95 g CO₂/km for 2021 [1]. New driving concepts such as electric drives are currently developed to achieve the emission standards. These alternative drive concepts include battery electric vehicles (BEV), fuel-cell technology and hybrid technology. One major aspect for hybrid technology applications - and also for still produced conventional driving systems - is the continuous improvement to enhance the efficiency of internal combustion engines and consequently reduce emissions to achieve the aims. A method to improve internal combustion engines is the substitution of heavy gray-cast iron liners by thin, smooth functional cylinder-bore coatings with a coating thickness less than 100 μm. The specific coatings reduce frictional losses significantly compared to gray-cast iron liners with their typical honing structures at the surface [2–4]. Cylinder-bore coatings can be produced by several procedures. These include e.g. plasma-transferred wire arc (PTWA) [5], rotating single wire (RSW) [6], twin-wire arc-spray (TWAS) [2, 3], cold spray (CS) [7], high-velocity oxygen fuel (HVOF) [8] and atmospheric plasma spray (APS) [9, 10].

Additional techniques to reduce emissions for example nitrogen oxides (NOₓ) emissions include an increase of exhaust-gas recirculation (EGR) rates [11, 12]. Other options to decrease emissions are water injection [13, 14] and diesel exhaust fluid (DEF) injection [15]. All efforts to lower emissions result in new conditions within the combustion chamber of the engine. These conditions can lead to a higher corrosion rate at the cylinder-bore coating. Figure 1a shows possible causes of corrosion on thermally sprayed cylinder-bore coatings.
Besides the emission-reducing methods, the wide variety of fuel qualities also has an influence on corrosion phenomena within the cylinder-bore. High sulfur contents in fuels can lead to the formation of sulfuric acid ($H_2SO_4$) inside the cylinders of combustion engines, resulting in a high corrosion potential [16]. An overview of the maximum sulfur content in diesel fuels worldwide is displayed in figure 1b. In a lot of countries especially in South America, Africa, the Middle East and South East Asia, high sulfur contents are still permitted [17]. In addition to the poor diesel fuel quality in numerous regions, high sulfur gasolines are also present in many countries around the world [18]. Moreover, biogenic fuels are increasingly added to fossil fuels to reduce emissions. Due to their ethanol content, biofuels exhibit hygroscopic behavior that can lead to corrosive reactions [19].

Furthermore, the use of hybrid technology can lead to situations where the internal combustion engine is rarely used. These can occur for particular driving profiles that exclusively use the electric powertrain for short distance drives for example in urban traffic. This circumstance cause the pistons to remain in a certain position for a longer period than in a conventional combustion engine with the same driving profile, which can lead to corrosion between the piston rings and the cylinder-bore coating. To meet all the increasing technical requirements for modern internal combustion engines and to further advance the efficiency and performance, Mercedes-Benz AG advances the NANOSLIDE® technology.

Figure 1. a) Sources for corrosion on cylinder liner coatings and b) worldwide maximum sulfur limits for diesel fuel (2020) reproduced with permission from Stratas Advisors [17].

1.1. NANOSLIDE® technology - coating of cylinder liners
The NANOSLIDE® technology contains all process operations to produce thin functional cylinder-bore coatings in modern aluminum crankcases for diesel and gasoline engines. The start of the process chain is a mechanical roughening process of the cylinder liner surface. The process, also called Nissan mechanical roughening process (NMRP), produces a characteristic cylinder surface with micro- and macrostructures to create ideal conditions for adhesion between the coating and the substrate by mechanical interlocking and metallurgical bonding [3]. Subsequently, the roughened surfaces are coated with a twin-wire arc-spray process (Germ. LDS). The as-sprayed coatings are machined by a fine boring process followed by several honing steps to create the final mirror-like surface with finely distributed pores, serving as oil-retention volumes.

This study presents the latest research and development results to enhance the corrosion resistance of thermally sprayed cylinder-bore coatings for internal combustion engines. The paper proposes an approach to improve the corrosion behavior for low and high alloy spraying materials by altering the microstructure and the functional surface of the coating based on computational fluid dynamic (CFD) simulations.
2. Experimental and materials

The spray materials used in this study were 1.0479 (13Mn6), 1.4021 (X20Cr13) [20] and 1.4122 (X39CrMo17-1) [21]. 13Mn6 represents the state of the art that is utilized for coating of cylinder-bores. Table 1 displays the three coating materials with their individual chemical composition.

