Synthesis of catalytic coatings in arc plasma jet

Dr. Viktorija Grigaitienė

Lithuanian Energy Institute, Plasma Processing Laboratory

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Introduction

• Plasma is considered to be 4th state of matter next to solid, liquid, gas.
• “A gas in which an appreciable number of atoms or molecules are ionized is called Plasma”
• It was first identified in Crookes tube by Sir William Crookes as Radiant Matter in 1879.
• Later in 1923 it was named as PLASMA by an American Physicist Langmuir. For him it resembled to be as Blood Plasma.
• He says, “In Crookes tube experiment, except near the electrodes, where there are sheaths containing very few electrons, the ionized gas contains ions and electrons in about equal numbers so that the resultant space charge is very small. We shall use the mane plasma to describe this region containing balanced charges of ions and electrons.”
Plasma properties

• Plasma is the normal state of matter at temperatures of the order of 20 000K or even more.
• Sun and stars are condensed high temperature plasmas. The ionosphere of earth also contains plasma.
• Plasma is a mixture of electrons, ions, neutral atoms and molecules having different kinetic energies. Plasma is electrically neutral. Electrons in it have highest energy and molecules at least. The presence of a non negligible number of charge carriers makes the plasma electrically conductive, so, that it responds strongly to electric fields.
• If a magnetic field is applied to plasma, it behaves as a diamagnetic medium having a small, but negative susceptibility. Radio waves are reflected by plasma, as if it were a mirror.
Plasma - 4\textsuperscript{th} state of matter

Plasma properties
Plasma categories

- Cold Plasma
  - $T_e >> T_i$, $T_i$ near to home temperature

- Low temperature plasma

- Hot Plasma
  - $T_e = T_i$, $T_i = 2000 \sim 20000$ K

- High Temperature Plasma
  - Nuclear fusion, $T_e = T_i$, $T_i = 10^8 \sim 10^9$ K
Current applications

Plasma can be utilized in 2 ways:
• as a heat source
• as a carrier of medium

In material processing plasma is used as both as a heat source and carrier medium.

Current applications in material processing include welding, cutting, spraying, surface heat treatment, melting, sintering, etc.
Thermal spraying methods

- flame spraying
- arc spraying
- plasma spraying.
Flame spraying process
Arc spraying process
Arc spraying process

- The temperature generated in the arc is in excess of 4000°C, which is more than sufficient to melt any metal likely to be required.

- As with flame spraying, the molten metal is then atomized and projected onto the work piece by compressed air.

- The coating produced has a greater bond strength than that achieved by flame spraying, and it does not require an oxy-gas supply only an electrical source and a compressed air supply.
Plasma Spraying

- The high intensity plasma heat allows for designing compact systems;
- Temperature unlimited (T > 15000 °C);
- Gases used for the plasma creation: Argon, Helium, Hydrogen, Nitrogen, Air, Oxygen, Steam and their mixtures. It is not a combustion process;
- Materials for spraying: Solid (powders), metals, metal oxides, or their mixtures, ceramics. Liquids. Gases (hydrocarbon gases (CH₄, C₂H₂ etc.));
- No by-products (reduced by-products);
- Vacuum not applied.
Plasma Spraying

The scheme of a typical atmosphere plasma spray process.
Plasma Spraying

- Molten metallic or non metallic material is sprayed on to a prepared substrate to form a coating.
  - The sprayed material is in the powder form. It is propelled by a stream of ionized gas on to the substrate. The particles striking the surface, gets flattened to form thin platelets.
  - The substrate surface, which can be kept below ~470 K, eliminating metallurgical changes in base material.
  - The temperature is as high as ~2000 °C. The powder size is 10-70 microns for free flow. Spherical powders are best.

Splat pattern of a single particle

- Complete melting of the particle is critical for uniform coating
- Residual stress due to uneven thermal expansion is important
Residual Thermal Stress

Tensile force applied by substrate due to coating particle shrinkage.

Compressive force applied to substrate by coating particle.

Coating stress greater than bond strength.

Molten Droplet

Each Individual Splat Attempts to Contract During Cooling

Solid Particle at High Velocity Impact

Coating Underneath is "Peened"

Residual Tensile Stress

Residual Compressive Stress
Splat formations after the impact of the spherical powder during spraying.
Plasma sprayed coatings

- Theoretically thermal coating spray thicknesses have no limit, but in practice thickness of coating is 25 microns to 10 mm.
- Most spray coated surfaces tend to be slightly porous, with coatings reaching approximately 85-90 percent of wrought metal density.

