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Catalytic Effect of Plasma Sprayed Coatings on Combustion Gases Afterburning Improvement

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Summary. Important types of environmental noxiousness connected with carbon monoxide and toxic gases emission are characterized in this paper. Presented methods allow to reduce pollutants emission in the afterburning processes, especially catalytic afterburning.

Results concern the catalytic effect of plasma sprayed ceramic coatings on burning surfaces and ceramic blocks. The catalytic afterburning processes are realized in tube furnaces, water heaters and in a model chamber with ceramic blocks sprayed with catalytic coatings placed in combustion gas ducts. Results confirm the purposefulness of plasma sprayed catalytic coatings application for afterburning processes.
Key words: catalytic sprayed coatings, NO_x, fuel gasses, pollution emission in the afterburning processes.

INTRODUCTION

In the last year about 4 million tons toxic waste gases are emitted in Poland, whereof only 15% are neutralized thereupon pollutant emission losses amount 17% of the national income. The most polluting industries are the commercial power engineering and transport. Pollutants emitted during burning process constitute dusts, pitchy substances, solid micro-particles, sulfur, nitrogen oxides and carbon dioxide and other about 50 substances, including As, Cr, V, Si, Mg, Fe. About 14% of Poland territory (Upper Silesian Industrial Region, Copper Region, and Cracow) are the polluted areas in which fuel burning process is the main source of pollutants [3, 8, 19]. The pollutants emission limit have been established in Poland only for boilers, and values are automatically transferred onto industrial furnaces and municipal boiler furnaces. However there are no limits for motorcar engines emissions. The penalties for exceeding the emission limit are only 10% of national economy losses.

Carbon monoxide because of its high toxicity is one of the most harmful burning product. Beside CO, the major pollutants include: hydrocarbons (CH), carbon soot (C_s), dusts, pitchy substances, nitrogen oxide (NO_x), sulfur oxide (SO_2) and organic micro-particles. According to the subject, almost all elementary carbon from the fuel burning process goes through the CO stage. For this reason, carbon oxidation acceleration to CO_2 is highly required in constrast to reduction of its formation during burning process. The elementary reactions of carbon oxidation are well known, however the mechanism of its formation not completely.

Significant improvement of coal burning processes negative effect might be possible through:
– implementation of the coal enrichment technologies,
– application of fluidized-bed furnaces,
– implementation of NO_x low emission powdered-fuel burners,
– implementation of SO_2 removing equipment from combustion-gas.

Authors studies on catalyzing of combustion gas afterburning and NO_x emission reduction may have a substantial contribution to the environmental conditions improvement and are results of power engineering, metallurgical, transport industry and economy demands [10, 11, 15].

One of the solution is covering with high-melting, high-hardness materials plasma sprayed coatings of furnaces, boilers, heat exchangers and other industrial equipment walls in order to protect against corrosion and erosion but also to induce catalytic action. Generally, coatings are sprayed on metallic, ceramic operating surfaces of the equipment both new or after exploitation often without removing the elements from the operating area.

According to active complex theory (refer to as the transition state theory), which claims that the collision of the active particles occurs easier on the burning space walls and reaction chains are shorter if the wall-contained surface area ratio is greater to the reaction space volume [7, 16]. However the problem is to select the coating types and parameters of spraying, and also their wear resistance.

CARBON MONOXIDE OXIDATION AND NITROGEN OXIDE DECOMPOSITION CATALYZING MATERIALS

During carbon monoxide oxidation process, high activity demonstrates platinum and palladium. In the presence of these metals at temperature of 470 K, 100% amount of CO is being burnt in the oxygen atmosphere. The fourth group oxides also catalyze CO oxidation however process proceeds at higher temperature and has lower rate.

The greatest catalytic activity is demonstrated by cobalt, copper, manganese and nickel oxides in contrast to zinc, titanium, vanadium, and iron oxides which are less active [9]. However copper, nickel and manganese oxides have also found other technical applications as catalyzing materials. For these oxides CO oxidation activation energy (at a normal temperature) is from 12.5 to 25 kJ/mole, and 62 to 110 kJ/mole at temperatures of 470 to 670 K. Lanthanide oxides also decrease the activation energy of the CO oxidation process, with the following order towards their decreasing activity: CeO_2, La_2O_3, Nd_2O_3, and Dy_2O_3.