Table 1. Chemical composition of the spraying materials 1.0479 (13Mn6), 1.4021 (X20Cr13) and 1.4122 (X39CrMo17-1) [22, 23].

|            | C     | Mn    | Si    | P     | Cr    | Ni   | Cu    | S     | Mo    |
|------------|-------|-------|-------|-------|-------|------|-------|-------|-------|
| 13Mn6 (%)  | 0.08 -| 1.35 -| 0.30  | ≤ 0.025| ≤ 0.12| ≤ 0.12| ≤ 0.17| ≤ 0.25| -     |
|            | 0.14  | 1.65  | 0.45  |       |       |      |       |       |       |
| X20Cr13 (%)| 0.16 -|       | ≤ 1.50| ≤ 1.00| 12.0  |      |      | ≤ 0.03| -     |
|            | 0.25  |       |       |       | 14.0  |      |      |       |       |
| X39CrMo17-1| 0.33 -|       | ≤ 1.50| ≤ 1.00| 15.5  |      |      | ≤ 0.03| 0.08 -|
|            | 0.45  |       |       |       | 17.5  |      |      |       | 1.30  |

2.1. Coating experiments

All coating experiments in this study were conducted on aluminum crankcases (AlSi8Cu3) for diesel engines with a cylinder diameter of 82 mm. The twin-wire arc-spray coating system was a CBC200 module from Gebr. Heller Maschinenfabrik GmbH, Germany. The primary and secondary atomizing gas for the coating experiments was nitrogen with a ratio of 3:1. Special masks were placed at the cylinder head sealing surface and at the lower end of the cylinder liner near the crankshaft space to protect these surfaces of the crankcase from overspray and coating material. A vane anemometer (Model Testo 445, Testo AG, Germany) was used to measure the extraction velocity at the cylinder head sealing surface for one cylinder bore while the remaining cylinders were covered to reproduce the conditions equal to the coating process. The extraction velocity was adjusted to 2.0 m/s ± 0.5 m/s. These configurations result in oxygen-rich coating conditions in the top and bottom region and oxygen-poor conditions in the middle of the cylinder bore during the coating process [3]. Figure 2a shows a part of an image of a honed cylinder bore surface with different porous sections.

Figure 2. a) Partial image of a coated cylinder-bore surface with porous (oxygen rich) and less porous (oxygen poor) sections, b) schematic overview of the coating atmosphere for an extraction velocity of 2 m/s.

The expansion of the porous and less porous surface is rotationally symmetric. Samples cut out from the top of the cylinder bore (oxygen rich) exhibit a layer structure with many inhomogeneities like pores,
lamellar structures and splat boundaries at the surface and throughout the layer structure. Instead, specimens taken from the middle of the cylinder bore (oxygen poor) show a more homogeneous layer structure with a considerably reduced level of lamellar structures, pores and boundaries between the individual splats. The experimental setup and the coating system are equivalent to the current large-scale production process at Mercedes-Benz AG.

2.2. Characterization of the corrosion behavior

For a quantitative analysis of the corrosion resistance of different coating materials, samples were examined in an alternating immersion test. The specimens were exposed to a synthetic exhaust-gas condensate (K1.2). The condensate was used according to VDA 230-214 for applications with high sulfuric fuels. It consists of nitric acid (HNO$_3$), sulfuric acid (H$_2$SO$_4$), sodium chloride (NaCl) and demineralized water [24]. The alternating immersion test is based on an internal Mercedes-Benz test guideline. Cylinder liners were cut out of the crankcases and prepared to an outer diameter of 95 mm. The samples were taken from the top of the cylinder bore (oxygen-rich coating atmosphere) and from the middle of the cylinder-bore (position 80 mm – oxygen-poor coating atmosphere). The height of each sample was 25 mm. All samples were cleaned in a bath with petroleum gasoline for 24 h to create comparable test conditions. The mass of each sample was measured with an analytical balance (Sartorius RC250S, Sartorius AG, Germany) before and after the test to determine the mass loss. The aluminum substrate was covered with a corrosion-resistant polyester masking tape BT-220 (Christian Zang GmbH, Germany) to ensure that the corrosive agent exclusively attacks at the cylinder-bore coating. All samples were alternately immersed in the synthetic condensate for a period of 60 s and placed above the immersion bath for 180 s to drip off. This procedure was repeated for a total time of 8 h. The temperature of the bath was adjusted to 60 °C. After the alternating cycles, a 16 h ageing phase took place above the heated exhaust-gas condensate. The entire cycle was repeated over a duration of five days. Then, the samples were removed from the test facility after the immersion loop and dried for another 48 h at ambient temperature. After the test, the weakly adherent corrosion products were removed by mechanical cleaning under water. The still remaining corrosion products were removed by chemical cleaning methods [25]. The stripping solution for the coating material 13Mn6 contained hexamethylenetetramine (C$_6$H$_{12}$N$_4$), hydrochloric acid (HCl) and distilled water and for X20Cr13 and X39CrMo17-1 nitric acid and distilled water [26]. The cylinder segments were weighted again to determine the mass loss of each sample. The alternating immersion test was performed for each coating material and microstructural condition in a double determination with three differential measurements of each sample mass.

