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APPLICATION OF THE EBSD TECHNIQUE FOR INVESTIGATIONS INTO MICROSTRUCTURE OF Pt-Rh ALLOY THIN WIRES USED FOR GAUZES IN CATALYTIC AMMONIA OXIDATION PROCESS

ZASTOSOWANIE TECHNIKI EBSD DO BADAŃ MIKROSTRUKTURY CIENKICH DRUTÓW ZE STOPU Pt-Rh PRZEZNACZONYCH NA SIATKI DO PROCESU KATALITYCZNEGO UTLENIANIA AMONIAKU

The work covered investigations into microstructure of wires made of Pt-Rh alloys and Pt-Rh alloys modified with microaddition of boron and addition of yttrium as well as determination of correlation between crystallographic orientation and susceptibility to selective catalytic pickling of grain surfaces.

It is very difficult to investigate both texture and grains orientation on surface of wires of diameter about 0.060 mm when using traditional X-ray methods, but it can be possible by Electron Backscatter Diffraction (EBSD) techniquee.

Topography of the surface and analysis of crystallographic orientation of individual grains on the surface of wires made of PtRh8 alloy have shown that during their operation in industrial installation a selective pickling of surface takes place which leads to exposing of crystallographic planes {111}. The results of investigations indicate that because of the rate of catalytic pickling of the wire surface the more advantageous is a structure of large grains with small grain surface energy, and consequently with small disorientation and of parallel, or almost parallel crystallographic planes {111} to the surface of the wire. It was established that formation of such a microstructure becomes facilitated by introduction of microadditives such as boron or yttrium into the alloy.

Keywords: .....

Cele pracy obejmuje badanie mikrostruktury drutów ze stopów Pt-Rh oraz stopów Pt-Rh modyfikowanych mikrododatkiem boru i dodatkiem itru oraz próbę ustalenia współzależności pomiędzy orientacją krystalograficzną a podatnością na selektywne, katalityczne wytrawianie powierzchni ziaren.

Modelowanie struktury drutów ze stopów Pt-Rh przeznaczonych na siatki do procesu katalitycznego utleniania amoniaku prowadzone jest na drodze zmiany ich tekstury poprzez głównie, wprowadzenie mikrododatków lub dodatków składników stopowych do bazowego stopu Pt-Rh. Badanie zarówno tekstury jak i orientacji ziaren na powierzchni drutów o średnicy około 0,060 mm jest znacznie utrudnione tradycyjnymi metodami rentgenowskimi, natomiast jest możliwe przy zastosowaniu techniki dyfrakcji elektronów wtórnie rozproszonych (EBSD – Electron Backscatter Diffraction).

Stosowane w procesie otrzymywania tlenku azotu siatki katalityczne na osnowie stopów Pt-Rh po określonym czasie eksploatacji ulegają fizycznemu zużyciu w wyniku erozyjnego oddziaływania temperatury i środowiska przepływających gazów. Erozja drutów wchodzących w skład siatek zachodzi selektywnie i jest zależna od wielkości i orientacji krystalograficznej ziaren na powierzchni pojedynczych drutów.

Topografia powierzchni i analiza orientacji krystalograficznych pojedynczych ziaren na powierzchni drutów ze stopu PtRh8 wykazała, że w trakcie ich eksploatacji w instalacji przemysłowej zachodzi selektywne wytrawiania powierzchni prowadzące do odsłaniania płaszczyzn krystalograficznych {111}. Wyniki badań wskazują, że ze względu na szybkość katalitycznego wytrawiania powierzchni drutów korzystniejsza jest struktura w której istnieją duże ziarna o małej energii powierzchni ziaren, a zatem o małej dezorientacji i o takim położeniu, kiedy płaszczyzny krystalograficzne {111} są równoległe, lub niemal równoległe do płaszczyzn powierzchni drutu.

Praca ma charakter oryginalny i może być wykorzystana do usprawnienia technologii wytwarzania drutów ze stopów na osnowie Pt-Rh przeznaczonych na siatki do procesu katalitycznego utleniania amoniaku.

