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Microstructure stability of the PtRh alloys used for catalytic ammonia oxidation

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Materials

ABSTRACT

Purpose: The aim of this work was to investigate the possibility of increasing performance of the PtRh alloys used in industrial processes of catalytic ammonia oxidation.
Design/methodology/approach: In order to reach this objective, the extensive studies have been carried out, which were aimed at better understanding of the phenomena taking place on a surface and inside the wires of catalytic gauzes during the process. The electron microscopy methods (SEM, TEM, HRTEM), optical microscopy and microanalysis were used to examine the alloys under investigation.
Findings: It was found that the performance and lifetime of the catalytic gauzes is closely related with structural stability of the alloys and with the stability of parameters of the ammonia oxidation process.
Practical implications: The PtRh10-based alloys modified with boron and yttrium have been developed, which are characterised by more stable structure than the classical PtRh10 alloy and enable significant reduction of the grain growth effect during the use of the gauzes. This should contribute to the improvement of the process efficiency and selectivity, and increase the lifetime of the catalytic gauzes.
Originality/value: The developed alloys are new and original.
Keywords: Metallic alloys; Multifunctional materials; Mechanical properties; Microstructure

1. Introduction

Over several dozen million tons of nitric oxide (NO) is produced annually in Europe and processed into nitric acid. This considerable scale of production evidences its massive use not only in the chemical industry and agriculture (fertilizers) but also in fabrication of plastics for application in automotive industry, household goods, power engineering, electrical engineering and electronics. The most frequently used method for obtaining this compound is based on the ammonia oxidation on the platinum-rhodium catalysts.

The catalytic platinum-rhodium gauzes exhibit high activity and selectivity, high strength and stability under operating conditions, and considerable lifetime. Besides, they can be easily replaced over a short period of time, and the technology for their fabrication and regeneration is known and mastered. Some drawback of these gauzes are platinum and rhodium losses amounting from 0.04 to 0.35 g per 1 t of HNO_3., in dependence on the type (pressure) of the installation, which considering high

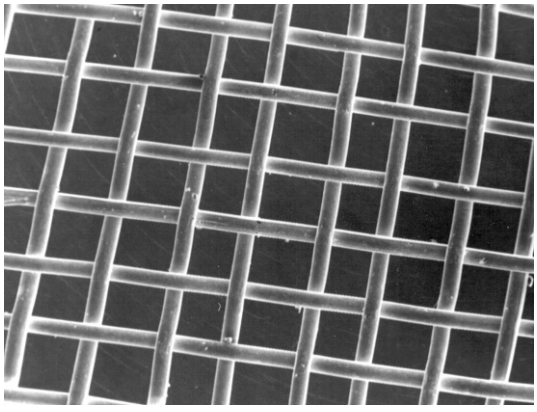
price of both metals is of great economic importance. Therefore, in order to increase efficiency of nitric acid production, the typical catalytic packs are used together with the catalyst-catchment packs of gauzes made from palladium alloys, most frequently with gold [1-7].

The costs of nitric oxide fabrication are influenced mainly by the ammonia consumption, which is strongly dependent on the efficiency, selectivity and stability of the oxidation process, and consequently, on the quality of the materials used in catalytic packs. It is also of great importance to recover precious metals from the catalyst-catchment gauzes and to minimise the costs of refining spent gauzes. Therefore, the value of precious metals contained in the gauzes takes the second position in the overall costs of nitric oxide fabrication.

2. Operating environment of the catalysts used in the processes of ammonia oxidation

As stated above, production of nitric acid is based on catalytic ammonia oxidation to nitric oxide (NO). The process parameters are different in various industrial installations. In general, the process is based on passing a mixture of ammonia with air through the platinum-rhodium catalyst.

a)



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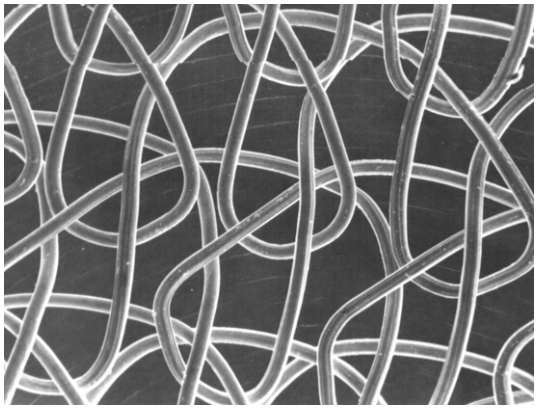


Fig. 1. a) The exemplary images of a woven gauze, SEM, 40x; b) The exemplary images of a knitted gauze, SEM, 40x

This mixture, containing 10-12 vol. % of NH_3 at the pressure of 0.1-1.0 MPa, is heated to the temperature of 80-220^{0}C, and while it comes into contact with a catalyst for the period of about 10^{-4} second about 92 to 98 % of ammonia undergoes oxidation into NO, and the rest – into N_2 and N_2O.