The qualitative analysis of corrosion phenomena on cylinder-bore coatings was accomplished with the Kesternich test method. Samples were exposed to a saturated atmosphere in the presence of sulfur dioxide (SO$_2$). One cycle of the test was divided into two sections. In the first section, the specimens were heated to a temperature of 40 °C and exposed to the sulfur dioxide atmosphere for a period of 8 h. Then, the test chamber was ventilated for 16 h during the second phase. The temperature was set to ambient temperature. The samples were cut out of the cylinder bore at a position of 6 mm (oxygen rich) and 91 mm (oxygen poor) below the cylinder head sealing surface in order to get liner segments with different layer structures. The specimens’ dimension was 11.95 mm x 14.30 mm. All surfaces of the tested samples were cleaned with ethanol prior the corrosion test and subjected to a two cyclic test.

2.3. Characterization of the functional properties of the coating

Contact-angle measurements were done with the OCA 200 system (DataPhysics Instruments GmbH, Germany) to analyze the surface wetting behavior of the various cylinder-bore coatings. The static contact-angle measurements were carried out with the test liquids ethylene glycol, diiodomethane and thioglycol with a drop volume of 2 μl. In addition, dynamic contact-angle analyses were done to determine the roll-off behavior of liquid droplets from the surface of the coatings. Therefore, the samples were tilted in a range between 0° and 87.5° with a tilting base unit TBU 100 (DataPhysics Instruments GmbH, Germany) in combination with the OCA 200 system. The water drop volume was set to 22 μl.
Specimens were taken from the top of the cylinder bore (oxygen rich) and from position 80 mm (oxygen poor). The size was 75 mm x 50 mm.

The functional description of the surface structure was determined by the characteristic $V_{oil}$ value. This parameter represents a measure for the oil-retention volume of the pores at the surface of the cylinder-bore coating and is normalized to an area of 1 mm$^2$. The tactile measurements of the surface characteristic were done with the roughness measuring system Hommel-Etamic T8000 (Jenoptik Industrial Metrology Germany GmbH, Germany). A structural separation of the measurement profile is used in order to distinguish the machining profile of the surface and the pore profile [27]. Each measurement consists of three measuring paths with a respective length of 15 mm.

Supplementary analyses of the cylinder liner were done with the Visionline B100 system (Jenoptik Industrial Metrology Germany GmbH, Germany). The 360° lens system creates high-resolution images from the surface of the entire length of the cylinder-bore coatings. The images were used to map and quantify the expansion of the porous surface structures (e.g. figure 2a).

The microstructural analyses of the coatings were performed on cross section specimens cut out of the cylinder bores, embedded in resin (Allylharz Glasfiber, Presi GmbH, Germany) and polished (Swing-Plus, Microdiamant AG, Switzerland). An Axio Observer microscope (Carl Zeiss AG, Germany) was used to take light microscope (LM) images from the microstructures. Furthermore, investigations were carried out with a field emission scanning electron microscope (SEM) (Mira3 XMU, Tescan Orsay Holding, Czech Republic) (15 kV, $WD = 15$ mm) in combination with a Quantax XFlash®5030 detector (Bruker Corporation, USA) for energy dispersive X-ray spectroscopy (EDS) to analyze the microstructure and the element distribution.

**3. Results and discussion**

The investigations in this study focus on the characterization and improving of the corrosion resistance properties for cylinder-bore coatings. Quantitative and qualitative analysis of the microstructure and surface of the coatings were carried out in order to gain more insights in the various layer systems.

