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M.G. BANNIKOV, cand. of science, GIK Institute, Topi, Pakistan,
I.P. VASILEV, cand. of science, EUNU, Lugansk

PROPERTIES AND EFFICIENCY OF CATALYSTS PRODUCED BY AN ION BEAM PROCESSING TECHNOLOGY

Приведены свойства и результаты испытаний катализаторов, полученных путем ионной имплантации. По сравнению с катализаторами, полученными обычными технологиями, опытные катализаторы показывают те же значения коэффициента нейтрализации при значительно меньшем содержании благородных металлов. Показано, что ионная бомбардировка не уменьшает эффективную поверхность носителей.

Paper presents the test results and properties of catalysts produced by an ion implantation technique. New catalysts showed the same efficiency with much lower expense of noble metals as compared with the catalysts produce by an impregnation. Also shown, that the ion bombardment did not reduce the specific surface area of the catalyst.

Catalysts are widely used to clean the industrial and automobile exhausts from oxides of nitrogen (NO_x), carbon monoxide (CO) and unburned hydrocarbons. The effectiveness of catalysts is determined, in part, by technology of their production. Impregnation as a base method of catalysts manufacturing has some drawbacks [1]. The properties of the carrier are changed, and in some cases the specific area of a catalyst is reduced. Unequal distribution of catalytic materials on the carrier surface and their agglomeration has been observed. High expense of catalytic materials is inherent to impregnation technology and this is of very importance when noble metals are used as a catalyst. Ion beam processing (IBP) technology has been used as a means of surface modification [2], tool hardening [3] and in-cylinder catalyst coating [4]. With this technology practically any chemical element can be implanted into the surface of any solid by a high velocity ion beam. This paper demonstrates the application of IBP for catalyst coating.

Experimental.
Catalysts have been fabricated by an ion implanter that consists of a vacuum chamber with a magnetron sputtering arrangement as the metal ion source [5]. This provided an ion beam with a diameter of 200 mm, a current density of 130 $\mu A/cm^2$ and a non-uniformity of 5 per cent along the cross-section. For implantation, the

ions could be accelerated from 0 to 40 keV. For catalyst surface to be coated evenly the installation has been equipped with a vibration mechanism. Catalysts were fabricated in a single cycle. The vacuum chamber was loaded with the substrates and vacuumed up to 0.013 Pa. Then coating started. This process, in turn, comprised two steps: surface degasing and coating. The first step was fulfilled at the voltage of 10 kV for about 10 minutes. The voltage of the second step determined the depth of ion penetration into the carrier and depended on materials processed. In our case it was around 20 kV. The duration of the second step depended on the catalytic material loading required. The mass of the substance implanted is proportional to the current density, duration of implanting and processed surface area. Details of an evaluation of an expense of materials during implantation are discussed in paper [6].

Several samples of catalyst on various substrates with different Platinum loading were prepared. Details of catalysts are given in tabl. 1 and tabl. 2. Prior to coating catalyst C3 the steel filament was pressed into tablets with porosity of around 70 %. tabl. 2 also provides details of the commercially produced platinum coated C5 and base-metal-based C6 catalysts that were fabricated by impregnation.

Table 1

Details of the Platinum coated catalysts and their NO_x conversion efficiency

Notation	C1	C2	C3
Carrier	γ-Al_2O_3		Steel
Size and shape	Extrudate ø 4 − 6 mm, L 5 – 7 mm	Rounded granules ø 3 – 7 mm (France)	Tablets ø 70 mm, L 5 mm from filament ø 0.1 mm
Fixation method	Implantation		
Catalyst loading, wt %	Pt = 0.11	Pt = 0.11	Pt = 0.114
NO_x conversion efficiency at 280 ºC, %	75	70	77

Table 2

Details of catalysts and their CO conversion efficiency

Notation	C4	C5	C6
Carrier	γ-Al_2O_3		
Size and shape	Rounded granules ø 3 to 6 mm		
Fixation method	Implantation	Impregnation	
Catalyst loading, wt %	Pt = 0.0135	Pt = 0.2	$CuO : Cr_2O_3 = 5 : 5$
CO conversion efficiency at 340 ºC, %	85	87	40

The pore structure of catalysts was investigated by mercury porosimetry method when mercury is pressed into pores. With mercury porosimetry only pores with radius more than 3.7 nm are accessible. That is why specific surface area of catalysts was also measured by nitrogen physisorption method. From the adsorption isotherm at liquid nitrogen temperature the surface areas of catalysts were calculated using BET equation. With BET surface area measurement pores with radius up to 0.32 nm are accessible.

Results and discussion.

First alumina extrudate, alumina pellets, and wire tablets were implanted by Platinum. This resulted in catalysts C1, C2, and C3 respectively. The implantation dose was chosen in such a way as to obtain a Platinum loading of catalysts two times less than that of commercially produced catalyst C5. The latter was manufactured by impregnation. Catalysts were tested in reaction of NO_x reduction in presence of NH_3. Such technology is used in industry to protect environment from NO_x pollution. Test results are in tabl. 1. All catalysts showed satisfactory conversion efficiency but Platinum content was still too high to make an ion implantation technique the competitive one.