Advantages
- Oxidation of powder is minimal
- Highly dense coating are produced
- Mechanical and metal surgical properties are superior due to high temperature and high velocity as well.
- Decomposition of powder is minimized.

Disadvantages
- Very high temperatures are required
- Complicated torch design
- Process is noisy, can reach 110 dB.
- Radiation hazards and toxic fumes.
Factors Effecting The Thermal Spray Coating Process

**3 STAGES**
1. Generation of thermal/kinetic energy
2. Interaction of energy with spray material
3. Interaction of spray particles with substrate

**SPRAY STREAM** (flame, plasma etc.)
- Composition
- Temperature
- Velocity
- Spray distance
- External environment
- Turbulence

**GUN**
- Nozzle Geometry
- Power
- Gas flows
- Gas composition

**MATERIAL FEED**
- Particle size and shape or wire size
- Feed rate
- Injection method and geometry
- Carrier gas, flow and velocity
- Chemical and physical properties

**SUBSTRATE**
- Surface contamination
- Surface profile
- Temperature
- Chemical and physical properties
- Relative speed to gun
Carrier Gas Flow Rate a) too low b) correct c) too high.

Building of a database for a given coating with specific conditions

The interaction of the surrounding atmosphere within a plasma jet exiting from a nozzle
Schematic of a typical thermal spray powder process.

Defects of the plasma sprayed coatings

Fig. 1: Structure of a plasma sprayed coating with all the possible defects (exaggerated):
1: substrate, 2: adhesion defect, 3: cohesion defect between two passes, 4: cracks parallel to
the substrate due to macroscopic residual stresses, 5: microcracks within a lamella, 6: cracks
orthogonal to the substrate and open porosity, 7: closed porosity, 8: well molten particles: splats,
9: unmolten particles, 10: gas inclusion between splats [70].

Plasma sprayed porous coatings

porous

more dense

High reactive surface:

50 μm

2 μm
Plasma sprayed porous coatings

All conventionally thermally sprayed coatings contain some porosity (0.025% to 50%). Porosity is caused by:

- Low impact energy (unmelted particles / low velocity)
- Shadowing effects (unmelted particles / spray angle)
- Shrinkage and stress relieve effects

The above interactions can make the coatings very different from their starting materials chemically and physically.

SEM image of precursor Al(OH)₃ powder (a) and catalytic coating supported with Al₂O₃ (b)
Characteristics of some plasma sprayed materials:

- Excellent stability, good mechanical properties (hardness, wear resistance, strength), relatively low cost

![Graph showing oxides and temperatures](image)

- **$\text{Al}_2\text{O}_3$** - Starting from $\alpha$ phase $\rightarrow \gamma$ phase upon spraying at $1000^\circ\text{C}$ $\gamma \rightarrow \alpha$ with vol. increase 4% $\rightarrow$ peeling off, not too sensitive to oxygen losses

- **Main applications:**
  - Wear resistance
  - Heat barrier
  - Dielectric (electronic - microwave)
  - High porosity
Plasma sprayed coatings

- Some Properties Thermally Sprayed Coatings can Provide:
  - Tribological (wear, resistance).
  - Corrosion resistance.
  - Heat resistance.
  - Thermal barrier.
  - Electrical conductivity or resistivity
  - Abradable or abrasive.
  - Textured surfaces.
  - Catalyst and prosthetic properties,
  - Restoration of dimension.
  - Copying of intricate surfaces.
## Environmental pollution

The main toxic pollutants, %

<table>
<thead>
<tr>
<th>The source</th>
<th>SO₂</th>
<th>Solid particles</th>
<th>NOₓ</th>
<th>CₘHₙ</th>
<th>CO</th>
<th>In total</th>
</tr>
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<tbody>
<tr>
<td>Transport</td>
<td>3</td>
<td>13</td>
<td>40</td>
<td>54</td>
<td>91</td>
<td>~58</td>
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<tr>
<td>Industry</td>
<td>35</td>
<td>26,5</td>
<td>20</td>
<td>23</td>
<td>2</td>
<td>~15</td>
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<tr>
<td>Heating plants</td>
<td>43</td>
<td>26,5</td>
<td>20</td>
<td>9</td>
<td>2</td>
<td>~15</td>
</tr>
<tr>
<td>Domestic appliances</td>
<td>19</td>
<td>34</td>
<td>20</td>
<td>14</td>
<td>5</td>
<td>~13</td>
</tr>
<tr>
<td>In total</td>
<td>19</td>
<td>7,6</td>
<td>1,3</td>
<td>11</td>
<td>49,5</td>
<td>100</td>
</tr>
</tbody>
</table>

The main emissions of a car engine are:

**Nitrogen gas** (N\textsubscript{2}) - Air is 78-percent nitrogen gas, and most of this passes right through the car engine.