The heat of the reactions taking place makes that the temperature of gases flowing through the catalyst increases to 790-940^{0}C. In spite of the existence of many catalysts of this process, these are usually platinum catalysts. They consists mostly of the packs of 3-20 dense gauzes (1024 meshes/cm^2) made of a wire, 0.060 or 0.076 mm in diameter, from platinum- rhodium alloys such as PtRh10, PtRh8, PtRh5, PtRh5Pd5, PtPd4Rh3.5 and PtPd15Rh3.5Ru0.5. The gauzes are manufactured by the weaving or knitting methods. A typical catalytic pack consists of three platinum-rhodium gauzes and three catalytic-catchment gauzes made of the PdAu20 alloy. Figure 1 shows exemplary images of a surface of knitted and woven gauzes before their use. The woven gauze was made of wires, 0.076 mm in diameter, and the gauze density was 1024 meshes per cm^2. The knitted gauze was made of wires 0.060 mm in diameter and their unit mass (in g/m^2) was similar to that of a woven gauze.

3. Examination of the catalyst gauzes removed from use

A study was undertaken, which was aimed at explaining the reasons for decreased efficiency of catalytic ammonia oxidation process and for the occurrence of an excessive brittleness of the gauzes, which might influence the safety of the process. Samples of the gauzes were taken from different installations, where the process had to be finished or interrupted due to its insufficient efficiency. The gauzes subjected to this examination were used in the industrial installations for a period from 3000 to 8000 hours. The changes, which took place on their surface and over the whole volume are illustrated in Figs 2-7. Distribution of rhodium on a diameter of the PtRh8 wire, from which the gauze was knitted, is shown in Fig. 8.

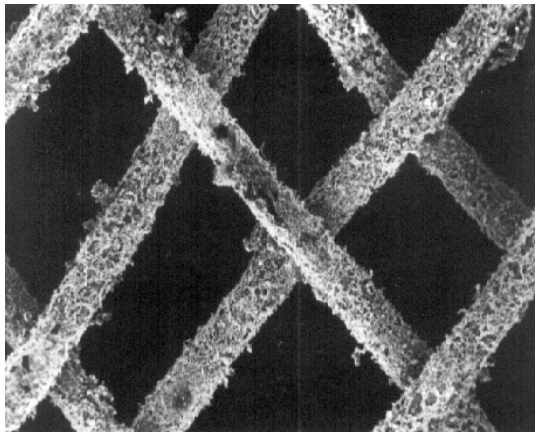


Fig. 2a. Surface of the PtRh10 catalyst gauze after 4000 hours of operation, SEM, 100x

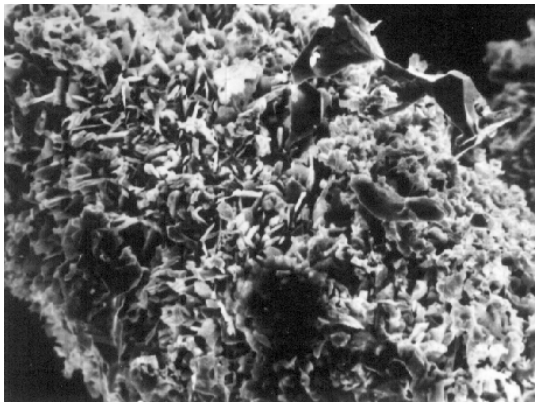
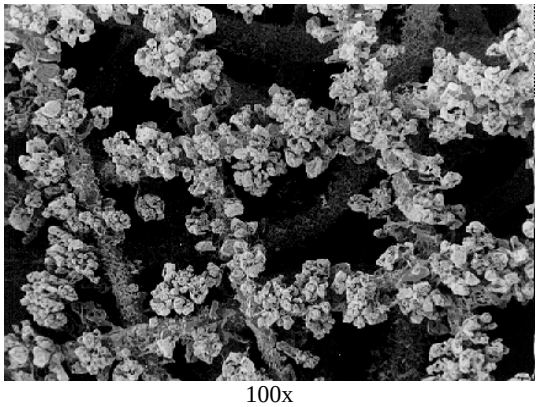
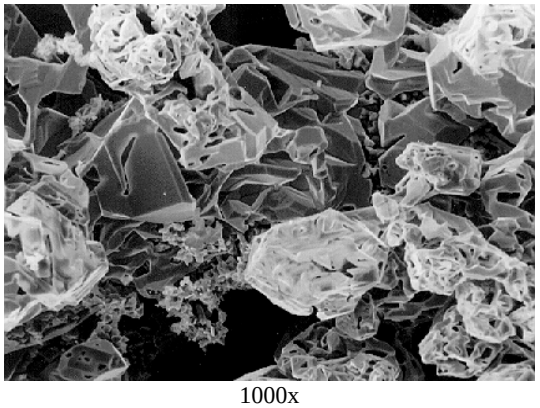