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1. Introduction

The catalyst gauzes made from Pt-Rh alloys, which are used in the processes of fertilisers production, undergo physical wear after some period of operation under erosive influence of the flowing gases. The production process consists in passing an ammonia-air mixture through the platinum-rhodium catalyst. The mixture containing 10-12 vol.% NH_3 is heated to the temperature of 80–220°C, which makes that from 92% to 98% of the ammonia is oxidised into NO, and the rest are N_2 and N_2O gases. The heat of the reactions taking place makes that the temperature of the gases flowing through the catalyst increases to 790–940°C. The catalysts are usually used in this process in a form of packs consisting of 3–20 gauzes each, made from platinum-rhodium wires, 0.060 or 0.076 mm in diameter and of a mesh density of 1024 mesh/cm^3. The gauzes are fabricated by knitting or weaving technologies [1]. The wire surface erosion (catalytic etching) proceeds selectively and it depends on a size and crystallographic orientation of the grains present on a surface of particular wires. In this work, selected results from microstructure examination carried out for the Pt-Rh alloy and its modifications by micro-addition of boron and an addition of yttrium are presented. Moreover, relationship between crystallographic orientation and an aptitude to selective catalytic etching of the grain surface was investigated.

2. Material and investigation method

The materials investigated under this work were wires from the PtRh10, PtRh10B and PtRh10Y alloys, 0.80 mm in diameter, subjected previously to drawing. Before the examination, the wires were annealed and etched. The main objective of annealing, conducted at a temperature of 1200°C for 2 hours, was to eliminate internal stresses and to recrystallise the wires. Besides, this operation was also aimed at diversifying some crystallographic parameters of the wires (texture and grain size) in dependence on micro-addition (boron) or an addition (yttrium) introduced to the original PtRh10 alloy. After annealing, the wires were etched with aqua regia in order to eliminate a bloom arising during annealing and to reveal microstructure of a surface layer. For the comparison, samples of the wires from classical PtRh10 alloy were also taken from worn gauzes and subjected to examination.

Because traditional X-ray methods can hardly be applied for the examination of the texture and grains orientation on a surface of wires about 0.60 mm in diameter it was decided to use the Electron Backscatter Diffraction method (EBSD). The equipment used for this examination was mainly X-ray micro-analyser with the OPAL measuring and analytical system [2-4]. The OPAL system enables measurements of grains orientation in selected points using computer-based analysis of Kikuchi diffraction patterns. Up to 50 000 analysis points can be selected for the analysis. The obtained set of orientations is subjected to numerical treatment, which aims at:

- preparation of grains orientation distribution maps upon the selected plane of a sample,
- presentation of grains misorientation distribution within determined angular ranges,
- visualisation of grain boundaries with the determined misorientation degree,
- preparation of the histograms illustrating grains misorientation distribution and grain size distribution,
- graphical and tabulated presentation of the values of lattice coincidence coefficient (Σ),
- preparation of the pole figures, inverse pole figures and orientation distribution functions,
  and
- identification of stresses in micro-areas.

3. Results from the texture and grain boundaries examination for the samples of wires 0.8 mm in diameter

The microtexture of investigated wires was analysed based on experimental pole figures <100> obtained from orientation measurements made for 3072 points from the selected area 0.12×0.12 mm in size. Due to small diameter of the wires, an increase in the analysed area had negative effect on the results. The pole figures, which were typical for particular materials, are shown in Fig. 1.

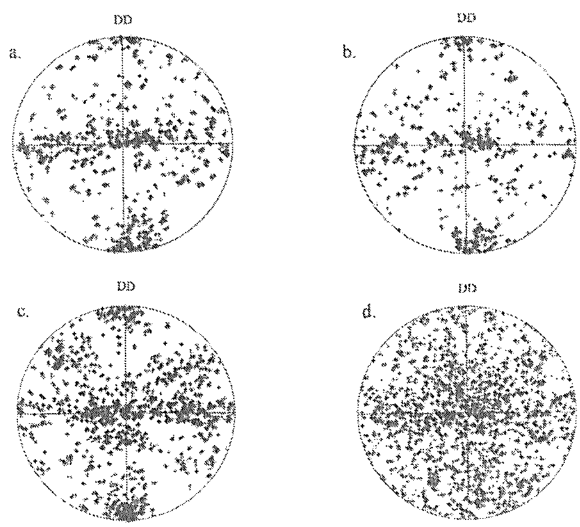

Fig. 1. {100} pole figures for the alloys examined. a. – PtRh10 (of an axial texture character), b. – PtRh10 (of a fibre texture character), c. – PtRh10+Y, d. – PtRh10+B. DD – drawing direction

The pole figures obtained for the PtRh10 wire (without micro-additions), which are shown in Figs 1a and 1b, prove the existence of rather strong texture close to the axial <100> texture, although some deviations from the ideal texture have been observed, namely:

- crystalline lattice rotation by about 100 around an axis perpendicular to the wire axis, and
- poles of the figures tend to such agglomeration that the texture exhibits some features similar to those of the {001} <100> sheet texture so that its ideal character of an axial texture disappears.