Conversion efficiency of the catalyst depends not only on the amount of a catalytic material implanted but on how much of it is exposed to reagents. While selecting process parameters the following is to be taken into account. Energy of ions determines the depth of their penetration into the surface of a substrate. If ions are implanted into depth more than 1 μm they probably will not be accessible to reagents. Besides, duration of ion bombardment and current density effect the specific area significantly. Nickel ion bombardment with the dose of 5×10^6 ions/cm^2 increased the specific area by factor of four [1].

Preliminary work has been carried out to optimise the process parameters and the catalyst C4 with low Platinum content and rather high conversion efficiency has been obtained. tabl. 2 shows that the new catalyst C4 has the same CO conversion efficiency as the commercially produced C5 but with the fifteen times less Platinum content. It should be mentioned that base-metal-based impregnated catalyst C6 is only half as effective.

It is of great interest how an ion bombardment and impregnation affect such properties of carrier surface as a specific area, pore volume, and pore radius distribution. To investigate a change of carrier properties the mercury porosimetry test of pore structure of catalysts has been carried out. Figure 1 shows that curves of

pore volume distribution versus pore radius have nearly the same shape for all samples tested. Pore structure of samples is characterised by two kinds of pores: macropores with radius from 200 to 1000 nm, and mesopores with radius from 3.7 to 8 nm. As seen from Figure 2, catalysts surface areas measured by mercury porosimetry and BET methods differ significantly. This indicates the presence in samples of tiny pores with radius from 0.32 to 3.7 nm. This is also confirmed by the incomplete shape of the integral curves in fig. 1.

The difference in surface areas of carrier and catalysts C4 and C6 shown in fig. 2 is comparable with measurement error of methods used. Hence, the firm conclusion can be made that ion implantation has not decreased the specific surface area of catalyst.

For further investigation of the processes occurring in a solid body under ion bombardment, structural changes of the surface of the piston of diesel engine processed by high intensity ion beam were investigated by X-ray analysis [7]. Analysis of the shapes of diffraction lines has revealed: (a) the widening from planes (111) and (200) towards smaller angles, and (b) the presence of phase which has arisen immediately after implantation.

As the path length of bombarding ions is of orders of magnitude less than the thickness of the surface stratum of the aluminium alloy participating in X-ray diffraction, it seems to be impossible to fix structural changes in such lamina. The most plausible reason of that one could fix structural changes in the surface stratum can be reorientation of crystals (formation of texture). Further investigation of structural changes in the surface layer processed by the ion beam would make it possible to get more understanding in mechanisms of catalysis and to obtain surfaces with beforehand given properties.

Conclusions.