Fig. 2b. Surface of the PtRh10 catalyst gauze after 4000 hours of operation, SEM, 1000X

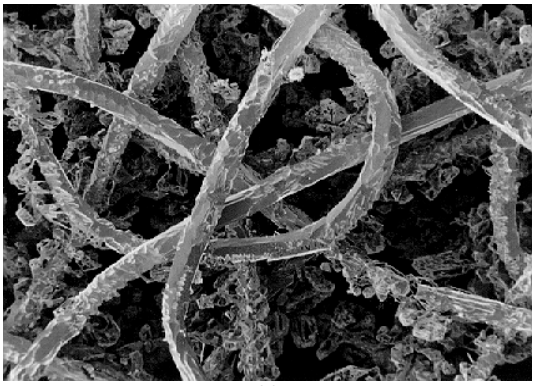


100x

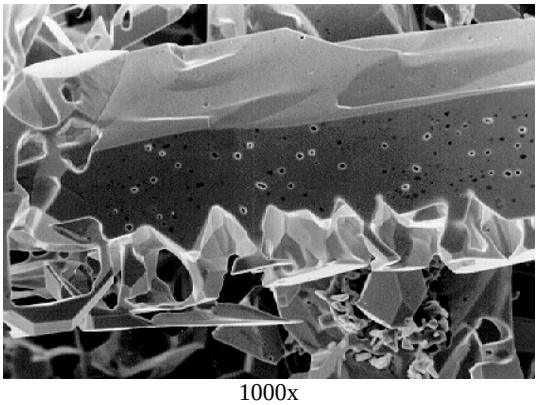


1000x

Fig. 3. SEM images of the first, woven PtRh10 gauze removed from operation (3500 hours)



100x



1000x

Fig. 4. SEM image of the lower surface of the third, PtRh8 knitted gauze (3500 hours)

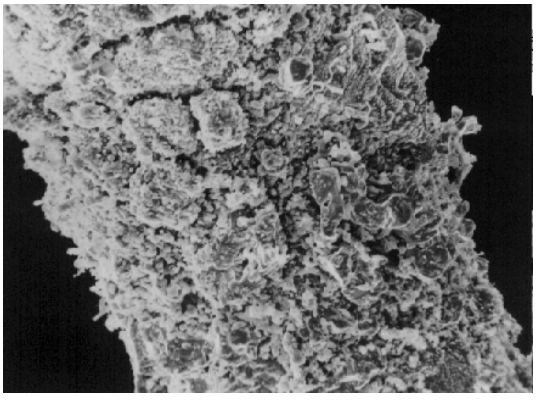


Fig. 5a. Exemplary image of an extremely brittle gauze (3000 hours), SEM-1000x [8,9]

The catalytic ammonia oxidation process results in the changes in surface topography of the catalytic gauzes and catalytic-catchment gauzes, which depend on the position of specific gauze within a pack. In general, an effective diameter of the catalytic gauze wire undergoes gradual reduction, whereas that of the catalytic-catchment gauzes in increasing. It was found that the process efficiency is significantly affected by the refinement of the initial microstructure and its stability during the process. The initial grain size and its stability depends of the content of rhodium in a gauze material. After extremely long period of time (several thousand hours) the grain diameter can be comparable with the diameter of a gauze wire (in Fig. 5b, the initial diameter of a gauze wire was 0.076 mm).

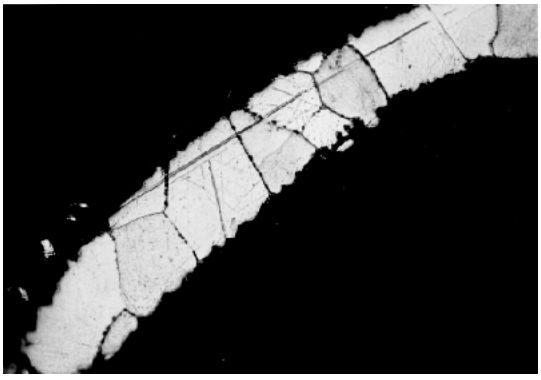
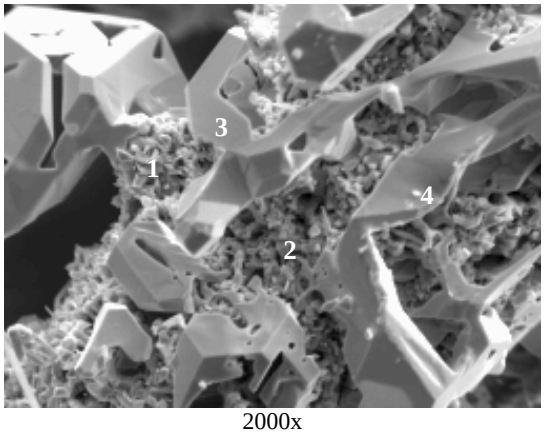