3.1. Quantitative analysis of the corrosion behavior

Since the cylindrical samples for the alternating immersion tests consist of the aluminum substrate and the coating, the measured loss of mass was related to a theoretical coating thickness of 100 μm. The theoretical coating mass $m_t$ is estimated from the volume $V$ and density $\rho_c$ (without pores) of the coating material as shown in equation (1). The coating mass loss $m_{loss}$ is determined by the difference between the mass of the sample before ($m_1$) and after ($m_2$) the alternating immersion test in relation to the theoretical coating mass (equation (2)).

$$m_t = V \cdot \rho_c = \pi \cdot (R^2 - r^2) \cdot h \cdot \rho_c$$  \hspace{1cm} (1) \\
$$m_{loss} = (m_1 - m_2) \cdot (m_t)^{-1}$$  \hspace{1cm} (2)

$R$ corresponds to the cylinder radius without coating (41.1 mm), $r$ represents the final measure of the cylinder bore after the honing process (41 mm) and $h$ stands for the sample height of 25 mm. Figure 3 displays the percentage mass loss of the three analyzed materials and the two coating structures (oxygen rich and oxygen poor) based on a theoretically layer thickness of 100 μm (minimum distance between coating surface and the top of the roughening structure). Two alternating immersion tests were performed for each material and layer structure. The largest mass losses (> 40 %) occurred with the material 13Mn6 of the coatings separated from the top of the cylinder which represents the oxygen-rich atmosphere during the coating process. The minimal mass loss was found for the material X39CrMo17-1 coated in oxygen-poor conditions. The mass loss decreased from 13Mn6 to X20Cr13 to X39CrMo17-1. X20Cr13 and X39CrMo17-1 are capable to create a protective passive layer against corrosion in contrast to the low-alloy material 13Mn6 [21]. The analysis in figure 4 presents the mass loss of the coatings normalized to the state of the art material and microstructure. By altering the wire material, improvements of the corrosion resistance up to 66 % for X20Cr13 and 97 % for X39CrMo17-1 were
achieved without changing the coating atmosphere. An additional change in the coating atmosphere lead to a reduction in mass loss by 81 % for the coating material X20Cr13 and 98 % for X39CrMo17-1.

Figure 3. Absolute percentage mass loss of coatings related to a theoretical coating thickness of 100 μm.

Figure 4. Normalized mass loss based on the sample with the low-alloy coating material (13Mn6) and sprayed in an oxygen-rich atmosphere.

The results show that the specimen from the middle of the cylinder bore coated in an oxygen-poor atmosphere generally exhibit lower mass losses in the alternating immersion test regardless of the material. Figure 5 indicates the percentage of improvement for the individual materials determined by equation (3). By changing the coating atmosphere, the microstructure of the coatings was influenced in such a way that the corrosion resistance properties were increased by 15 % for the material 13Mn6, 45 % for X20Cr13 and 46 % for X39CrMo17-1.

\[ m_{rel} = \frac{(\Delta m_{O_2-poor} - \Delta m_{O_2-rich}) \cdot (\Delta m_{O_2-rich})^{-1}}{\Delta m_{O_2-poor}} \]  

(3)

The negative gradient of the two linear regressions lines in figure 6 demonstrate that the mass loss decreases depending on the chromium content of the coating. The higher the chromium content in the alloy materials, the lower the mass loss regardless of the coating conditions. These results reveal that the stability of the protective passive layer depends on the chromium content in the alloy. Happek (2015) determined similar relations for twin-wire arc sprayed metallic coatings, Zhang et al. (2016) indicated an increased stability of the passive layer for porous coatings with a higher chromium content [21, 28].

Figure 5. Decrease of mass loss due to spraying in an oxygen-poor atmosphere relative to spraying in an oxygen-rich atmosphere in relation to the spray material.

