

The Catalytic Etching of Platinum and Rhodium-Platinum Gauzes

CRYSTALLOGRAPHIC CHANGES DURING AMMONIA OXIDATION

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Surface morphological and X-ray examinations have been carried out on catalyst gauzes exposed to the conditions encountered during the oxidation of ammonia. A model, based upon observations of platinum and rhodium-platinum single crystals is proposed to explain the structural changes that occur on rhodium-platinum alloys during industrial use.

A major concern during the process of ammonia oxidation is the loss of platinum from the rhodium-platinum catalyst gauze, which occurs simultaneously with its deactivation. The use of rhodium-platinum or palladium-rhodium-platinum alloys causes a noticeable rise of mechanical strength of the gauze, without a significant loss of catalytic efficiency.

Previous studies have shown that the wires of a new catalyst gauze are essentially smooth (1-8). During use they become roughened and etching occurs along grain boundaries. The process spreads into the interior of the grains and ultimately well developed facets appear, the character of which varies from grain to grain. After a prolonged period of use deep etch-pits, often with very regular shape and developing into channels which penetrate the interior of the grains, are also observed. Finally irregular cauliflower-like growths appear on the surface.

During catalyst use, segregation of the components and enrichment of the surface layers with rhodium occurred on rhodium-platinum gauzes, and X-ray examination revealed the formation of rhodium oxide (1, 4, 7, 9, 10). This rhodium oxide layer can form a very compact, thick envelope which can be separated from the gauze wire core (11, 12).

The facets observed on the surface of the grains have a very regular form. This suggests that they are crystallographically oriented and

it is reported that their character depends on local structural features (2, 6, 8, 13).

Experiments with single crystals in the form of small diameter balls have shown that faceting depends upon the local orientation of the surface, its curvature and the flow velocity of the reactant gases (14, 15).

In the present paper results are presented of studies with scanning electron microscopy (SEM) of surface morphology, and X-ray examinations of platinum and rhodium-platinum alloys exposed to industrial conditions for ammonia oxidation. To explain the structural changes observed in commercially used rhodium-platinum gauzes a model is proposed, based on the observed changes of surface morphology of single crystals of platinum and rhodium-platinum alloys.

Experimental Conditions

All the samples were exposed in an experimental reactor designed to follow industrial practice. The samples were placed between the first and second gauzes in a pack of four with the examined surface facing the reaction gas stream. The experiments were performed at pressures of 3.5 to 4.8 atm, the concentration of the ammonia in the gas being 6.3 to 6.8 wt. per cent. The average gas temperature was 820 to 900°C, and the catalyst gauze loading was either 24.5, or more generally 49N cubic metres

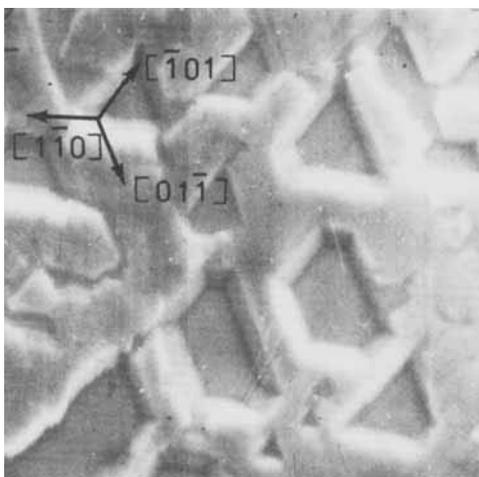


Fig. 1 A platinum (111) surface, which had been shielded by the gauze, showing an early stage of catalytic etching ×3400

of nitrogen per hour while the exposure times were 5 to 100 hours (for single crystals 5, 10 and 100 hours), except for gauzes obtained directly from industrial plant.

High purity platinum and rhodium-platinum polycrystalline wires of 150 and 60 μm diameter, respectively, were used; the 60 μm wires being in both the as-produced condition and as taken from catalyst gauzes. In addition flat polycrystalline samples, with surface dimension 5 \times 5 mm, were cut from rods used in the production of gauzes.

Single crystals of platinum and 10 per cent rhodium-platinum with surface orientation (100), (111), (110) were cut by spark-erosion from randomly oriented single crystal rods of 4 to 6 mm diameter. The samples were polished with diamond paste and then annealed in vacuum by an electron beam at a temperature of about 1200°C. Berg-Barrett X-ray topographs of the cut and annealed samples displayed a highly developed mosaic structure, which, in the case of the platinum single crystal, was noticeably reduced only after the third annealing treatment.

The 10 per cent rhodium-platinum samples were annealed at much lower temperatures and for shorter periods of time than the platinum. This reduced segregation of rhodium, but did

not allow the formation of large mosaic blocks.

The characteristic feature of any wire is the longitudinal structure (texture) resulting from directional plastic deformation during wire production. This structure is usually non-uniform, and changes with the distance from the longitudinal axis of the wire. Wires of face centred cubic metals generally exhibit an axial structure with $\langle 111 \rangle$ direction as the axis or with mixed $\langle 111 \rangle + \langle 100 \rangle$ axes (16).

