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Oxygen interaction with Pt–Pd–Rh catalytic alloys

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The effect of molecular oxygen interaction with Pt 92.5%–Pd 4%–Rh 3.5% and Pt 81%–Pd 15%–Rh 3.5%–Ru 0.5% (wt%) alloy gauzes was studied. The investigation was carried out at temperatures of 1163 and 1373 K under oxygen pressure of 0.094 MPa. Reaction of the alloys with oxygen leads to the formation of volatile oxides α-PtO_2, RhO_2 and PdO and to changes in the surface topography and chemical composition of the gauzes. Using atomic absorption spectroscopy, scanning electron microscopy and electron probe microanalysis methods the rate of the volatile oxide formation and the characteristics of the surface changes were determined. The rate of the oxide formation decreases with increasing palladium concentration in the alloys. The distributions of elements on the oxidized surfaces are non-uniform; grain facets are enriched with platinum and grain boundaries with rhodium and oxygen, probably in the form of Rh_2O_3. However, distinct differences in palladium distribution were not observed.

1. Introduction

The industrial process for ammonia oxidation to nitric oxide is catalysed by Pt–Rh gauzes containing 5 to 10% of rhodium. Lately, Pt–Pd–Rh alloy gauzes have been applied for this purpose as well [1, 2]. The available information on the industrial applications of these alloys indicates that the selectivity of the oxidation of NH_3 to NO is about 94 to 97%, i.e. the same as that obtained with Pt–Rh gauzes.

Numerous studies of industrial Pt–Rh alloy gauzes prove their erosion under technological conditions [3–10]; losses of catalyst mass are also observed [5, 6, 11]. These processes are connected with the formation of volatile PtO_2 and, as has been found recently, with the volatility of a small amount of RhO_2 [12]. Simultaneously, rhodium from the surface layer of gauzes is oxidized to the superficial nonvolatile Rh_2O_3 and the catalyst becomes deactivated. Thus, oxygen from the air – ammonia reaction mixture can be responsible for the catalytic erosion.

As yet, there are no data on the surface changes of Pt–Pd–Rh alloy gauzes used for the ammonia oxidation process. It was simply noticed that mass losses were lower than in the case of the Pt–Rh catalyst [1]. Thus, it seems to be important to determine the influence of oxygen upon catalytic alloys containing palladium.

In the present study it was important to find out: (i) the quantitative composition of the volatile products of oxygen reaction with alloys, (ii) the changes in surface topography and chemical composition of the gauzes, and (iii) the influence of palladium upon changes in the rate of the mass losses.

2. Experimental details

The investigation was carried out with Pt 92.5%–Pd 4%–Rh 3.5% and Pt 81%–Pd 15%–Rh.3.5%–Ru 0.5% alloy gauzes in the form of wire of 90 μm diameter and 900 mesh cm^{-2}. Alloys were supplied by Almaz–Juveler Export, USSR.

The alloy gauzes were exposed to oxygen in a Pyrex glass reactor under static conditions. The procedure of the experiments and construction of the reactor were described previously [12]. The alloys were oxidized at temperatures of 1163 or 1373 K for 70 h under an oxygen pressure of 0.094 MPa. This pressure corresponded to the partial pressure of oxygen in the 10% HN_3–air mixture for the medium-pressure (0.51 MPa) industrial process. Also, the temperature of 1163 K was characteristic of this process.

During oxygen interaction with Pt–Pd–Rh alloy samples the volatile products of this reaction were condensed on the reactor walls. Simultaneously the gauzes underwent erosion, and changes in their surface topography and chemical composition were detected. The condensed reaction products were dissolved in hot concentrated HCl_{aq} and the quantities of platinum, rhodium and palladium determined by atomic absorption spectroscopy (AAS). Changes in surface topography were observed by scanning electron microscopy (SEM), whereas changes in surface chemical composition were studied by electron probe microanalysis (EPMA). The surface distributions of platinum, rhodium, palladium and oxygen were recorded, X-ray radiation was excited with a primary electron beam of energy 20 keV. Special attention was needed for the recognition of the palladium