**Carbon dioxide** (CO\textsubscript{2}) - This is one product of combustion. The carbon in the fuel bonds with the oxygen in the air.

**Water vapor** (H\textsubscript{2}O) - This is another product of combustion. The hydrogen in the fuel bonds with the oxygen in the air.

These emissions are mostly benign, although carbon dioxide emissions contribute to global warming.

Because the combustion process is never perfect, some smaller amounts of more harmful emissions are also produced in car engines.

**Carbon monoxide** (CO) is a poisonous gas that is colorless and odorless.

**Hydrocarbons** or **volatile organic compounds** (VOCs) are a major component of smog produced mostly from evaporated, unburned fuel.

**Nitrogen oxides** (NO and NO\textsubscript{2}, together called NO\textsubscript{x}) are a contributor to smog and acid rain, which also causes irritation to human mucus membranes.
Catalysis

In chemistry, a **catalyst** is a substance that causes or accelerates a chemical reaction without itself being affected. Catalysts participate in the reactions, but are neither reactants nor products of the reaction they catalyze.

**Heterogeneous catalysis** - the use of a catalyst in a **different phase** from the reactants. Typical examples involve a **solid** catalyst with the reactants as either **liquids or gases**.

The first research works on heterogenous catalyst were performed at the end of 18th century.

The catalytic converter was invented by **Eugene Houdry**, a French mechanical engineer and expert in catalytic oil refining, in the mid 1950s. United States Patent 2742437.
Most automobile spark-ignition engines in North America have been fitted with catalytic converters since 1975, and the technology used in non-automotive applications is generally based on automotive technology. While the regulatory requirement was for the 1975 model year, General Motors is documented as having fitted catalytic converters to the 1974 Camaro Type LT fitted with the 5.7L L65 and LM1 engines.

Vehicles emit most of their pollution during the first five minutes of engine operation before the catalytic converter has warmed up sufficiently to be effective.

In 1999, BMW introduced an electrically heated catalyst, which they called "E-CAT", in their 750iL sedan. Heating coils inside the catalytic converter assemblies are electrified just after engine start, bringing the catalyst up to operating temperature very quickly to qualify the vehicle for low emission vehicle (LEV) designation.

[Catalytic converters, nsls.bnl.gov]
Most modern cars are equipped with “three-way” catalytic converters. They consist of a ceramic structure coated with a metal catalyst, usually platinum, rhodium and/or palladium.

A “three-way” catalytic converter has three simultaneous tasks:

- **Reduction** of nitrogen oxides to nitrogen and oxygen: $2\text{NO}_x \rightarrow x\text{O}_2 + \text{N}_2$
- **Oxidation** of carbon monoxide to carbon dioxide: $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$
- **Oxidation** of unburnt hydrocarbons (HC) to carbon dioxide and water:
  \[
  C_x\text{H}_{2x} + 2 + [(3x+1)/2]\text{O}_2 \rightarrow x\text{CO}_2 + (x+1)\text{H}_2\text{O}.
  \]

### Typical Conversion Efficiencies
- NOx: 60-99%
- CO: 70-99%
- NMHC: 40-90%
- VOC: 60-99%
- CH$_2$O: 60-99%
- HAPs: 60-99%
Oxidation reactions with O2:
CO + ½ O2 → CO2
HC + ½ O2 → CO2 + H2O
HC + ½ O2 → CO + H2O
H2 + ½ O2 → H2O

Oxidation/reduction reactions with NO:
CO + NO → ½ N2 + CO2
HC + NO → N2 + H2O + CO2
HC + NO → N2 + H2O + CO
H2 + NO → ½ N2 + H2O
H2 + 2 NO → N2O + H2O
5/2 H2 + NO → NH3 + H2O
2 NO + 2 NH3 + ½ O2 → 2N2 + 3 H2O

Water-gas shift reaction:
CO + H2O → CO2 + H2

Reforming reactions:
HC + H2O → CO2 + H2
HC + H2O → CO + H2
Pt and Pd the most active catalysts, work in low temperatures.