Figure 6. Mass loss of the coating related to a theoretical layer thickness of 100 μm in relation to the chromium content of the spray material.
3.2. Analysis of the functional surface

Optical contact-angle measurements were carried out to analyze the wetting properties of cylinder-bore coating surfaces in order to infer the corrosion behavior. Therefore static contact-angles (CA) were investigated to determine the surface energy of the samples using the Owens, Wendt, Rabel and Kaelble (OWKR) model. Figure 7 shows that the surface energy for the different coating materials is almost the same for surfaces with $V_{\text{oil-pores}}$ values less than 100 $\mu$m$^3$/mm$^2$ and tends to decrease for higher values. The analyses of the individual coating materials reveal that the samples produced in an oxygen-poor atmosphere exhibit a slightly higher surface energy. Pores at the surface act as energy barriers, which influence the spreading behavior of the fluid drops [29]. The high surface porosity inhibit the propagation and thus the flattening of the drops more than smooth surfaces with less inhomogeneity. This effect leads to larger contact-angles that were interpreted to smaller surface energies in the OWKR-model. Nota bene: all analyzed samples show a hydrophilic characteristic (CA < 90°) independent of the material and surface properties of the coatings [30, 31].

![Figure 7. Surface energy of the various materials and surface textures in relation to the specific volume of the surface pores based on an area of one square millimeter.](image)

In addition to the static contact-angle measurements, dynamic measurements were conducted to characterize the roll-off behavior of droplets from the various cylinder-bore coatings. The roll-off angle $\alpha$ was determined by the first occurrence of a contraction from the base diameter of the drop. The base diameter represents the lateral expansion of the drop between the advancing contact-angle ($\theta_{\text{adv}}$) and receding contact-angle ($\theta_{\text{rec}}$). The results of the dynamic contact-angle measurements indicate that the rolling behavior of the drops depends on the structure of the coating surface (figure 8). The structure influences the adhesion properties and thus the hydrophobicity of the surface [32]. The water drop adhered at the surface for all samples coated in an oxygen-rich atmosphere, except one specimen of 13Mn6. However, all coatings sprayed in an oxygen-poor atmosphere showed a sliding of the drop after the tilting process. The fewer the amount of pores and inhomogeneity at the surface, the faster the roll-off behavior. The roll-off behavior thus influences the contact time between the corrosive agent and the coating. A longer contact time increases the period to cause corrosion reactions [31].

The analysis of the dynamic contact-angle measurement demonstrates that the roll-off behavior can be strongly influenced by the atmosphere in which the coating process occurs. An oxygen-poor spraying process positively effects the corrosion resistance properties by reducing the contact time between the less porous surface and a corrosive medium.

![Figure 8. Roll-off angle of water droplets for the three coating materials and surface textures in relation to the specific volume of the surface pores $V_{\text{oil-pores}}$.](image)

3.3. Microstructure-corrosion-relationship

The Kesternich test was utilized to systematically corrode the various cylinder-bore coating materials under comparable conditions. Afterwards, the microstructure of cross sections and the surface of the
coatings were examined. Figure 9 displays the surface of the samples after two cycles of Kesternich test. The coating material 13Mn6 shows in both samples from the top (oxygen-rich coating condition, figure 9a) and from the middle of the cylinder bore (oxygen-poor coating condition, figure 9b) loosely adherent corrosion products on the entire surface. The coating material X20Cr13 also reveals distinct corrosion reactions on the sample in figure 9c, which are reduced on the less porous surface (figure 9d). The fewest visible corrosion products were found on the surface of the material X39CrMo17-1 with the best result on the less porous surface (figure 9f). The corrosion attack depends on the coating material and the surface structure. An increased surface porosity \( V_{oil-pores} \) results in a greater active surface area that is exposed to the corrosion agent. Thus, the growth of the solid-liquid interface will lead to enhanced corrosion reactions on the coating surfaces. This phenomena was also identified for increased surface roughness of coatings [30].

These results coincide with the alternating immersion test and the contact-angle measurements. The corrosion resistance increases due to a higher chromium content in the coating material and denser surfaces with fewer pores.

After the Kesternich test method, cross sections of the coatings were made in order to further investigate the microstructure. The cross sections were analyzed by light microscope and scanning electron microscope. Figure 10a presents a LM image of a cross section from the coating material 13Mn6. The specimen cut out of the cylinder bore at position 6 mm below the cylinder head sealing surface (oxygen rich). The cross section shows a morphology with porous and lamellar structures that is characteristic for twin-wire arc-sprayed metallic coatings [3, 33–35]. This coating structure is also evident for the materials X20Cr13 (figure 10c, d) and X39CrMo17-1 (figure 10e). On the other hand, the samples that were created from the middle of the cylinder bore (position 91 mm – oxygen-poor coating conditions) show a more homogeneous layer structure with fewer lamellar structures and oxidized splat boundaries. Figure 10f displays an example of this microstructure for the coating material X39CrMo17-1. A detailed description for the effects that lead to the creation of the various microstructures can be found in [3]. Prior to the Kesternich test, a portion of the samples were covered with an anti-corrosion pad to provide a non-corroded reference section. These reference areas displays the typical smooth honed surface. The part of the 13Mn6 sample that was not covered with the anti-corrosion pad and exposed to the corrosive environment exhibits surface corrosion across the entire specimen as shown in figure 9a. The depth of the shallow corrosion attack is on average between 5 μm and 10 μm, also for the specimen coated in oxygen-poor spraying conditions. The SEM image in figure 10b presents a detailed view of the corroded surface of the material 13Mn6 with the resulting corrosion products on top of the coating.