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TABLE I Conditions of the EPMA determination of palladium and rhodium distributions using pentaerythritol (PET) as the diffraction crystal

Emission line	Detector position	Relative intensity
Rh$L\alpha$	147.25	100
Pd$L\alpha$	139.89	100
Rh$L\beta_1$	140.09	61
Pd$L\beta_1$	132.79	59
Rh$L\beta_2$	132.30	13
Pd$L\beta_2$	125.19	13

distribution on a sample with rhodium content, because of strong coincidence of $L\alpha$ and $L\beta_1$ emission lines from palladium with $L\beta_1$ and $L\beta_2$ lines from rhodium. The positions of these emission lines and their relative intensities are given in Table I. Thus, it was possible to determine rhodium distribution from the $L\alpha$ line and palladium distribution from the $L\beta_2$ line. However, due to the low intensity of the $L\beta_2$Pd emission line it was difficult to extract this signal from the background. Because of this difficulty, the intensities of platinum, rhodium ($L\alpha$ line) and oxygen emission lines were recorded independently, whereas the palladium distribution (from the $L\alpha$ and $L\beta_1$ lines) was recorded simultaneously with rhodium.

3. Results

3.1. Characteristics of the volatile reaction products

The results of the AAS analysis indicated the presence of platinum, rhodium and a small amount of palladium in the sample obtained after dissolution of the condensed reaction products in hot concentrated hydrochloric acid.

Previously performed, quantitative X-ray photoelectron spectroscopy investigation had revealed the presence of PtO_2 and RhO_2 in the volatile, condensed products of reaction between Pt–Rh alloys and oxygen [12]. In the case of Pt–Pd–Rh alloys the presence of PdO in the reaction products can be expected as well.

In Table II the values of the rates of the volatile oxide formation are collected. In the last column of this table the weight ratios m_{Pt}/m_{Rh} and m_{Pt}/m_{Pd} of the volatile oxides are presented. They can be compared with these ratios for initial metallic samples.

One can notice that the rate of the volatile oxide formation decreases with increasing palladium content in the oxidized alloys. Moreover, the relative palladium concentration in the oxides is dramatically lower than in the metallic samples.

3.2. Surface changes

In Fig. 1 SEM micrographs of the Pt–Pd–Rh gauzes after 70 h oxidation at 1163 K are shown. There are visible numerous pits, faceted regions, distinct grain boundaries and precipitates, along them. This character of the topographical changes is typical of all examined surfaces.

The results of the EPM analysis of the Pt 92.5%–Pd 4%–Rh 3.5% alloy surface after its oxidation at 1163 K are shown in Fig. 2: (a) the surface composition displayed with backscattered electrons and (b–d) the distributions of platinum, rhodium and oxygen. In the surface region these elements are distributed non-uniformly. The grain facets are enriched with platinum, whereas the grain boundaries are enriched with rhodium. The presence of oxygen is recorded mainly in areas where rhodium is accumulated. This result could indicate the appearance of rhodium sesquioxide in the surface region.

In Fig. 3 a backscattered electron image of the surface composition of the Pt 81% –Pd 15% – Rh 3.5%–Ru 0.5% alloy gauze is presented. Numbers (1 and 2) on this micrograph indicate the points at which the analysis for palladium and rhodium was performed. This result is shown in Fig. 4. The elemental concentrations were detected on the grain facet (Line 1) and at the grain boundary (Line 2). The relative intensities of recorded emission lines of palladium and rhodium are collected in Table III. The results presented suggest a slight increase in palladium concentration on the grain facets.

The SEM investigation of topographical changes caused by oxidation of the gauzes at 1373 K revealed effects of recrystallization of the wires and the presence of small precipitates on the grain facets (Fig. 5). However, using the EPMA technique no changes of elemental distribution on the sample surface could be detected.