Krylov summarized the data of catalytic metal oxides and put to a line according the catalytic activity:

\[
\text{MnO}_2 > \text{CoO} > \text{Co}_3\text{O}_4 > \text{MnO} > \text{CdO} > \text{Ag}_2\text{O}_3 > \text{CuO} > \text{NiO} > \text{SnO}_2 > \text{Cu}_2\text{O} > \text{Co}_2\text{O}_3 > \text{ZnO} > \text{TiO}_2 > \text{Fe}_2\text{O}_3 > \text{ZrO}_2 > \text{Cr}_2\text{O}_3 > \text{CeO}_2 > \text{V}_2\text{O}_5 > \text{HgO} > \text{WO}_3 > \text{ThO}_2 > \text{BeO} > \text{MgO} > \text{GeO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2.
\]

Several plasma spray systems will be used for deposition of wide range coatings. Plasma torches of special configuration will be adjusted for operating by feeding air, nitrogen, propane-butan, acetylene or CO$_2$ gases in the mixture with dispersed particles under the possibility of injection directly into the reacting arc zone.

Three types of plasma torches were developed for deposition of catalytic coatings. The power supply of the torch is connected with voltage rectifier of verified voltage. It includes current stabilization and precise regulation systems. The gas passes through the arc with dissociation-and-ionization process until it forms plasma, which is stabilized by direct-current source. The geometry of the copper anode forces the rapidly expanding gas to accelerate and results in the formation of a high velocity, high-temperature jet. The coating material is introduced as a powder or vapour in a jet of a carrier gas. The particles enter the jet either internally or externally.

The main parameters were used in the production of carbon coatings at atmospheric pressure: power supply – 35 kW, arc current – 180-200 A, the main flow rate of the working gas – 1.5-3·10^3 kg·s$^{-1}$, the additional flow rate of air – 1·3·10^3 kg·s$^{-1}$, the temperature of the gas leaving plasma torch – 3000-3500 K and the mean velocity – 500-650 m·s$^{-1}$. The heat flux density is 106-108 kW/m$^2$, the flux of particles in the torch ~1025 m$^2$·s$^{-1}$. 

PLASMA SYSTEMS AND PLASMA SOURCES

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PLASMA SYSTEMS AND PLASMA SOURCES
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Two-chamber</th>
<th>Three-chamber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power, $P$ (kW)</td>
<td>33–78</td>
<td>40–94</td>
</tr>
<tr>
<td>Arc current, $U$ (A)</td>
<td>175–245</td>
<td>175–285</td>
</tr>
<tr>
<td>Arc voltage, $I$ (V)</td>
<td>160–335</td>
<td>200–360</td>
</tr>
<tr>
<td>Cooling water flow rate, $G_v$ (kg s$^{-1}$)</td>
<td>0.16–0.18</td>
<td>0.16–0.18</td>
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<tr>
<td>Water temperature increment (*)</td>
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<td></td>
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<tr>
<td>Plasma torch</td>
<td>15–23</td>
<td>18–38</td>
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<tr>
<td>Cathode</td>
<td>1.1–1.53</td>
<td>1.004–1.75</td>
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<tr>
<td>Ignition section</td>
<td>1.08–2.16</td>
<td>1.15–3.0</td>
</tr>
<tr>
<td>Neutrode</td>
<td>—</td>
<td>2.2–6.0</td>
</tr>
<tr>
<td>Anode</td>
<td>13.0–19.3</td>
<td>13.7–27.3</td>
</tr>
</tbody>
</table>

Source gas flow rate ($10^{-3}$ kg s$^{-1}$)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Two-chamber</th>
<th>Three-chamber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode, $G_0$</td>
<td>0.54–1.0</td>
<td>0.54–1.2</td>
</tr>
<tr>
<td>Neutrode, $G_1$</td>
<td>—</td>
<td>1.2–3.6</td>
</tr>
<tr>
<td>Anode, $G_2$</td>
<td>1.85–7.6</td>
<td>1.0–3.0</td>
</tr>
</tbody>
</table>

Source gas flow rate ($10^{-3}$ kg s$^{-1}$)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Two-chamber</th>
<th>Three-chamber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode, $G_0$</td>
<td>0.54–1.0</td>
<td>0.54–1.2</td>
</tr>
<tr>
<td>Neutrode, $G_1$</td>
<td>—</td>
<td>1.2–3.6</td>
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<tr>
<td>Anode, $G_2$</td>
<td>1.85–7.6</td>
<td>1.0–3.0</td>
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</tbody>
</table>