Fig. 5b. Exemplary image of an extremely brittle gauze (3000 hours) longitudinal microsection, optical microscope -300x [8,9]



2000x

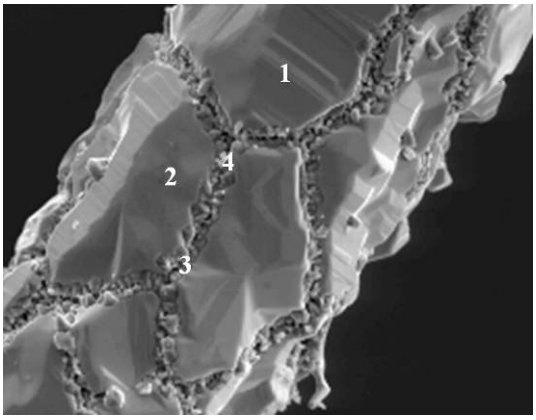
Point No	Pt [%]	Rh [%]	O [%]
1	15,09	66,89	18,06
2	7,86	73,67	18,47
3	87,24	12,76	-
4	84,98	15,02	-

Fig. 6. Chemical composition in micro-areas, woven gauze, top (5974 hours)

4. Examination of the properties and microstructure of the modified PtRh alloys

In order to eliminate grain size instability in a classical PtRh10 alloy used for catalytic gauzes the efforts were made to find suitable alloy modifiers. Taking into account that the gauzes operate in a chemically aggressive environment, the process temperature is high, diameter of a reactor is large and that flow rate of the gases is high, the following three criteria for selecting the alloys suitable for catalytic gauzes have been identified:

- economic criterion, reflecting the need to minimise the costs of nitric acid fabrication,
- process safety, the measure of which is the degree in which ammonia actually reacted with oxygen, or the concentration of non-reacted ammonia in the gases behind the catalyst,
- functional properties, to be met by the catalyst so as to obtain required quality of the produced nitric acid.



2000x

Point No	Pt [%]	Rh [%]	O [%]
1	89,67	10,33	-
2	83,27	16,73	-
3	7,50	74,01	18,49
4	4,55	76,79	18,66

Fig. 7. Chemical composition in micro-areas , knitted gauze, bottom (5974 hours)

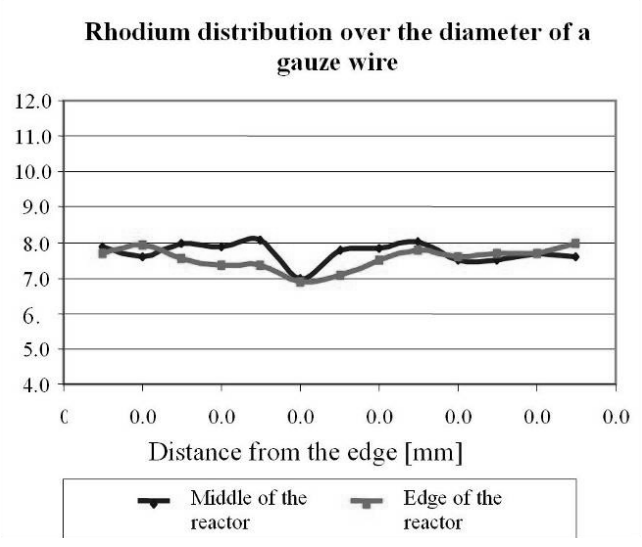


Fig. 8. Distribution of rhodium over the diameter of a gauze wire

In order to meet these criteria, particular emphasis during further work was put on the possibility of eliminating an excessive grain growth in the wires of gauzes made from

platinum-rhodium alloys through microstructure modification with micro-additions of boron (up to 10 ppm) and yttrium (up to about 0.2 %). The simulation studies of the process of boron diffusion to the grain boundaries [10,11] (Fig. 9), occurring at the temperatures similar to that in which catalytic ammonia oxidation takes place, gave rise to the expectation that the use of micro-addition of this element might be advantageous. It was also believed that an addition of yttrium should suppress the grain growth due to the formation of intermetallic compound of platinum with yttrium. Besides, both elements do not reduce catalytic properties of the PtRh alloys.