4. Discussion

The investigation previously performed upon interaction of molecular oxygen with Pt–Rh alloys (containing 5 or 10% Rh) indicated a decrease in the rate of volatile oxide formation with increase in rhodium concentration in oxidized alloy gauzes [12]. The rates determined were 15.00 and 12.80 $\mu g\,cm^{-2}\,h^{-1}$ at 1373 K, or 0.92 and 0.80 $\mu g\,cm^{-2}\,h^{-1}$ at 1163 K for alloys with 5 and 10% Rh, respectively. These values are higher than those presented in Table II. Taking into account the low concentration of rhodium in the Pt–Pd–Rh alloys studied one can conclude a

TABLE II Rates of volatile oxide formations during reaction of Pt–Pd–Rh alloys with molecular oxygen, and weight ratios in the volatile oxides*

Alloy (wt %)	T (K)	Rate ($\mu g\,cm^{-2}\,h^{-1}$)				m_{Pt}/m_{Rh}	m_{Pt}/m_{Pd}
		r_{PtO_2}	r_{RhO_2}	r_{PdO}	total		
Pt 92.5%–Pd4%–Rh 3.5%	1163	0.70	0.02	0.01	0.73	35.0	70.0
	1373	9.16	0.23	0.05	9.44	39.8	183.2
Pt 81%–Pd 15%–Rh 3.5%–Ru 0.5%	1163	0.67	0.02	0.01	0.70	33.5	67.0
	1373	7.78	0.32	0.06	8.16	23.6	130.0

*The weight ratios for the initial Pt–Pd–Rh alloys are as follows: m_{Pt}/m_{Rh} = 26.4 and 23.1, m_{Pt}/m_{Pd} = 23.1 and 5.4 for Pt 92.5%–Pd 4%–Rh.3.5% and Pt 81%–Pd 15%–Rh 3.5%–Ru 0.5% alloys, respectively.

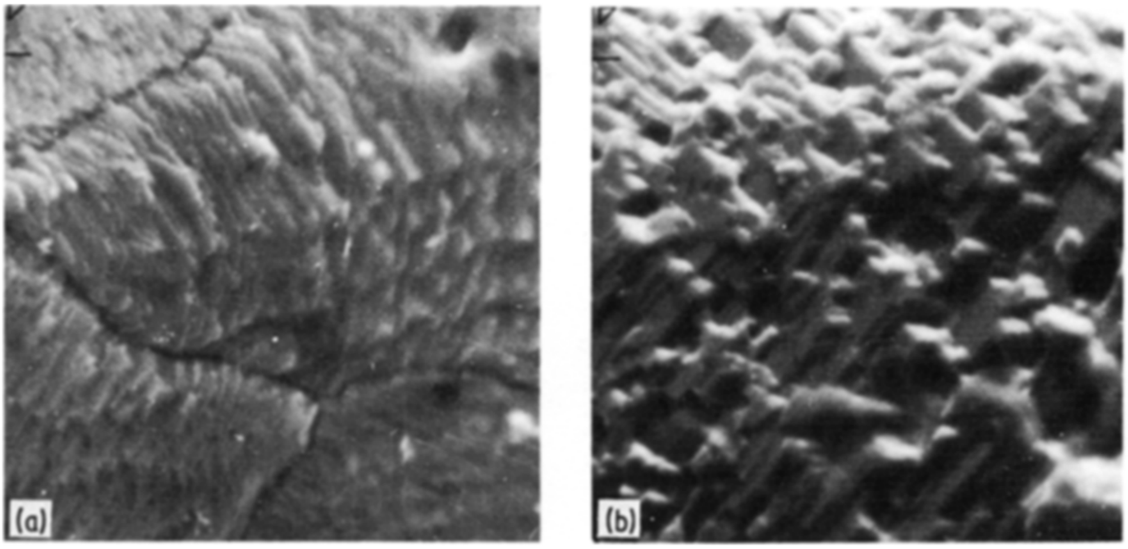

Figure 1 Topography of (a) Pt 92.5%–Pd 4%–Rh 3.5% and (b) Pt 81%–Pd 15%–Rh 3.5%–Ru 0.5% wire surfaces after 70 h oxidation at 1163 K. × 2400.