An EDS study of the microstructure shows the composition of corroded and non-corroded regions. The EDS spectrum of a non-corroded splat inside the coating (figure 10b-1) reveals the chemical composition of the coating material 13Mn6 (table 1). In contrast, oxygen and sulfur could be detected in the darker area at the top of the coating (figure 10b-2). Sulfur originates from the corrosion agent sulfur dioxide (SO2) used for the Kesternich test and oxygen from the oxidation reaction between the coating and the electrolyte. In contrary to 13Mn6, no surface corrosion with a quantifiable level of depth could be identified for the coating material X20Cr13 (figure 10c, d) and X39CrMo17-1 (figure 10e, f).
All high-alloyed coatings show the smooth honed surface. However, if defects occur on the surface for instance in terms of pores or lamellae structures, the corrosion medium can penetrate inside the layer and cause corrosion independent of the coating material composition and the general constitution of the microstructure (figure 10c-f) [28, 36].

Inside the layer, corrosion occurs preferentially at lamellar structures, splat boundaries and pores (e.g. figure 10c) [37]. These regions often exhibit a serrated and frayed contour. Defect structures, pores and oxidized splat boundaries that form the elongated lamellar structures are susceptible to chromium depletion and therefore vulnerable to corrosion [28, 38]. Furthermore, oxide layers at splat boundaries, pores and structural defects can lead to localized corrosion elements [36]. Coatings sprayed in an oxygen-rich atmosphere exhibit a higher oxide content within the microstructure and thus an enhanced susceptibility to corrosion. Figure 10c-e represent examples for corroded lamellar structures and pores even within the coating. These irregularities build potential paths for the corrosive agent. For specimen with an inhomogeneous microstructure, corrosion could often be detected even in deeper areas near the substrate, whereas homogeneous layers showed only corrosion attacks close to the surface. In general, a homogeneous layer structure reduces the probability that a connected network of lamellar structures and pores will be formed where corrosive media can penetrate inside the layer and in the worst case reach the interface between the substrate and the coating [28, 36].

Changing the mask geometry can significantly increase the oxygen-poor region during the coating process [3]. The development and implementation of an advanced coating process for the entire cylinder length and a large-scale application are currently in realization.

4. Conclusions
This paper presents a novel method to enhance the corrosion resistance of cylinder-bore coatings for internal combustion engines by changing the surface characteristics and microstructures of the coating and utilizing alternative materials. The results from the alternating immersion test demonstrate a significant improvement of the corrosion resistance up to 50 % through altering the microstructure of the coating and almost 100 % by additional changing the spraying material. The corrosion resistance property of the low-alloy material 13Mn6, that is currently applied for cylinder-bore coatings, could also be enhanced by 15 % through changing the microstructure to a more homogeneous layer formation. Contact-angle measurements indicate that the wetting behavior strongly depends on the oil-retention
volume of the coating. Less porous surface produced in an oxygen-poor coating atmosphere reveal shorter contact times and a decreased surface area between the coating and a corrosive agent and therefore have a positive influence on the corrosion resistance of the coatings. The results of the Kesternich test in combination with the analysis of the coating microstructures show that inhomogeneous areas (e.g. pores, lamellar structures, splat boundaries) at the surface and inside the layer are susceptible to corrosion in both low and high-alloy coating materials. The more homogeneous the microstructure at the surface and inside the coating, the lower is the probability of corrosive media penetrating into the layer system and causing corrosion.

The corrosion resistance of cylinder-bore coatings can be enhanced in general by specifically influencing the gas-flow conditions during the coating process to ensure a low-oxygen coating atmosphere. In addition to the presented model-based test methods further validation should be done by engine-test runs and vehicle tests to gain more knowledge about the corrosion behavior in true engine operation conditions.