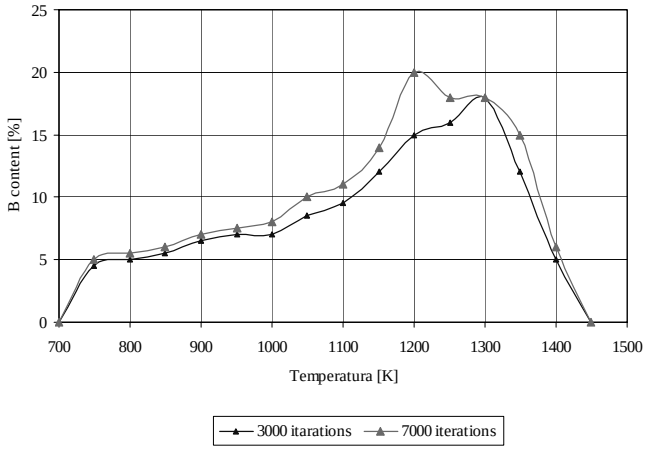


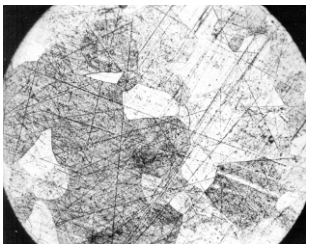
Fig. 9. Simulation results of boron diffusion to grain boundary in platinum

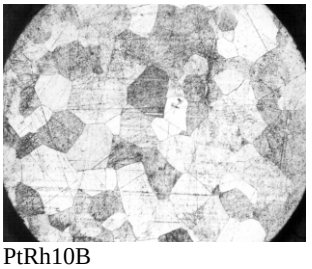
For that reason, further tests were made using the PtRh10B and PtRh10Y alloys, and the commonly-known PtRh10 alloy as a reference. The alloys were prepared by melting and casting in vacuum furnaces. It is worth noting that the content of impurities in these alloys was below 500 ppm. The technological details related to fabrication of wires 0.076 mm in diameter from these alloys have been presented elsewhere [12].

Their mechanical properties were preliminarily examined for wires drawn from the diameter of 3.20 mm to 0.80 mm, and the following results were obtained:

Alloy	Rm [MPa]	$R_{0.2}$ [MPa]	A_{10} [%]
PtRh10	665,1	588,6	5,7
PtRh10B	734,0	683,7	3,1
PtRh10Y	671,0	608,0	3,1
After annealing at the temperature of 950^{0}C for 10 hours:			
PtRh10	314,1	123,4	40,0
PtRh10B	408,7	181,1	38,6
PtRh10Y	-	-	-
After annealing at the temperature of 1250^{0}C for 10 hours:			
PtRh10	273,7	113,0	22,6
PtRh10B	-	-	-
PtRh10Y	276,5	106,8	26,6

The exemplary microstructure images of these alloys [13-15] are shown in Fig. 10.


PtRh10


PtRh10B

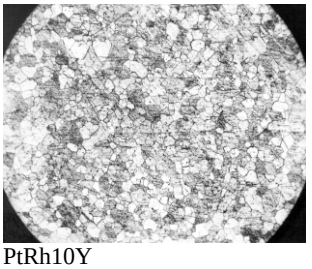

PtRh10Y

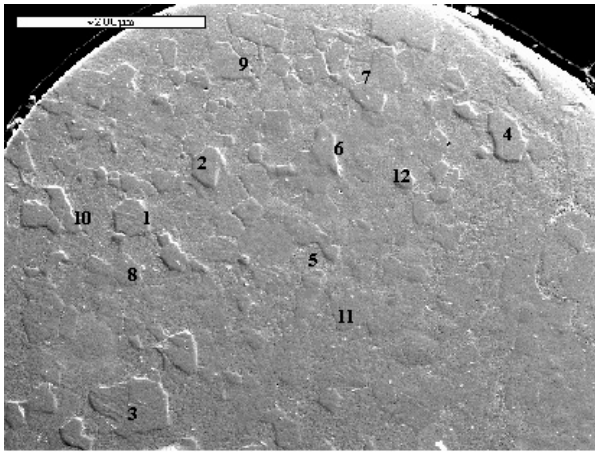
Fig. 10. Microstructure images of the platinum alloys after their annealing at the temperature of 950^{0}C for 100 hours. Optical microscope. Chemically etched micro-sections. Magn. 120x

The results of micro-hardness measurements, made by the Vickers method HV (200 g) on a wire cross-section transversely to the drawing direction, after annealing conducted at the temperature of 950^{0}C for 100 hours, were the following: PtRh10 (94,3; 92,0; 92,6), PtRh10B (97,1; 92,0; 90,6), PtRh10Y (105; 102; 107). The contents of boron and yttrium in micro-areas, determined after annealing conducted at the temperature of 950^{0}C for 10 hours, are given in Fig. 11.