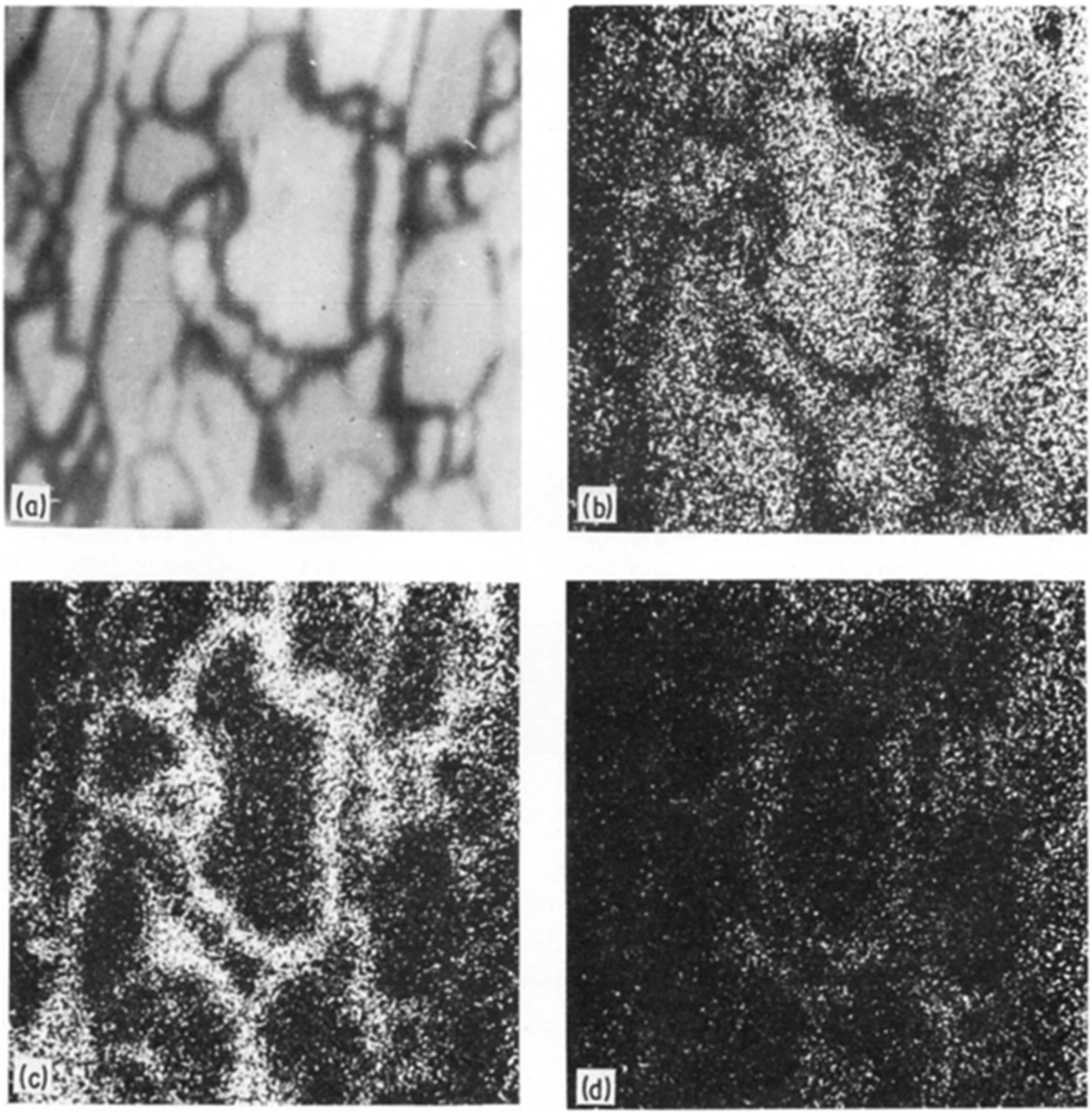

Figure 2 Results of EPM analysis of the Pt 92.5%–Pd 4%–Rh 3.5% wire surface after 70 h oxidation at 1163 K: (a) surface composition, (backscattered electron image); surface distributions of (b) platinum, (c) rhodium and (d) oxygen. × 1440.