Several samples of catalysts on various substrates have been prepared and tested. Platinum implanted catalyst showed the same CO conversion efficiency as the commercially produced impregnated one but with the fifteen times less Platinum content.
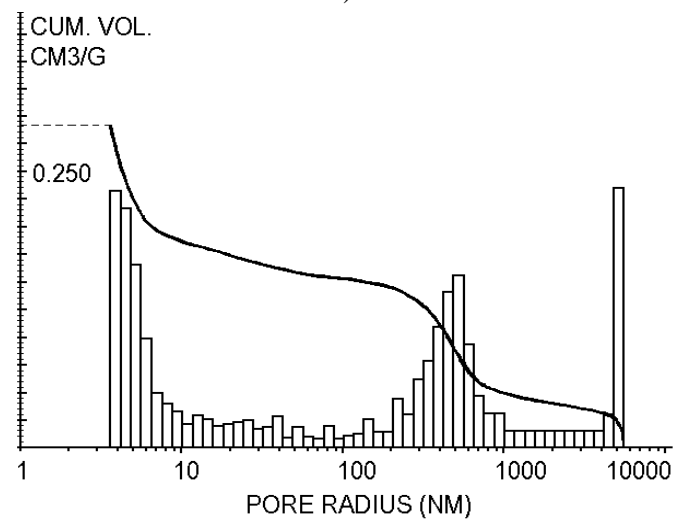
Pore structure test results showed that ion implantation did not decrease the specific surface area of the catalyst. Ion implantation results in the texturing of the surface. Ion beam processing technology can be considered as a potential means of production of noble-metal-based catalysts and research in this direction shall be continued.
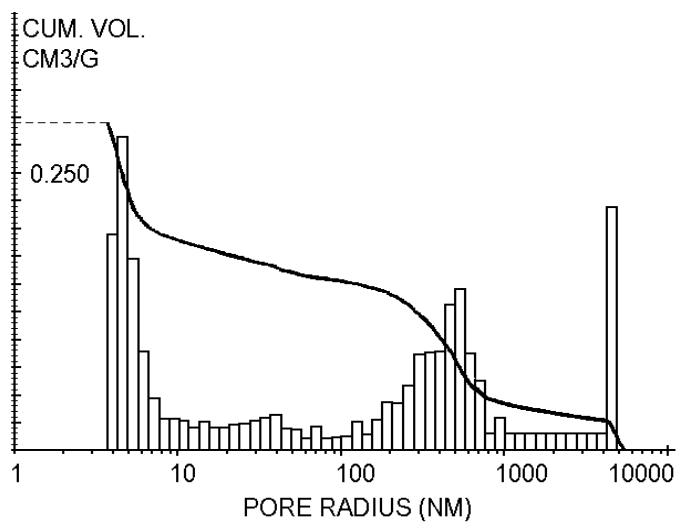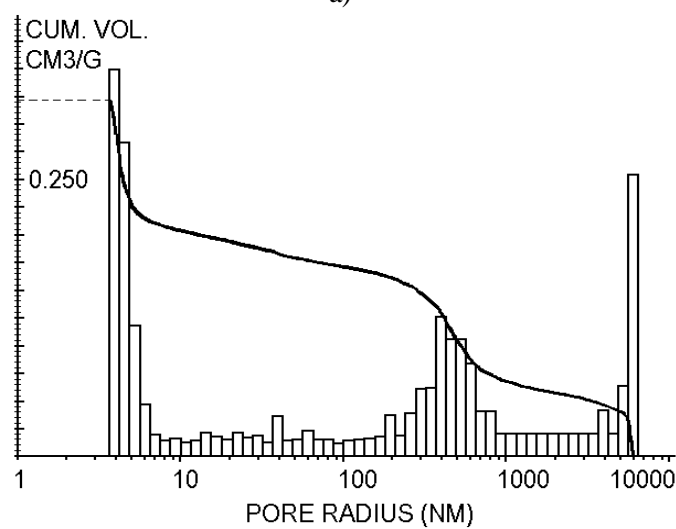
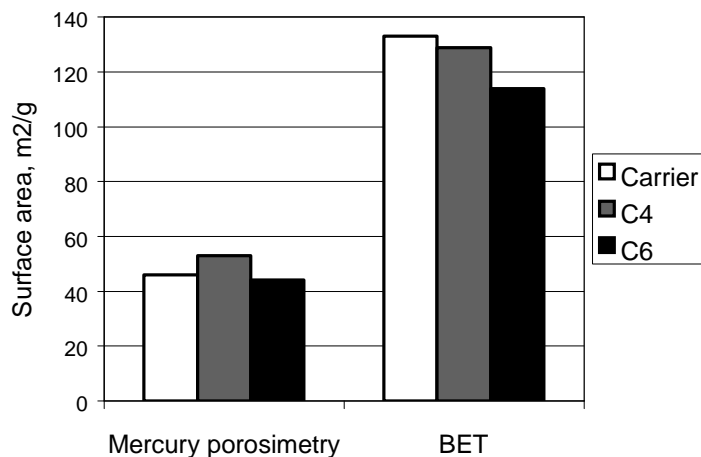Fig. 1. Pore volume distribution: a) carrier (γ-Al$_2$O$_3$ pellets), b) catalyst C4, c) catalyst C6

Fig. 2. Surface area of catalysts

Acknowledgment.

References: 1. *Mychlenov I.P.* Catalysts Technology / *I.P. Mychlenov.* – L.: Chemistry, 1979. – 272 p. **2.** *Hirvonen J.K.* Ion Implantation / *J.K. Hirvonen* // Academic Press. – 1980. **3.** *Zlobin V.N.* Hardening of Cutting Tool Inserts by Ion Implantation / [*V.N. Zlobin, M.G. Bannikov, P.H. Draper et al.*]: Proceedings of 7th International Symposium on Advanced Materials (ISAM-2001), (Islamabad, September 2001). – P. 470 – 472. **4.** *Bannikov M.G.* Reduction of NO_x Emission of Diesel Engines by In-cylinder Catalysis / [*M.G. Bannikov, P.H. Draper, J.A. Chattha et al.*] // Proc. Instn Mech. Engrs, Part A, Journal of Power and Energy. – 2003. – 217/A1. – P. 101 – 106. **5.** *Zlobin V.N.* Potential of Use of Ion Implantation as a Mean of Catalysts Manufacturing // [*V.N. Zlobin, M.G. Bannikov, I.P. Vasilev et al.*] // Proc.Instn Mech. Engrs, Part D, Journal of Automobile Engineering. – 2002. – 216/D5. – P. 385 – 390. **6.** *Bannikov M.G.* Evaluation of an expense of materials during ion implantation / [*M.G. Bannikov, V.N. Zlobin, A.V. Zotov et al.*]: Proceedings of 8th International Symposium on Advanced Materials (ISAM-2003), (Islamabad, September 2003). – P. 473 – 475. **7.** *Bannikov M.G.* Investigation of Properties and Structure of Surfaces Processed by an Ion Implementation Technique / [*M.G. Bannikov, V.M. Gromenko, J.A. Chattha et al.*]: Proceedings of International Conference on Frontiers of Advanced Engineering Materials (FAEM-2004), (Lahore, September 20-22). – 2004. – P. 270 – 273.