Source gas inlet velocity (m s$^{-1}$)

<table>
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<th>Parameter</th>
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<tbody>
<tr>
<td>Cathode, $v_0$</td>
<td>70–130</td>
<td>70–150</td>
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<td>Neutrode, $v_1$</td>
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<td>70–210</td>
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<tr>
<td>Anode, $v_2$</td>
<td>55–220</td>
<td>66–180</td>
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Plasma jet mean temperature, $T_f$ (K), equation (9)

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Three-chamber</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>3460–5200</td>
<td>3480–5170</td>
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Plasma jet mean velocity, $w_f$ (m s$^{-1}$), equation (10)

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<tr>
<td></td>
<td>350–1000</td>
<td>500–1000</td>
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Efficiency, $\eta$

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<th>Three-chamber</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0.58–0.78</td>
<td>0.6–0.77</td>
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</tbody>
</table>

Reaction chamber diameter ($10^{-3}$ m)

<table>
<thead>
<tr>
<th>Parameter</th>
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</thead>
<tbody>
<tr>
<td>$d_1$</td>
<td>4.0</td>
<td>4.0</td>
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<tr>
<td>$d_2$</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>$d_3$</td>
<td>12.0</td>
<td>12.0</td>
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</tbody>
</table>

Section length ($10^{-3}$ m)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Two-chamber</th>
<th>Three-chamber</th>
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<tbody>
<tr>
<td>$l_1$</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>$l_2$</td>
<td>—</td>
<td>26.0</td>
</tr>
<tr>
<td>$l_3$</td>
<td>64.0</td>
<td>56.0</td>
</tr>
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</table>
Sprayed materials

Specific attention has been focused on the deposition and investigation of micro- and nanostructured coatings from inorganic oxide materials: Cu, CuO, CrO, Cr$_2$O$_3$, Ni, Al$_2$O$_3$, TiO, zeolites, etc. and their mixtures for catalytic application. Air, argon, hydrogen, nitrogen and their mixtures were used as plasma forming gas.

The used mixtures of powder for coatings deposition:
- Al–Al(OH)$_3$–CuO–Cr$_2$O$_3$
- Al–zeolite;
- Al–CuO–zeolite;
- Al–Al(OH)$_3$–zeolite;
- Al–Al(OH)$_3$–Cr$_2$O$_3$–zeolite;
- Al–CuO–Cr$_2$O$_3$–zeolite;
- Al–Al(OH)$_3$–CuO;
- Al–Al(OH)$_3$–Cu;
- Al–Al(OH)$_3$–Cu–Cr$_2$O$_3$.
- Al – Al(OH)$_3$-TiO$_2$ – Ni
- Al – Al(OH)$_3$ - TiO$_2$ – Cu
Schematic representation (a) and real view (b) of the plasma spray technique
Temperatures and velocities of sprayed particles

Distribution of temperatures (a) and velocities (b) of Al\textsubscript{2}O\textsubscript{3} particles and plasma jet determined by measurements along the spraying distance. 1, 2 show plasma jet experimental and numerical simulation results respectively, 3, 4 and 5 represent particles of 75, 50 and 35 µm in diameter respectively. x/d is a dimensionless distance.
The chemical composition of powder for plasma spraying

<table>
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<tr>
<th>Nr.</th>
<th>Layers</th>
<th>Quantity, %</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
<td>Al(OH)$_3$</td>
<td>Cr$_2$O$_3$</td>
<td>CuO</td>
<td>Cu</td>
</tr>
<tr>
<td>1</td>
<td>Inner layer</td>
<td>8</td>
<td>92</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>Active layer</td>
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<td>10</td>
<td>10</td>
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<td>Inner layer</td>
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<td>92</td>
<td>-</td>
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<td>87</td>
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<td>5</td>
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<tr>
<td></td>
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<td>-</td>
<td>85</td>
<td>5</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>Inner layer</td>
<td>50</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Active layer</td>
<td>-</td>
<td>85</td>
<td>5</td>
<td>-</td>
<td>15</td>
</tr>
</tbody>
</table>
Standard Pt, Rh supported catalytic converters: a – honeycomb structure, b - ceramic beads
Catalytic monolithic reactor