TABLE III Intensities of palladium and rhodium emission lines recorded during EPM analysis of the Pt 81%–Pd 15%–Rh 3.5%–Ru 0.5% wire surface

Emission lines	Intensity	
	Grain facet	Grain boundary
Rh$L\alpha$	170	800
Pd$L\alpha$ + Rh$L\beta_1$	480	570
Pd$L\beta_1$ + Rh$L\beta_2$	300	190

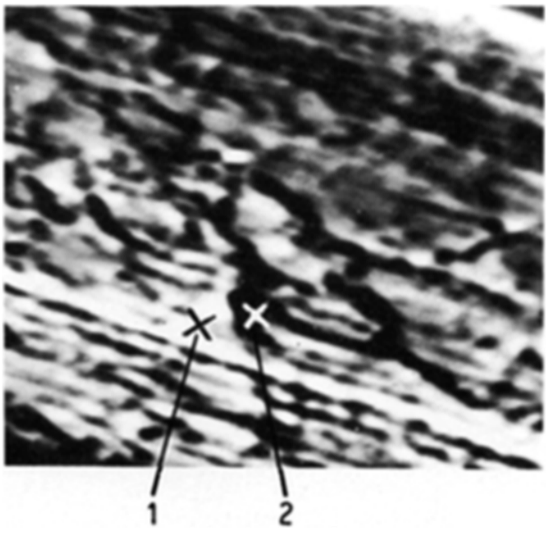

Figure 3 Surface composition of the Pt 81%–Pd 15%–Rh 3.5%–Ru 0.5% wire after 70 h oxidation at 1163 K (backscattered electron image). × 1000. Point 1, grains facet; Point 2, grain boundary.

palladium influence upon the decrease in the rate of volatile oxide formation. In order to find an explanation for this phenomenon the chemical composition of the surface region of the exposed alloys has to be considered.

Previously, we had noticed the presence of metallic platinum on the grain facets and Rh_2O_3 at the grain boundaries and adjacent areas on Pt–Rh gauzes oxidized at 1163 K. A very similar situation has been observed during the present study. This time it is necessary to consider the chemical state of palladium on the sample surface. The results of studies [13–16] of the oxidation of metallic palladium sponges and powders proved that under an oxygen pressure of 0.094 MPa the equilibrium temperature of PdO dissociation did not exceed 1100 K. Furthermore, Schmidt and Chen [17] did not notice the formation of PdO during oxidation of Pt–Pd alloys with low (up to 10 wt %) concentration of palladium. These data indicate clearly that palladium oxide should not appear on the alloy surfaces under the present experimental conditions.

The above discussion leads to the conclusion that gauze surfaces oxidized at 1163 K may contain metallic alloy components and rhodium sesquioxide, whereas surfaces oxidized at 1373 K are oxide-free.

However, palladium differs from the other alloy components because of one important reason. The sublimation enthalpy of palladium (340 kJ mol^{-1} [18]) is distinctly lower than those of platinum and rhodium (about 565 kJ mol^{-1} [18] in both cases). Thus, palladium can segregate to Pt–Pd–Rh alloy surfaces and produce relatively high concentrations of this element. Unfortunately, the quantitative confirmation of this suggestion by EPMA or another analytical technique is impossible because of the circular geometry of the samples and the roughness of investigated surfaces.

During the present study, it was noticed that palladium formed a volatile oxide but the rate of this reaction was many times lower than in the case of PtO_2 and RhO_2. The formation of volatile PdO was previously detected [19] only at temperatures higher than 1573 K. It seems that at temperatures of 1163 and 1373 K palladium oxide is formed not by surface reaction (as for platinum and rhodium dioxides), but is due to the evaporation of palladium to the gas phase and subsequent oxidation in this phase. Thus, the sublimation enthalpy can once more be an important factor which influences the difference between palladium and other alloy components.