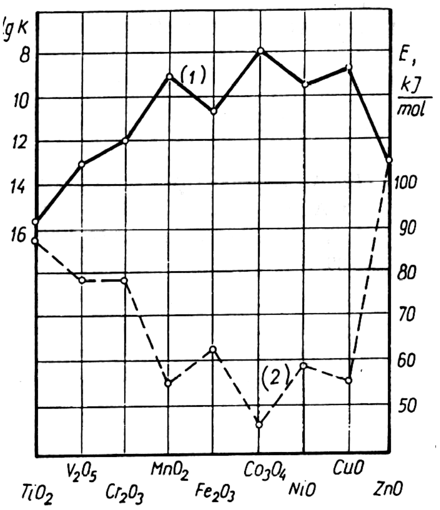

Fig. 1. Logarytmic relation beetwen reaction-rate velocity (1) and activation energy (2) of fourth group elements for $CO + O_2$ reaction [1]

The hydrocarbons oxidation is strongly influenced by the cobalt, nickel, and copper oxides. Because of the symmetrical structure of CH_4 molecule its oxidation is a complicated process and the greatest catalyzing is demonstrated by Co_3O_4, NiO, CuO and MnO_2. Great capability of methane oxidizing is possessed by the cerium and terbium oxides. Factors which affect the formation of nitrogen oxides beside burning temperature, are also connected with the parameters which influence on the burning process as: fuel, burner type, air preheating, excess air ratio, fuel flow rate, flame form and also design parameters as furnace geometry, burners design and position, temperature distribution of furnace wall and combustion gas [12, 13, 20]. On the other hand when combustion gas temperature decrease, metastable nitrogen oxides decompose, but several requirements have to be meet as:

- slowly cooling of NO combustion gas,
- oxygen depletion in combustion gas,
- systematic removal of oxygen from NO decomposition by bonding it with incompletely burnt constituents.

The NO decomposition rate can increase by presence of the catalysts as: platinum, palladium, and some oxides which strongly accelerate CO, CH_4, and H_2 burning reactions. The afterburning of these components is realized using oxygen generated from the NO decomposition reaction while presence of these catalysts increases the intensity NO decomposition and afterburning of incompletely burnt components [2, 5].

ASSUMPTIONS OF THE RESEARCHES

Combustion gases flowing out through burning chamber consists of NO_x, CO, CH_4, C_nH_m, other unburned constituents and also free oxygen. It is assumed that by the proper set of the thermochemical parameters, it is possible to make conditions which enable thermal decomposition processes of NO_x and its nonselective reduction by incompletely burnt constituents of combustion gas. It result in a reduction of NO_x emission and incompletely burnt constituents. The effect of CO reduction in the combustion gas by catalytic coatings is obtained in the previous studies. However since an excess air ratio of 0.9 – 1.0 is used in these studies, it can be assumed that the afterburning of incompletely burnt constituents is also influenced by oxygen formed as a result of NO_x decomposition [4, 14, 18]. In researches realized in the model combustion-gas duct exothermal effect of nitrogen oxide reduction and CO, CH_4, C_nH_m afterburning reactions is changed into heat in the water heaters. In the industrial conditions it means that heat recovered by NO_x reduction and CO, CH_4, C_nH_m afterburning reactions might increase overall thermal efficiency of furnaces, boilers etc [1, 6, 17].

METHODS AND RESULTS

The studies are realized in two stages. At first stage, three types of coating are sprayed onto ceramic blocks (beds) choosing greatest catalyzing capabilities in NO_x reduction and CO afterburning reactions. These coatings are made of the IV period transition metals oxide mixtures, called **K, M, C** oxides, with additions of high wear and high temperature erosion resistance materials. Considering small porosity (<3%) of the coatings, they form tight, impervious barrier to the gaseous corrosion of the metal substrate (steel boiler tubes). Prepared mixtures of coatings based on IV period metal oxides are sprayed on ceramic substrate of 1.5 m-long and 0.1 m-inner diameter catalytic cartridges (stacks) of high permeability (30% of voids). The catalytic cartridges (stacks) are placed within a ceramic duct built over at the outlet of burning chamber – Fig. 2.

The dimensions of the chamber where natural gas is burnt using a low-emission burner are as follows: length – 2.5 m, diameter – 0.5 m. Four test series are realized using a different type of coating sprayed on the cartridge (catalytic stack). The greatest catalytic effect on the reduction of NO_x and CO contents had coatings sprayed from the **K**

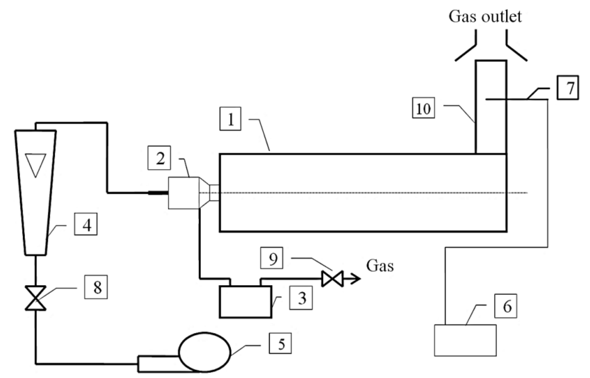

Fig. 2. Equipment for coatings catalytic effect testing stage I: 1 – ceramic burning chamber, 2 – burner, 3 – gas meter, 4 – air rotameter, 5 – burning air fan, 6 – PEMAC 3000 combustion-gas analyzer, 7 – measuring probe, 8 – air valve, 9 – gas valve, 10 – combustion-gas ducts with catalysts

type oxide-based mixtures. The NO_x conversion was up to 80% and CO afterburning was complete. In the case for coatings sprayed with the **M** type oxide-based coatings, the NO_x conversion values were 2-3% smaller, however CO conversion was also 100%. For the coatings sprayed from the **N** and **C** type oxide mixtures, NO_x conversion was 55-65%. The conversion in the presence of the coatings sprayed from the **N** or **C** type oxide-based mixtures were approximately 10% lower than the values of the **K** or **M** type oxide-based coatings.