The active CMR unit made of flat and corrugated coatings
## Properties of the catalytic converter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>The value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area of the substrate</td>
<td>0,26 m²</td>
</tr>
<tr>
<td>The density of microchannels</td>
<td>66·10⁴ m⁻²</td>
</tr>
<tr>
<td>The length</td>
<td>0,09 m</td>
</tr>
<tr>
<td>The diameter</td>
<td>0,03 m</td>
</tr>
<tr>
<td>The area of the cross section</td>
<td>0,615·10⁻³ m²</td>
</tr>
<tr>
<td>The active area of the cross section</td>
<td>0,431·10⁻³ m²</td>
</tr>
<tr>
<td>The volume</td>
<td>55,4·10⁻⁶ m³</td>
</tr>
<tr>
<td>The active volume</td>
<td>38,8·10⁻⁶ m³</td>
</tr>
</tbody>
</table>
The morphology and composition of catalytic coatings
The morphology and composition of catalytic coatings

SEM view of Al(OH)$_3$+Cu coatings at different injection locations of dispersed particles into plasma jet: a – injection into the reactor; b – into the arc; c and d – the same under magnification of 2000 times respectively. Hydrocarbons containing gas was not supplied.
The XRD analysis results of Al coatings covered with metal oxides of Al(OH)$_3$, Cu, CuO.

The XRD analysis results of Al coatings covered with Ni, Zr$_2$O$_3$. 
XRD patterns of as-sprayed coatings with different composition: A – anatase, R – rutile, S – support.
XRD patterns of the fresh, thermal processed and used coating containing CuO(5 wt.% Cu)/Al₂O₃. ◊ – Cu₂O, ○– Cu, □ – CuO.
TG and DSC curves of initial mixture (top) and coating (bottom) of Ni–Cu/TiO$_2$–Al$_2$O$_3$
The research on catalytic activity

Scheme of the experimental set-up for the investigation of catalytic coatings’ properties: S1–S6, T1–T15, P1–P3 – thermocouples; 1 – burner; 2 – gas combustion chamber; 3 – stabilization section; 4 – catalytic combustion chamber; 5 – CMR.
Catalytic activity of the coatings

Catalytic combustion behaviour in the CO oxidation. Initial CO concentration 3%, flow rate 1.5 g/s. 1 – Al+Al(OH)$_3$, Cr$_2$O$_3$(10%), CuO(10%); 2 – Al+Al(OH)$_3$, CuO (7%); 3 – Al+Al(OH)$_3$,Cu(5%); 4 – Al+Al(OH)$_3$, Cr$_2$O(5%), Cu(10%); 5 – Al+Al(OH)$_3$, Cr$_2$O$_3$(5%),Cu(15%); 5 – a standard Pt catalyst.
Catalytic activity of CuO/Al₂O₃ at the different flow rates: 1 g/s; 1.5 g/s and 2 g/s
Catalytic conversion of NOx

NO conversion as a function of temperature
A) over Ni–Cu/TiO$_2$–Al$_2$O$_3$ (●), Cu/TiO$_2$–Al$_2$O$_3$ (■), Ni/TiO$_2$–Al$_2$O$_3$ (▲) and Pt/cordierite (×) catalysts, and during the blank test (○) at the space velocity of 2100 h$^{-1}$,
B) over Ni–Cu/TiO$_2$–Al$_2$O$_3$ catalyst at the space velocity: (●) 2100h$^{-1}$, (■) 3250 h$^{-1}$, (▲) 6300h$^{-1}$. 
Catalytic ignition and extinction. Emission gas flow rate 1.5 g/s, 3% CO (T=300 °C)
Catalytic reforming of glycerol

Experimental setup of thermal decomposition of glycerol fraction. 1,2 – overheated water vapor supply, 3 – 8 – glycerol gasification system, 9– 18 – gas products collecting system, 19 – heated channel for catalytic reactions
Reforming of glycerol

\[
\begin{align*}
C_2H_8O_3 + 3H_2O & \rightarrow 7H_2 + 3CO_2 \quad \text{(Glycerol steam reforming)} \quad (1) \\
C_3H_8O_3 & \rightarrow 4H_2 + 3CO \quad \text{(Direct decomposition - pyrolysis)} \quad (2) \\
CO + H_2O & \rightarrow H_2 + CO_2 \quad \text{(water-gas shift reaction - WGS)} \quad (3) \\
CH_4 + H_2O & \rightarrow CO + 3H_2 \quad \text{(CH}_4 \text{ steam reforming)} \quad (4)
\end{align*}
\]
Catalytic reforming of glycerol
Thank you!
The End