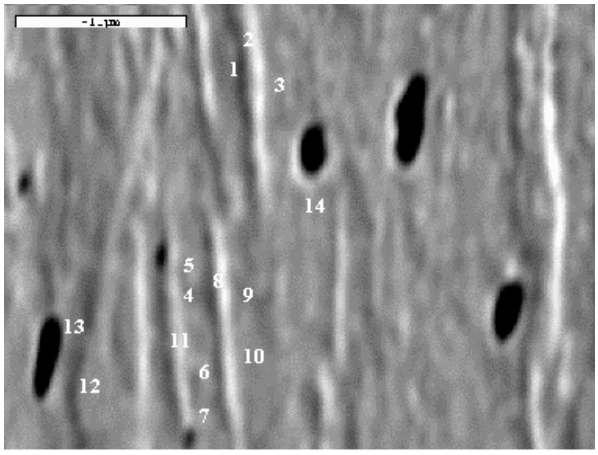
An effect of micro-additions of boron and yttrium on the grain size modification was investigated by the transmission electron microscopy using the samples in a form of thin foils. The exemplary microstructure images of the alloys under investigation are shown in Fig. 12. An average size of grains and sub-grains for the PtRh10B and PtRh10Y alloys, and for the reference PtRh10 alloy, after their annealing at the temperature of 950^{0}C for 1 hour, was the following:

PtRh10 0.0464 mm,
PtRh10B 0.0052 mm,
PtRh10Y 0.0061 mm.

These data clearly demonstrate an effect of alloy modification on the grain size.



PtRh10B

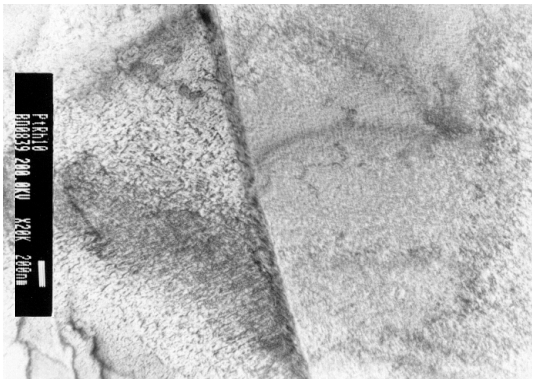


PtRh10Y

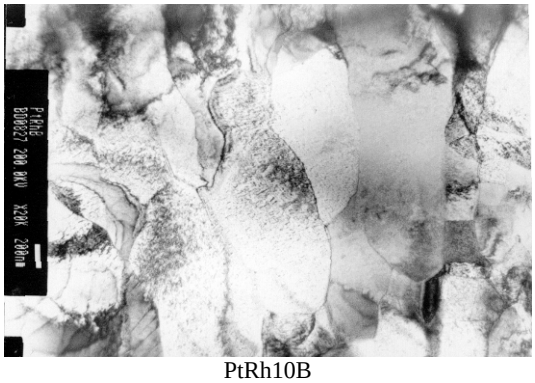
Element	Analysis point			
	1	**2**	**3**	**4**
Boron [%]	0,030	0,000	0,000	0,000
Yttrium [%]	0,174	0,155	0,238	0,061
Analysis point	**5**	**6**	**7**	**8**
Boron [%]	0,040	0,060	0,070	0,040
Yttrium [%]	0,005	0,198	0,228	0,203
Analysis point	**9**	**10**	**11**	
Boron [%]	0,050	0,080	0,000	
Yttrium [%]	0,208	0,262	0,257	

Fig. 11. Microstructure and distribution of boron in the PtRh10B alloy and of yttrium in the PtRh10Y alloy after annealing conducted at the temperature of 950^{0}C for 10 hours

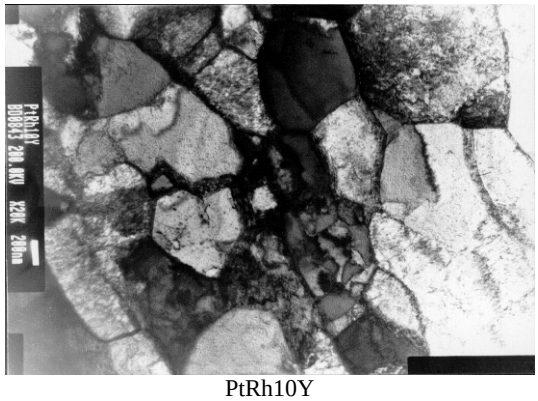
It is seen in this figure that the modifying effect of boron as a micro-addition is demonstrated mainly by the formation of a sub-structure (sub-grains), which is not observed in a classical PtRh10 alloy (not modified with boron). The mechanism of microstructure refinement by micro-addition of boron to the PtRh10 alloy has not been fully elucidated so far, since it is impossible to determine exactly its distribution within the alloy volume. Based on the results of structural examination (Figs 13a and 13b) it can be presumed that this effect can be attributed to the synergy of boron interaction with other elements referred to as impurities (their overall content is at the level of 500 ppm). Such explanation is justified by the fact that the fine precipitates restraining the growth of grains and sub-grains are observed in the matrix and on the grain boundaries. In spite of similar content of impurities, no precipitates were found in an alloy not modified with boron, even when the HRTEM technique was used.



