Advanced Chromium Carbide Coatings on Piston Rings by CVD: A Highly Adaptable

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Various surface treatment methods are currently used on cylinder piston group (CPG) components to increase service life of internal combustion engines and improve efficiency. Galvanic chrome plating of piston rings is the most common way to improve engine performance. Hard chrome electroplating reduces friction and increases wear resistance of the cylinder working surface, thereby increasing service life of medium-speed engines to 20,000 hours\textsuperscript{[11]}. Nearly 15 to 20% of piston rings produced in the world are manufactured with hard chrome plating.

Disadvantages of galvanic chrome plating include difficult burnishing, low heat stability, poor oil adhesion on its surface, high internal stress (which leads to cracking and chipping), and formation of large amounts of aqueous waste containing highly toxic Cr (VI) in the chrome-electroplating process\textsuperscript{[2-5]}. While improvements in galvanic chrome plating technology are being made, alternative methods to apply chromium and chromium-nitride (CrN) coatings have been developed including vacuum, flame, plasma, and electric arc. Antifriction coatings based on diamond-like carbon (DLC), metal containing diamond-like carbon (Me-DLC), and a number of similar composite materials are often used in industry\textsuperscript{[2-5]}. Limitations of most industrial DLC coatings are poor adhesion, high internal stresses, and low bearing capacity\textsuperscript{[6]}. Adhesion of Me-DLC coatings is better, but they are relatively unstable under intense stress\textsuperscript{[6-7]}. Further improvement can be achieved using a multilayer coating combining the useful properties of carbon and metal; for example, multilayer chromium-carbide coatings (CCC) on piston rings\textsuperscript{[8-10]}. Optimizing coating structure increases abrasion and corrosion resistance and reduces friction\textsuperscript{[6, 7, 11, 12]}. Multilayer CCC have been produced using physical vapor deposition (PVD), such as magnetron sputtering technique.

This article discusses development of the chemical vapor deposition (CVD) process to deposit advanced chromium-carbide coatings.

Background on proposed technology
Preparing chromium coatings from the gas phase is based on the thermal decomposition of organometallic compounds (OMC) of chromium. A BARCHOS chromium-organic liquid manufactured according to Russian TU (technical specification) 6-01-1149-78 was used in this work. The liquid is a mixture of chromium bis (ethyl benzene) homologues with general formula \([\text{C}_6\text{H}_6-x(\text{C}_2\text{H}_5)x]\text{Cr}\) (where \(x = 1, 2, 3\)) containing admixtures of aromatic and chlorinated compounds.

The chromium OMC is evaporated between 200 and 260°C, and the vapor is contacted with a heated substrate (350 to 550°C) where thermal decomposition of the OMC vapors occurs. Metallic chromium and its carbides are deposited on the substrate as a compact uniform coating (pyrolytic chromium carbide coating, or PCCC). Coating formation can be described by

\[\text{[C}_6\text{H}_{6-x}(\text{C}_2\text{H}_5)x\text{Cr} \rightarrow \text{Cr + C}_6\text{H}_{6-x}(\text{C}_2\text{H}_5)x}\]  (1)

Formation of chromium carbides and carbon are the parallel processes: \(\text{Cr}_2\text{C}, \text{Cr}_3\text{C}_2, \text{Cr}_2\text{C}_3, \text{Cr}_7\text{C}_3\)\textsuperscript{[13]}. Gaseous products of thermal decomposition are removed from the reaction zone by the vacuum system and condensed in a trap cooled with liquid nitrogen.

PCCCs are dispersed-crystallite compositions containing 10 to 80 nm chromium-carbide particles and chromium metal, which are stabilized by carbonaceous impurities. The relative content of the components and their
structural characteristics are determined by process conditions. Hence, physical and mechanical properties of coatings are controlled in accordance with changes in their composition and structure[13, 14]. The color of the prepared coatings changed from light yellow-silver or gold to mirror-bright, depending on the original substrate surface finish treatment. The relief of the surface coatings is generally smooth, and the internal microstructure is layered.