These both phenomena refer to the wire surface and they can suggest that the tools (drawhole) influence the development of a drawing texture and next, have an effect on recrystallisation texture. Assuming some simplification it can be stated that the mechanisms taking place on a surface of wire deformed during drawing can be referred to as similar to the mechanisms of sheet surface deformation during rolling, particularly at small values of 1/h [5]. Similar phenomenon of the formation of the so-called fibre texture was also observed by other authors, who examined the texture of wire surfaces and of the tubes [6].

Some negative effect on the analysis results, which applies to all wires examined under this work, had the fact that only convex surfaces of wires were inspected, and none of them were flat. The PtRh10 wires with an addition of yttrium exhibited also considerable degree of texture development, although the pole figures obtained, such as that shown in Fig. 1c, contain generally only a weak texture component close to <111> orientation, besides strong <100> texture component. The pole figures obtained for the PtRh10 alloy with an addition of boron (see Fig. 1d) illustrate the statistical, random distribution of grains orientation. Only in a few cases weakly outlined poles can be seen, which probably originate from the <100> texture.

It can be concluded from analysis of the pole figures obtained for recrystallised wires from the PtRh10 alloy with micro-additions that the element strongly modifying the wire structure is boron, which very efficiently limits an excessive grains growth during recrystallisation. This is evidenced by the grain size analysis presented in Table 1 and by a random distribution of orientations on the pole figures. In other words, a clear texture is not observed although recrystallisation took place.

An addition of yttrium, which exhibits some modifying effect but on a smaller scale, can influence stacking fault energy, which results in a change of wire drawing texture and, consequently, of a recrystallisation texture, in which a component close to the <111> orientation starts to appear.

The grain boundary analysis was performed for all examined grades of wires, including determination of misorientation degrees, analysis of coincidence boundaries by the Σ CSL (Coincidence Site Lattice) coefficients method, and also grain size measurements were made. The grain boundaries were analysed under the same conditions, which were used in texture examination.

Figs. 2a, 2b and 2c show misorientation distributions for grain boundaries within the same angular ranges, and the values of Σ CSL coefficients determined for the materials examined are given in Fig. 3. The results from this examination are summarised in Table 1, where the average data from the analysis performed in 20 points on a surface of wires from particular material grades are presented.

Based on the results obtained under this work it can be concluded that there is a strong correlation between misorientation degree of the grain boundaries, type of coincidence boundary and the grain size for particular materials studied. Both the wires with an addition of yttrium and oron had smaller grain size compared to that of an original PtRh10 material. However, the smallest grain size in comparison to the initial PtRh10 alloy had the wires with an addition of boron (about 11 μm^2 for misorientation angle of 5°).

It was also found that the content of grain boundaries with high coincidence degree (low Σ) within a range of Σ 3÷5 was the highest in a wire with boron and reached about 88% (see Table 1 and Fig. 3), and at the same time this material exhibited the highest content of high-angle grain boundaries (42%) over the maximum analysed angular range of 40-60° (see Fig. 2c). According to the literature data [7, 8, 9], large content of high-angle boundaries with low values of Σ coefficients is characteristic for higher-order twin boundaries, which is observed in recrystallised metals.