PtRh10



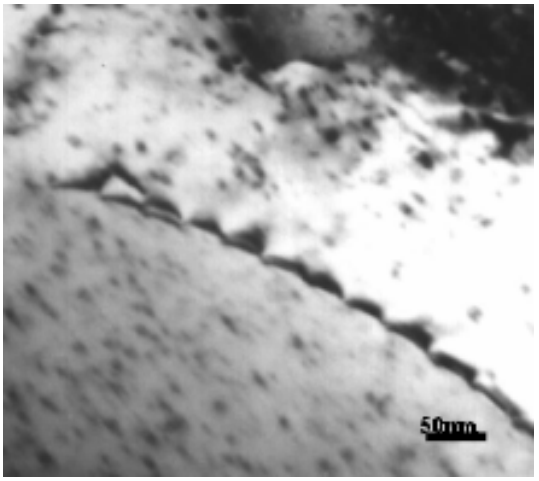
PtRh10B



PtRh10Y

Fig. 12. Microstructure of the PtRh10, PtRh10B and PtRh10Y alloys after the annealing conducted at the temperature of 950^0 C for 1 hour ; TEM

a)



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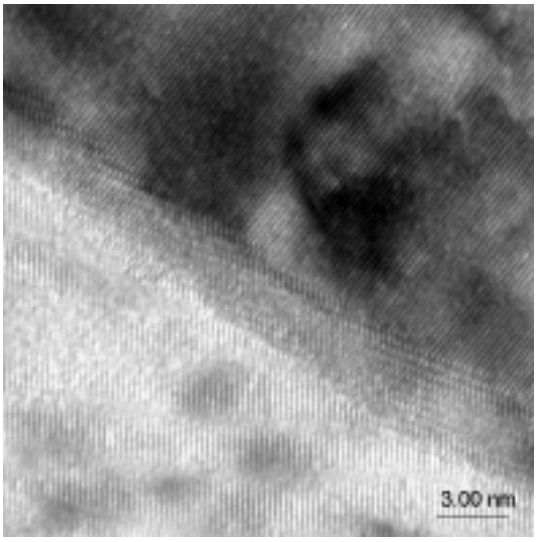


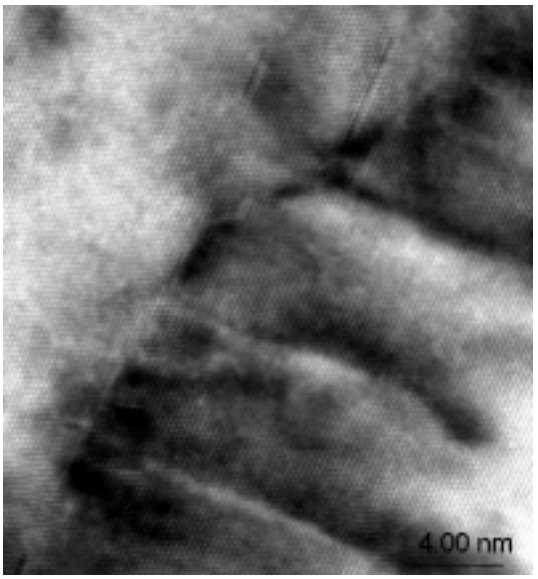
Fig. 13. Comparison of microstructure images observed near grain boundaries in the PtRh10 alloy (a) modified with micro-addition of boron (TEM); (b) without alloy modification (HRTEM)

Application of the PtRh10 alloys modified with micro-addition of boron in the catalyst gauzes enables significant increase of their life. This also enables raising the temperature of the ammonia oxidation process thus improving performance and selectivity of oxidation and reducing emission of harmful N_2O to the atmosphere.

It should be emphasised that introduction of greater amount of yttrium to the PtRh10.