Results of this study and published data [15-17] suggest that:

• PCCCs are often nonporous even at thicknesses of 4 to 5 µm
• Coatings exhibit high adhesion (about 100 MPa) to most construction materials
• Microhardness of PCCCs reaches 20 to 25 GPa (2.5 to 3.0 times higher than the microhardness of hardened steel and chromium electroplating coatings and 1.2 to 1.5 times higher than the microhardness of carbide VC-type built-up layers)
• Relative durability of PCCCs is nearly two time higher than that of tungsten hard alloys and electroplated “hard” chromium
• PCCCs exhibit high antifriction properties
• Corrosion resistance is close that of noble metals

Use of the advantages of PCCCs to improve the wear resistance of the friction parts of the piston group (primarily oil scraper and compression rings) was evaluated. This work led to the design of special pilot units for chrome coating of rings, selection and optimization of conditions to apply PCCCs to piston rings, and producing and testing pilot lots of CPG components.

Experimental equipment

Figures 1 shows the unit used for CVD coating the outside (working) surface of oil scraper and compression rings, and the principal operating scheme is shown in Fig. 2. Technical characteristics of the pilot unit are listed below.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of coating deposition</td>
<td>1 µm/min max</td>
</tr>
<tr>
<td>Quantity of rings/single process</td>
<td>60</td>
</tr>
<tr>
<td>Ring diameter, mm</td>
<td>250 max</td>
</tr>
<tr>
<td>Deposition nonuniformity within ring perimeter, %</td>
<td>3 max</td>
</tr>
<tr>
<td>Deposition nonuniformity along mandrel height, %</td>
<td>5 max</td>
</tr>
<tr>
<td>Dimensions (height/width/length), m</td>
<td>1.7/0.5/2.0</td>
</tr>
<tr>
<td>Max power consumption, kW</td>
<td>4</td>
</tr>
<tr>
<td>Average productivity, rings/hour</td>
<td>120</td>
</tr>
</tbody>
</table>

The main component of the pilot unit is a horizontal vacuum reaction chamber (Fig. 2). In the coating process, parts (rings and imitators) are degreased, washed, and dried; attached to the holder (2), and the chamber is closed and evacuated. Parts are heated to the working temperature (350 to 450°C) and rotated while passing through the deposition zone (13). Simultaneously, BARHOS OMC flows from the feeder (4, 5) to the evaporator (6) placed above the holder. OMC is adsorbed on the ring surface and decomposes to form compact solid PCCC and gaseous reaction products, which are removed from the chamber by vacuum pumps (7, 8).

Research methodology

PCCC was deposited on 12 mm diameter × 45 mm high cylindrical and 30 mm × 30 mm × 1 mm thick flat pieces made of cast iron, stainless steel, and tool steel to determine the interaction of the coating-substrate pairs. The substrate material retains its properties upon heating to a temperature between 400 and 450°C in a vacuum, which allows application of quality coatings. Coating adhesion to the substrate was greater than 100 MPa.

Typical CPG components are 121-mm diam. (23/2H30) scraper piston rings of Raba-Man diesel engines for the Ikarus bus and 215-mm diam. (D100.04-018, D100.04-016-2-017-D100.042) compression and oil scraper rings for 10D100 diesel engines. Coating working parameters were:

• Heat to 400 to 420°C
• Feed chromium-organic liquid in the reaction zone at a rate of 45 to 60 ml/h
• Maintain a coating thickness of 10 to 20 µm

Various techniques were used to determine coating properties and characteristics including thickness (gravimetric and metallographic); composition, properties, and structure (x-ray diffraction analysis and electronic and op-
tical spectroscopy); microhardness (diamond pyramid indentation); adhesion (tensile); porosity (red blood salt), and tribometric (roller-roller and roller-block methods). Tribological studies of coated cast iron parts were performed on a friction machine. Chromium coated rings were tested on a machine with a reciprocal motion, which simulates wear conditions, mechanisms, and the interaction between the moving parts of a vehicle engine.

Standard piston rings were made of SChHN cast iron with surface roughness ranging from 0.15 to 1.25 µm. Coated-ring pairs were tested; sleeve cylinder roughness was 0.15 - 0.75 µm. Chemical composition of ring materials is given below.

### Results and discussion

Parameters were optimized to produce a ring coating with uniform shine. Coating was carried out using the following parameters after parts were degreased, rinsed, and dried:

- Vacuum of 1 to 5 Pa
- Substrate temperature in heating zone of 440±5°C
- Ultimate substrate temperature in deposition zone of 400±5°C
- Working pressure of 15±5 Pa

- BARHOS OMC supply rate of 50±5 ml/h
- Deposition time of 20 to 30 min

These conditions produced smooth PCCCs with a thickness of 10 to 20 µm. Average growth rate of the coating did not exceed 0.50 to 0.65 µm/min. Coatings had an opaque mirror appearance with the separate light golden areas on the front surface of the rings (Figs. 3 and 4).