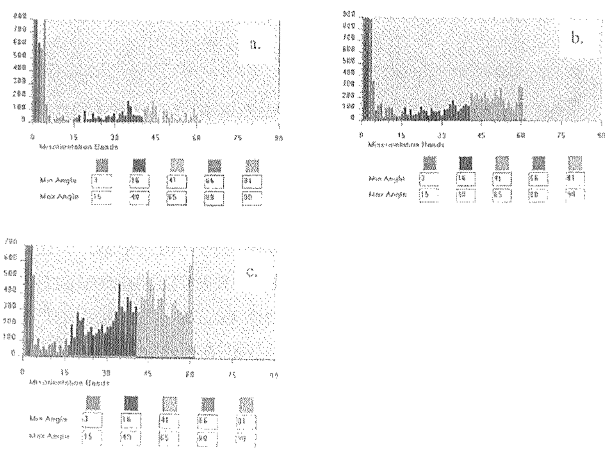

Fig. 2. Distributions of grain boundary misorientation for particular angular ranges: a – PtRh10, b – PtRh10 + Y, c – PtRh10 + B

An effect of yttrium on the grain size stabilisation is smaller. Based on analysis of the results presented in Table 1 and in Fig. 3 it can be concluded that this results from lower content of the boundaries characterised by low values of Σ CSL coefficient (77%) and from significantly reduced content, compared to boron, of the boundaries with high misorientation degree (25%).

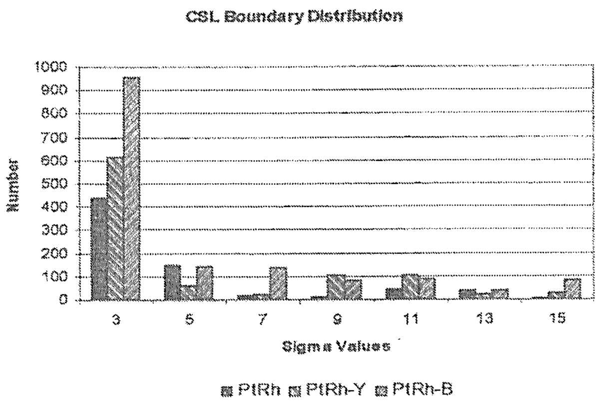

Fig. 3. The Σ CSL values for the materials examined

TABLE 1

Misorientation degree of the grain boundaries, the values of Σ CSL coefficient and grain size in recrystallised PtRh10 wires with micro-additions of yttrium and boron

Material examined	Misorientation degrees of the grain boundaries [%]		Content of coincidence boundaries for Σ 3÷15°, [%]	Grain size [μm^2] as a function of misorientation angle	
	3÷15°	40÷60°		5°	20°
PtRh10	53	18	70	52,8	70,4
PtRh10+Y	48	25	77	29,5	32,4
PtRh10+B	40	42	88	11,9	12,2

4. Results from the examination of grain orientation on a surface of catalytic wires after industrial exploitation

The wires from catalyst gauzes removed from industrial operation were examined. The analysis was made both for woven and knitted gauzes. Diameter of wires used in both types of gauzes was 0.050-0.060 mm. The result of long-term exposure of the wires to ammonia and air, and to high pressure and high temperature, were characteristic changes observed on a surface of wires from the PtRh10 alloy demonstrating itself by the presence of strongly grown grains (sometimes 1-2 grains over the whole wire cross-section) with protruding selectively etched boundaries (faceting), frequently covered with rhodium oxides. The wire surface topography (Fig. 3) and analysis of crystallographic orientation of single grains indicate that the selective etching takes place during wires operation, leading sometimes to revealing subsequent crystallographic planes.

It was found that, in accordance with crystallography basics, etching becomes inhibited and is sometimes significantly slowed down when the {111} planes are revealed, which are characterized by the most dense atoms packing and are resistant to chemical interactions.

The analyses have been carried out showing that the angular differences between crystallographic plane parallel to the wire surface and the {111} plane are initially large, but in subsequent stages of the etching process the planes increasingly distant from the primary distinguished orientation (surface) are gradually revealed, which are closer to the {111} plane, e.g. {112}, {113}, etc. This explanation is confirmed by the wire images shown in Figs 4c and 4d, where the greatest grain surfaces can be identified as the {111} crystallographic planes. Further slow down in etching the {111} planes proceeds mainly through the formation of thin jogs, which are seen in Figs 4a and 4b, and through systematic etching of their edges, which are the crystallographic planes of higher indexes, different from {111}.

Typical examples of this phenomenon are visible in Fig. 4d. The jogs start to form at the grain boundaries.