Acknowledgments
This study was carried out as part of a research and development project at Mercedes-Benz AG. The authors acknowledge the Institute of Materials Science and Engineering, Chemnitz University of Technology and the Mercedes-Benz AG, Stuttgart, for supporting the research. We would also like to thank all colleagues from process development and materials technology department at Mercedes-Benz AG for the intensive and interdisciplinary cooperation.

References
[1] European Parliament and the Council of the European Union 2019 Regulation (EU) 2019/631 of the European Parliament and of the Council - of 17 April 2019 - setting CO2 emission performance standards for new passenger cars and for new light commercial vehicles, and repealing Regulations (EC) No 443 / 2009 and (EU) No 510 / 2011
[2] Schmidt M, Spieth H, Haubach C and Kühne C 2019 100 Pioneers in Efficient Resource Management: Best practice cases from producing companies (Berlin, Heidelberg: Springer Berlin Heidelberg)
[3] Schilder B, Garling A, Reimer F, Hamann M, Joos R, Hüger J, Pöhlmann M and Lampke T 2020 CFD Enhanced Thermal Spray Process for Coating of Cylinder Bores of Car Engines J. Therm. Spray Technol. 29 546–59
[4] Schommers J, Scheib H, Hartweg M and Bosler A 2013 Minimising Friction in Combustion Engines MTZ Worldwide 28–35
[5] Bobzin K, Öte M and Königstein T 2018 Effect of Different Atomization Gases on the Properties of Cylinder Bore Coatings Adv. Eng. Mater. 21 1800853
[6] Hanke W 2019 Friction Reduction in Power Cylinder Systems of Commercial Vehicle Engines MTZ Worldwide 80 18–23
[7] Aubanel L, Lefeivre L, Delloro F, Jeandin M and Sura E 2019 Cold Spray Coatings for Automotive Cylinder Block Application ITSC 2019: International Thermal Spray Conference and Exposition : 2019 New Waves of Thermal Spray Technology for Sustainable Growth ITSC 2019 (Yokohama, 26.05.2019-29.05.2019) ed F Azarmi (Materials Park, OH: ASM International) 433-440
[8] Hahn M and Fischer A 2010 Characterization of Thermal Spray Coatings for Cylinder Running Surfaces of Diesel Engines J. Therm. Spray Technol. 19 866–72
[9] Barbeza G 2005 Advanced thermal spray technology and coating for lightweight engine blocks for the automotive industry Surf. Coat. Technol. 200 1990–3
[10] Grund T, Paczkowski G, Lampke T, Liborius H, Nestler A and Schubert A 2020 Finish Turning of FeCr17Ni2C0.2 Iron-based Sprayed Coatings: Influences of Substrate Preparation, Cutting Speed and Feed on the Coating and Surface Properties J. Therm. Spray Technol. 29 308–18
[11] Praveena V and Martin M L J 2018 A review on various after treatment techniques to reduce NOx emissions in a CI engine J. Energy Inst. 91 704–20
[12] Nun J, Wieler A, Andres C and Betz T 2019 The First Mercedes-Benz Four-cylinder Diesel Engine Complying with RDE Step 2 MTZ Worldwide 80 46–53
[13] Mingrui W, Thanh Sa N, Turkson R F, Jinping L and Guanlun G 2017 Water injection for higher engine performance and lower emissions J. Energy Inst. 90 285–99
[14] Fan Y, Wu T, Di Xiao, Xu H, Li X and Xu M 2021 Effect of port water injection on the characteristics of combustion and emissions in a spark ignition direct injection engine Fuel 283 119271
[15] Nova I and Tronconi E 2014 Urea-SCR Technology for deNOx After Treatment of Diesel Exhausts (New York, NY: Springer New York)
[16] Distelrath-Lübeck A, Scherer V and Außmiller M 2017 Corrosion of Cylinder Bore Materials MTZ Worldwide 78 52–7
[17] Stratas Advisors 2020 Five Countries Move in Top 100 Ranking on Diesel Sulfur Limits (Stratas Advisors)
[18] Stratas Advisors 2019 Stratas Advisors Ranks Top 100 Countries with Lowest Sulfur in Gasoline (Stratas Advisors)
[19] Käfer S, Melz T, Engler T and Oechsner M 2019 Impact of Biogenic Fuels on the Fatigue Behavior of Steels MTZ Worldwide 80 100–5
[20] Özdeniz E A 2016 Entwicklung korrosions- und verschleißbeständiger thermisch gespritzter Zylinderlaufbahnen für Verbrennungsmotoren Dissertation Fakultät für Maschinenbau, Technische Universität Chemnitz
[21] Happek B 2015 Tribologische und elektrochemische Untersuchungen an lichtbogendrahtgespritzten Beschichtungen aus nichtrostendem Stahl für die Zylinderlaufbahnen von PKW-Dieselmotoren Dissertation Maschinenbau und Verfahrenstechnik, Universität Duisburg-Essen
[22] DIN Deutsches Institut für Normung e. V. 2014 Stainless steels: Part 3: Technical delivery conditions for semi-finished products, bars, rods, wire, sections and bright products of corrosion resisting steels for general purposes (DIN EN 10088-3) (Berlin: Beuth Verlag GmbH)
[23] DIN Deutsches Institut für Normung e. V. 1980 Round wire rod for welding filler metals: Technical terms of delivery (DIN 17145) (Berlin: Beuth Verlag GmbH)
[24] Verband der Automobilindustrie e. V. 2018 Resistance of metallic materials to condensate corrosion in exhaustgas-carrying components (VDA 230-214) (Berlin)
[25] DIN Deutsches Institut für Normung e. V. 2009 Corrosion of metals - Corrosion testing: Part1: General guidance (DIN 50905-1) (Berlin: Beuth Verlag GmbH)
[26] DIN Deutsches Institut für Normung e. V. 2020 Corrosion of metals and alloys: Removal of corrosion products from corrosion test specimens (DIN EN ISO 8407) (Berlin: Beuth Verlag GmbH)
[27] Boehm J, Hartweg M, Hercke T, Izquierdo P, Michel M, Schweickert S and Rau G 2012 Thermisch beschichtetes Bauteil mit einer reibungsoptimierten Laufbahnoberfläche und Verfahren zur Bauteil-Beschichtungsüberflächensimulation eines thermisch beschichteten Bauteils DE102012002766 (A1)
[28] Zhang S D, Wu J, Qi W B and Wang J Q 2016 Effect of porosity defects on the long-term corrosion behaviour of Fe-based amorphous alloy coated mild steel Corros. Sci. 110 57–70
[29] Duursma G R, Seifiane K and David S 2010 Advancing and receding contact lines on patterned structured surfaces Chem. Eng. Res. Des. 88 737–43
[30] Ramachandran R and Nosonovsky M 2015 Coupling of surface energy with electric potential makes superhydrophobic surfaces corrosion-resistant Phys. Chem. Chem. Phys. 17 24988–97
[31] Tejero-Martin D, Rezvani Rad M, McDonald A and Hussain T 2019 Beyond Traditional Coatings: A Review on Thermal-Sprayed Functional and Smart Coatings J. Therm. Spray Technol. 28 598–644