Coatings were amorphous and their metallographic slices (without etching) exhibited a horizontal layered structure parallel to the substrate. Typical microstructure and surface morphology are shown in Fig. 5.

Relief of the coating surface was dome-shaped and smooth with some spheroidal globules (Fig. 5a). Two types of layers observed are white and gray/dark (Fig. 5b). Light layers are thicker than dark layers. Layer-by-layer analysis showed that the chromium content in white layers was 95 to 96%, and 92 to 94% in the dark layers. Carbon content varied from nearly 5 to 6-8% in the same layers, respectively. To convert amorphous coatings, samples were heated to 900°C in an inert atmosphere. Analysis of annealed coatings showed the presence of chromium carbides Cr23C6 and Cr2C (Fig. 6).

Coating porosity tests for the model samples with a 12±2 mm thick coating showed they are nonporous. Coating microhardness on cast iron substrates was 16.5±2 GPa. Microhardnesses of PCCC and other types of coatings are shown below [3-7, 17]. The hardness of PCCC is similar to, or higher than, most other materials used in the production of the piston rings.

<table>
<thead>
<tr>
<th>Type of coating</th>
<th>Microhardness, GPa</th>
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<tbody>
<tr>
<td>Chromium flame</td>
<td>3.2–11.2</td>
</tr>
<tr>
<td>Chromium plasma</td>
<td>5.0–11.8</td>
</tr>
<tr>
<td>Chromium plating</td>
<td>8.0–11.3</td>
</tr>
<tr>
<td>Ductile cast iron</td>
<td>3.0–8.2</td>
</tr>
<tr>
<td>Chromium nitride</td>
<td>17.2–18.0</td>
</tr>
<tr>
<td>PCCC</td>
<td>14–16</td>
</tr>
<tr>
<td>Multilayer C-Cr</td>
<td>14–24</td>
</tr>
</tbody>
</table>

PCCC adhesion was determined using SChNH cast iron, 08HN10T stainless steel, and 15H mild steel standard samples (“mushrooms”), which were ground to a grade 10 roughness before coating. Table 1 lists results, which confirm the exceptionally high adhesion of PCCC due to the formation of a chemical bond at the substrate-coating boundary.

<table>
<thead>
<tr>
<th>Chemical composition, wt%</th>
<th>Material grade</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>SChHN cast iron piston ring</td>
</tr>
<tr>
<td>C</td>
<td>2.7</td>
</tr>
<tr>
<td>Si</td>
<td>1.75</td>
</tr>
<tr>
<td>Mn</td>
<td>0.74</td>
</tr>
<tr>
<td>P</td>
<td>0.43</td>
</tr>
<tr>
<td>S</td>
<td>0.04</td>
</tr>
<tr>
<td>Cr</td>
<td>0.42</td>
</tr>
<tr>
<td>Ni</td>
<td>0.47</td>
</tr>
<tr>
<td>Mo</td>
<td>—</td>
</tr>
<tr>
<td>Cu</td>
<td>—</td>
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</table>

Tribometric laboratory tests were performed on certified friction machines using roller-block and roller-roller schemes. Wear ratio was determined by weighing to an accuracy of 0.1 mg. Averaged test results shown in Fig. 7 show that under the same conditions, wear of samples (rollers) with PCCC is smaller by 3.5 to 4.0 times than that

![Fig. 3 — Compression and oil scraper rings for the 10D100 diesel engine before (A) and after (B) coating with chromium.](image)

![Fig. 4 — Coating of the compression (C) and oil scraper (D) rings for 10D100 diesel-engine piston rings.](image)
with galvanized chromium coating. The wear resistance of the block joined with a roller with PCCC increases by 8 to 10 times compared to that of galvanic-chromium coating. Similar results were obtained for bearing interfaces. The wear intensity of the steel pairs with PCCC was 5 to 10 times smaller than that for galvanic chromium coatings\(^\text{[18]}\).