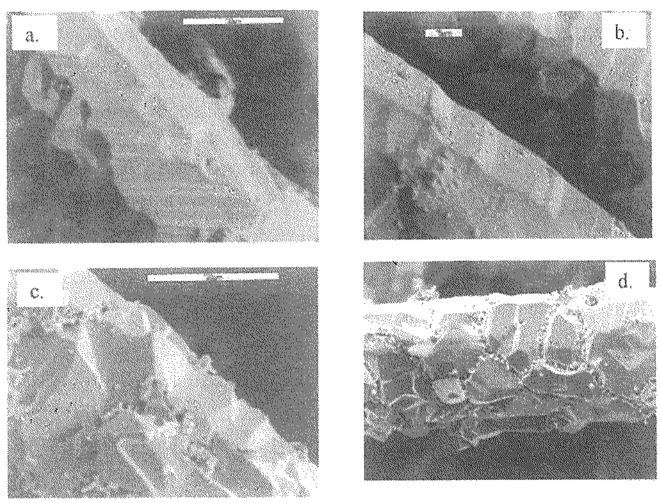

Fig. 4. Topography of the PtRh10 wire surface after industrial exploitation: a – knitted gauze (x2000), b – knitted gauze (x3000), c – woven gauze (x2600), d – woven gauze (x2600)

It is seen in Figs 4c and 4d that the etching process proceeds most slowly on the revealed octahedrons, whose outer surfaces are formed solely from the {111} planes protruding over the surface of trisoctahedron grains.

Based on this mechanism of the etching process proceeding on a wire surface in catalytic gauzes it can be expected that the grain refinement and weakening of a texture resulting from the presence of modifying additives can result in the increase of etching rate. The reason for that is that the areas close to grain boundaries, which exhibit elevated energy and, as a consequence, can be etched more easily, have greater share in the grains volume than large grains. Besides, the absence of a texture or a weak texture can increase the content of high-angle boundaries characterised by higher energy than that of the grain boundaries with similar orientations, which frequently occurs in strongly texturised materials.

5. Conclusions

Based on the results from this investigation the following conclusions can be drawn:

- A presence of the <100> axial texture of a diversified degree of formation was found in the PtRh10, PtRh10+Y and PtRh10+B wires examined,
- Wires from PtRh10 alloy and from PtRh10 alloy with an addition of yttrium are highly textured, and the pole figures obtained correspond to the <100> axial texture or are related to the {001} <100> fibre texture,
- A weak component close to the {001} orientation was found on the pole figures obtained for the PtRh10 alloy with yttrium,
- Pole figures obtained for the PtRh10 wire with boron represent statistically distributed poles of randomly oriented grains with poorly marked poles close to the <100> texture,
- The grain size misorientation analysis and analysis of coincidence boundaries performed by the Σ CSL coefficient method for all examined alloys have shown that the PtRh10 wires with boron are characterised by the highest content of high-angle boundaries within the range of misorientation angles of 40-60° and the highest content of coincidence boundaries with low values of Σ CSL coefficient (3-5). Besides, wires with an addition of boron exhibit the smallest grain size of misorientation angles of 5 and 20°,
- Analysis of surface topography and crystallographic orientation of the single grains on a surface of wires from the PtRh10 alloy has shown that during their operation in industrial installation selective etching takes place on a wire surface leading to revealing crystallographic planes {111}, and
- Etching of the {111} planes proceeds mainly through the formation of low jogs and systematic etching of their edges.

These results indicate that, considering the rate of catalytic etching of wires, the most beneficial is a structure consisting of large grains with low surface energy and, consequently, of low misorientation and with such an arrangement that the {111} crystallographic planes are parallel or almost parallel to the plane of a wire surface. The microstructure analysis of the examined wires proves possibility for modification of their operation properties either by application of alloy micro-additions or by specific drawing process.

REFERENCES

[1] Z. Rdzawski, Report IMN, No 57/2000.
[2] D. Dingley, Scanning Electron Microscopy, **11**, 74 (1984).
[3] V. Randle, B. Ralph, D. Drugley, Acta Metall **11**, 267 (1988).
[4] Oxford Instrument Guide Book, ser. OP/b/0997.
[5] K. Sato, F. Uchida, S. Takahashi, Metall **35**, 11, 119 (1981).
[6] M. Woch, B. Besztak, Report IMN, No 3904/I/1987.
[7] D. G. Grandon, The structure of high-angle grain boundaries. Acta Met. **12**, 813 (1964).
[8] S. R. Orther, V. Randle, Scr. Met. **23**, 1903 (1929).
[9] M. Grabski, Struktura granic ziarn, Ed. Wydawnictwo Śląsk, 1969.

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