It can be concluded from the observation of these microstructure images that the direct reason for grain growth inhibition and stabilisation of properties is that the size of precipitates of the PtY intermetallic phase is very small. They are plate-like on the grain boundary, several inter-atomic distances in thickness and from several to a dozen of such distances in length, and in the alloy matrix they are disc-like, of a similar thickness and 3-5 nm in diameter. It was found that these precipitates are not of an oxide character. The choice of an optimal content of yttrium in the PtRh based alloys should be related to the operating and environmental conditions, in which they are to be applied. The introduction of yttrium to these alloys is not technologically complicated and does not result in the increase of manufacturing costs.

a)



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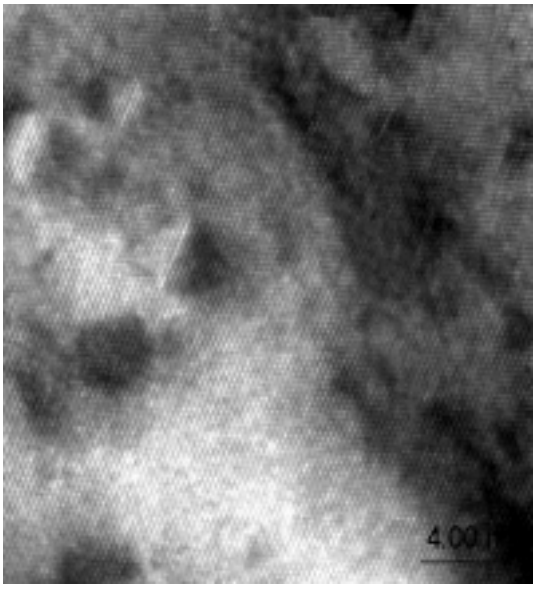

Fig. 14. Exemplary images of the precipitates in the PtRh10 alloy with 0.1 % addition of yttrium a – near the grain boundary; b – within the alloy matrix. HRTEM

5. Catalytic activity of the PtRh10, PtRh10B and PtRh10Y alloys

The catalysts operate in industrial installations for several thousand hours and it is impossible to take their samples in order

Table 1.
Results of catalytic activity examination carried out for wires from the PtRh10, PtRh10B and PtRh10Y alloys, 0.076 mm in diameter

No.	Description	Alloys under examination		
		PtRh10	PtRh10B	PtRh10Y
1	Power required to initialise the reaction [W]	3,17	3,01	3,15
2	Power necessary to initialise the reaction after 4 hours of catalysis [W]	2,04	1,98	1,94
3	Heat of the ammonia oxidation reaction [W]	8,6 – 9,0	9,1 – 9,3	8,3 – 8,6
4	Electric resistance of a new wire, measured at 22^0 C [Ohm]	3,59	3,36	3,57
5	Electric resistance measured after 4 hours of catalysis at 22^0 C [Ohm]	3,49	3,25	3,46

to study the changes taking place in the wires of gauzes in the early stages of their operation. The duration of tests performed in experimental installations is also too long so as to notice any changes. Therefore, in order to investigate the phenomena taking place and to assess catalytic activity of the materials under test, samples of wires from the PtRh10, PtRh10B and PtRh10Y alloys (0.076 mm in diameter) were subjected to the exposure in electric thermograph, using an industrial ammonia/air mixture [16]. The results obtained at the exposition time of 4 hours are shown in Table 1.

These results clearly demonstrate that the new alloys (PtRh10B and PtRh10Y) have the catalytic properties comparable with those of a classical PtRh10 alloy. It should be noted that in case of the PtRh10B alloy these properties are slightly better.

6. Conclusions

Based on the results of analysis of operating conditions and examination of microstructure and properties of the platinum-rhodium alloys the following conclusions can be drawn:

- An addition of boron to the PtRh10 alloy in an amount of about 5 ppm limits an excessive grain growth at high temperatures. Besides, it has beneficial effect on microstructure stability and homogeneity and improves mechanical properties thus contributing to greater lifetime of the catalyst gauzes.
- It is possible to increase the operating temperature of the gauzes, which should increase the yield and selectivity of the ammonia oxidation process and reduce N_2O emission to the atmosphere.
- An addition of yttrium to the PtRh10 alloy, in the amount of about 0.2 %, efficiently eliminates an excessive grain growth at high temperatures. Besides, it has beneficial effect on microstructure stability and homogeneity and improves mechanical properties thus contributing to greater lifetime of the catalyst gauzes.
- The manufacturing costs of the modified alloys are comparable with those of a classical PtRh10- alloy.

This investigation enabled also the formulation of other conclusions, which are very interesting from scientific point of view. It is, however, still necessary to fully elucidate the phenomena taking place on a catalyst surface. It would be interesting to know whether equally drastic changes in the chemical composition as those observed here in the investigated platinum-rhodium gauzes used in the processes of catalytic ammonia oxidation are also encountered on the surface and inside other catalytic materials. Full elucidation of this question might be helpful in developing of a comprehensive description of the process of catalysis so as to enable more precise choice of the chemical composition of a catalyst for specific application and the development of technology for its production.

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