[32] Mohamed A M A, Abdullah A M and Younan N A 2015 Corrosion behavior of superhydrophobic surfaces: A review Arabian J. Chem. 8 749–65

[33] Jandin G, Liao H, Feng Z Q and Coddet C 2003 Correlations between operating conditions, microstructure and mechanical properties of twin wire arc sprayed steel coatings Materials Science and Engineering: A 349 298–305

[34] Newbery A P and Grant P S 2006 Oxidation during electric arc spray forming of steel J. Mater. Process. Technol. 178 259–69

[35] Gedzevicius I and Valiulis A V 2006 Analysis of wire arc spraying process variables on coatings properties J. Mater. Process. Technol. 175 206–11

[36] Wu J, Zhang S D, Sun W H and Wang J Q 2018 Influence of oxidation related structural defects on localized corrosion in HVAF-sprayed Fe-based metallic coatings Surf. Coat. Technol. 335 205–18

[37] Sadeghi E, Markocsan N and Joshi S 2019 Advances in Corrosion-Resistant Thermal Spray Coatings for Renewable Energy Power Plants. Part I: Effect of Composition and Microstructure J. Therm. Spray Technol. 28 1749–88

[38] Zeng Z, Sakoda N and Tajiri T 2006 Corrosion Behavior of Wire-Arc-Sprayed Stainless Steel Coating on Mild Steel J. Therm. Spray Technol. 15 431–7