These considerations allow one to suggest the formation of a surface layer of palladium almost passive toward oxygen. This layer can probably inhibit the

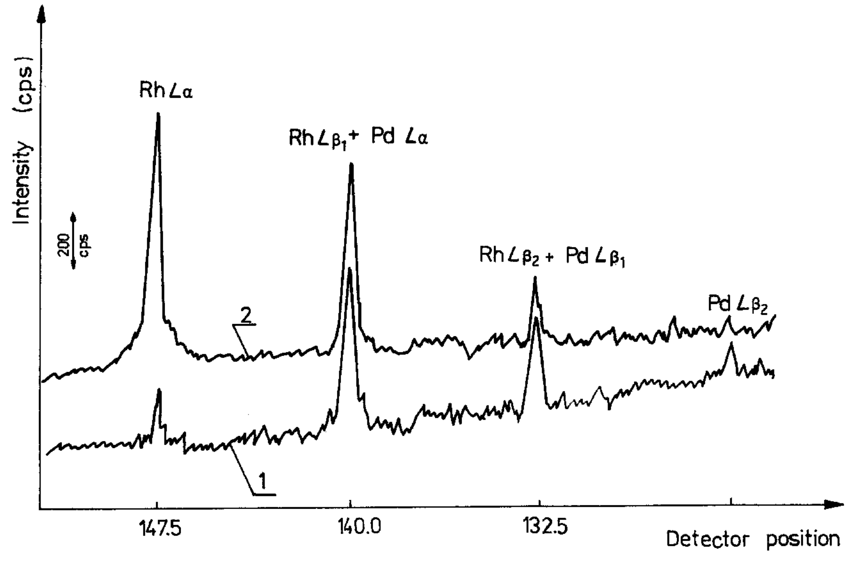

Figure 4 The EPMA determination of palladium and rhodium concentrations on the Pt 81%–Pd 15%–Rh 3.5%–Ru 0.5% wire surface after 70 h oxidation at 1163 K. Line 1, grain facet; Line 2, grain boundary.

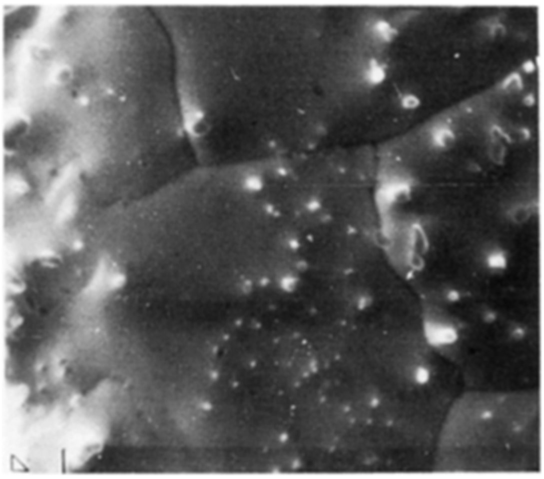

Figure 5 Topography of the Pt 92.5%–Pd 4%–Rh 3.5% wire surface after 70 h oxidation at 1373 K. × 2400.

rate of volatile platinum and rhodium dioxide formation, and may be a reason for the lowering of mass losses of Pt–Pd–Rh catalysts for ammonia oxidation.

In the case of Pt–Rh alloys exposed to oxygen it was possible to compare the surface changes with those detected on industrial catalytic gauzes; the changes were very similar to each other. Unfortunately, such a comparison is impossible in the case of the Pt–Pd–Rh alloys studied because of the fact mentioned in Section 1. However, during the industrial process of ammonia oxidation the catalyst composition, gauze temperature and oxygen pressure in the reaction mixture are the same as in the present study, and one can thus expect that the changes observed would be characteristic also of industrial gauzes during the early stages of their use.

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