The second stage of research are realized on a semi-industrial stand equipped in gaseous and liquid fuel burners. (fig. 3). The catalytic coatings from **K** and **M** type oxide-based mixtures were sprayed onto the chamotte and metal substrates. Thus obtained two catalytic cartridges (stacks) were placed in two of the three ducts, through which the combustion gas was flowing out of the burning chamber – Fig. 3, whereas the third – empty (without the cartridge) duct served for the combustion gas flowing out during the period of heating up and attaining a thermal equilibrium by the testing stand. The results of NO_x and CO conversion measurements revealed the need for building a stand with a longer burning chamber that would assure the complete burning of the supplied fuels (an imitation of the burning chamber in reverberatory furnaces and boilers).

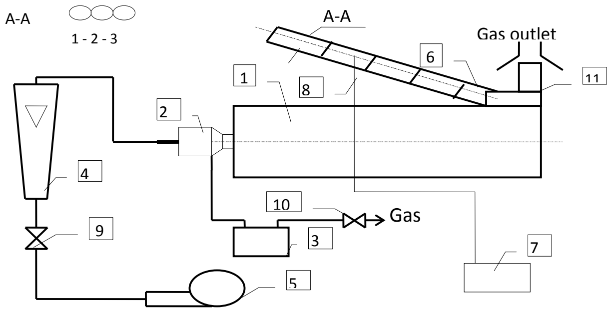

Fig. 3. Equipment for coatings kinetic effect testing stage II: 1 – ceramic burning chamber, 2 – burner, 3 – gas meter, 4 – air rotameter, 5 – burning air fan, 6- combustion-gasducts with catalysts, 7 – PEMAC 3000 combustion-gas analyzer, 8 – measuring probe, 9 – air valve, 10 – gas valve, 11 – short combustion gas-ducts

For combustion gases of natural gas in presence of the **K** type oxide coatings sprayed on the ceramic substrate, NO_x conversion exceeded 70%, while for **M** type oxide coatings about 60%. However when using coatings sprayed on the metal cartridges of furnace the NO_x conversion was approximately 10% lower than for the ceramic cartridges but for liquid fuel burner, the amount of NO_x in a combustion gas highly increased and thus effectiveness of the coatings was lower. Higher conversion degree is attained for the coatings applied on the metal substrate in compare to ceramic. Present studies are based on the nonselective reduction of NO_x using hydrocarbon fuels in the presence of **K** and **M** type coatings.

CONCLUSIONS

The multi-stage studies realized on presented equipment result in following conclusions:

1. The results have shown the purposefulness of catalytic sprayed coatings application on burning chamber surfaces and evaluation of **K, M, C** metal-oxide plasma sprayed ceramic coatings for catalyzing and thermal decomposition of NO_x and CO afterburning.
2. Coatings applied for the combustion gases of natural gas had the greatest catalytic properties (approximately 70% NO_x conversion and 100% CO afterburning) and are made of **K** and **M** type oxide mixtures, and tested at $T_{c.gas}$~900°C; excess air ratio, λ<1.05; and the combustion gas velocity 1.8 m/s.
3. In the natural gas-derived combustion gas, the **K** type oxide-based coatings show the highest activity if they are sprayed on the ceramic cartridges (stacks).
4. The NO_x conversion in the diesel oil combustion gas is not satisfactory and is the subject of further studies. The studies include also effect of temperature, catalyst surface loading with the combustion gas, and NO_x reduction process ratio of catalyzing surface to CO oxidation catalyzing coating surface.

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KATALITYCZNE ODDZIAŁYWANIE PLAZMOWO NATRYSKIWANYCH POWŁOK NA ZWIĘKSZANIE DOPALANIA PALIW GAZOWYCH

Streszczenie. W pracy zawarto najważniejsze typy zanieczyszczeń powiązanych z CO, NOx oraz innymi toksycznymi gazami. Zaprezentowano również metody redukcji emisji zanieczyszczeń w procesie spalania. Wyniki pomiarów w kolejnych etapach badań wykazały celowość natryskiwania katalitycznych powłok na powierzchnie ograniczające przestrzenie spalania oraz umożliwiły dokonanie jakościowej oceny przydatności powłok ceramicznych natryskanych plazmowo.

Słowa kluczowe: natryskiwanie katalitycznych powłok, NO_x, paliwa gazowe, zanieczyszczenia w procesie spalania.