Tests simulating operating conditions, wear mechanisms, and interaction of friction parts of vehicle engines were carried out on a friction machine with a reciprocating motion using M14V2 diesel oil as a lubricant. Samples were prepared from the materials for cylinder sleeves, pistons, and piston rings of the 10D100 diesel engine. Standard piston rings made of SChHN cast iron (purity grade surface Ra = 0.15 to 1.25 µm) were also used. Rings with PCCC were tested in pairs with cylinder sleeves (purity grade surface 0.15 to 0.75 µm). Mechanical and performance properties of oil scraper rings after surface hardening with chromium carbide were tested in comparison with standard oil scraper rings having phosphate and galvanic chrome coating. Test results are presented in Table 2.

PCCC increases wear resistance of oil scraper piston rings compared to rings coated with electroplated chromium by a factor of three. Frictional properties of PCCC were measured on a friction machine (2 MPa load) at a sliding rate of 1 to 6 m/s. Sliding friction coefficient of PCCC paired with SChHNMD cast iron (prepared by grinding) was 0.04 to 0.06, which is significantly smaller than that of cast iron-cast iron pair (0.95 sliding friction coefficient)\(^\text{[19]}\).

PCCC showed higher wear resistance than common galvanic chromium coatings under the conditions close to the operating conditions of piston rings. Full-scale tests in Ikarus bus engines showed that in the case of rings with PCCC, consumption of lubricant oil decreases by nearly three times despite being thinner (20 µm and 100 µm for PCCC and galvanic chromium coatings, respectively).

High tribotechnical properties of the coating are probably due to its layered structure (Fig. 5). This structural feature (spherical surface morphology) provides sufficient oil adhesion at a relatively small height of the spherical ledges on the coating surface. The layered coating structure is characterized by alternating chromium and chromium carbide layers with high-carbon interlayer. The authors believe that after wearing of a single PCCC layer (20-µm coating consists of 10 to 15 such layers), the surface is saturated with carbon from the interlayer, which imparts a lubricating effect. The coating upper layer wears intensely during burnishing, which "opens" the graphite layer. This prevents expansion of the jamming process. The ability of PCCC to prevent jamming and setting, as well as its resistance to thermal shock, can be successfully used in the construction of hydromechanical friction transmissions\(^\text{[20]}\).

PCCC offers a range of operating properties that are competitive with those of magnetron-grown chromium carbide multilayer coatings. They have excellent adhesion (more than 100 MPa for PCCC determined using the nor-
Friction pairs reached 95 to 100°C.

Temperature at contact point reached 60°C for roller coatings consisting of (left) 100-µm thick galvanic chromium plating, 8.7 GPa microhardness; (middle) 17 GPa microhardness; SCHhNMD cast iron block with 2.5 GPa microhardness; (right) 12-µm thick PCCC with 17 GPa microhardness; SCHhNMD cast iron block with 2.5 GPa microhardness. Temperature at contact point friction pairs reached 95 to 100°C.

Fig. 7 — Average wear intensity of roller-block pair tested for 5 hours under 1 kN load on CMC-2 friction machine using MS-20 lubricating oil. Roller coatings: (left) 100-µm thick galvanic chromium plating with 8.7 GPa microhardness; (right) 12-µm thick PCCC with 17 GPa microhardness; SCHhNMD cast iron block with 2.5 GPa microhardness. Temperature at contact point friction pairs reached 95 to 100°C.

Mal separation method versus 70 to 120 N for multilayered CCC determined using a scratch test with critical load), low coefficient of friction (0.04–0.06 and 0.05–0.07 for PCCC and CCC, respectively) high microhardness (14–18 GPa and 14–24 GPa for PCCC and CCC, respectively), and wear resistance 3 to 10 times higher than that of electroplated chromium[6-12].

PCCC is characterized by extremely low porosity, which is not detected using existing methods. This significantly improves the corrosion resistance of the substrate material, as well as resistance to blistering, cracking, and exfoliation. The absence of pores in the coating along with other factors increases the life of piston rings due to restricting diffusion of active substances from within the cylinder into the substrate.

Conclusion

Substitution of the environmentally friendly CVD process to produce PCCC for commonly used electrolytic chromium plating offers a way to increase wear resistance of piston rings and to provide high coating adhesion. With its high wear resistance, PCCC can be used as an anti-friction coating on machine parts that are subject to sliding friction on a steel surface. PCCC combines properties of relatively low coefficient of friction and high corrosion resistance. The CVD process is characterized by high adaptability and relatively low cost. A patent application has been filed[21].

References


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