Using CuK_{α} X-ray radiation, the half penetration depth for platinum is about 1.6 μm . Thus by dissolution it was possible to study changes in the structure as a function of the distance from the surface.

Observations and Results

As produced platinum wires had an axial $\langle 111 \rangle$ texture in the surface layer but in the interior there was a mixed axial texture of the $\langle 111 \rangle + \langle 100 \rangle$ type. X-ray photographs of the surface layers of pure platinum wire after treatment in the reactor for 10 hours showed a polycrystalline image. However, hardly any changes occurred at the interior of the wire.

Before treatment in the reactor the rhodium-platinum wires had a mixed $\langle 111 \rangle + \langle 100 \rangle$ axial texture near the surface. However, after the treatment the samples exhibited a

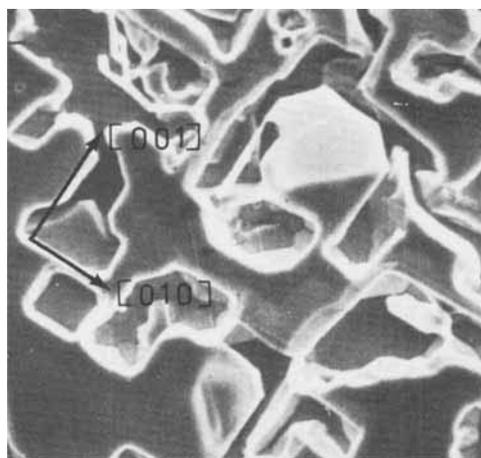


Fig. 2 A platinum (100) surface showing an early stage of catalytic etching. The relief developed on the surface corresponds to its symmetry ×3400

polycrystalline structure with a simultaneous increase of the $\langle 100 \rangle$ type of texture when examined by X-ray diffraction. The degree of $\langle 100 \rangle$ crystallographic orientation was greater in the 10 per cent rhodium-platinum than in the 5 per cent rhodium-platinum wire. The observed changes in the interior of the wires were those expected after a purely thermal treatment of the sample. The thick 150 μm diameter wires behaved similarly, except that after an initial 10 hours exposure, recrystallisation of the interior was less pronounced.

The platinum and rhodium-platinum wires obtained from catalytic gauzes behaved in the same manner. However, the curvature of the wires made X-ray identification of the texture more tedious.

The single crystal samples were treated under the same conditions as the wires. Before treatment the surfaces were optically smooth, except for a few scratches remaining from the mechanical polishing. After the treatment however, both the oriented platinum and rhodium-platinum single crystal samples exhibited some common features. Platinum crystals with surfaces parallel to (111), (100) and (110) planes and also the 10 per cent rhodium-platinum crystals with (111) and (100) faces, when treated for 20 hours, exhibited only a few pits; these were mostly along the

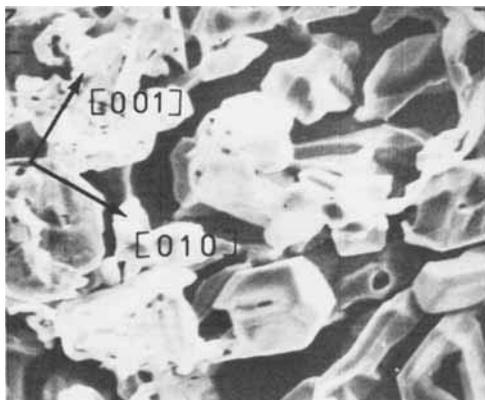


Fig. 3 A platinum (100) surface after 100 hours exposure to the direct influence of the reactant gases. Crystallites with well defined faces are visible, as are cauliflower-like growths ×3400

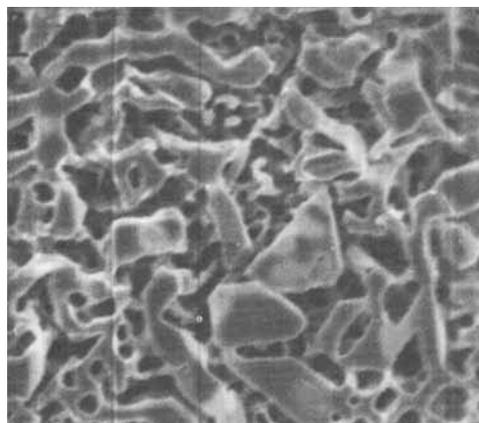


Fig. 4 A 10 per cent rhodium-platinum (100) surface after treatment for 100 hours. The surface is not as deeply etched as platinum after the same treatment time ×3400

mechanical scratches produced during the handling of the samples after preliminary SEM examinations. After 100 hours treatment, the whole surface of the samples exposed directly to the reactant gases was heavily etched. The places shielded by the gauze were attacked less and show the earlier stages of the etching process, see Figures 1 and 2. The analysis of the relief showed that the edges of the etch-pits are oriented along the directions of intersection of low-index planes with the single crystal surface. In the heavily etched areas, shown in Figures 3 to 6, the surface was covered with crystallites of varying regularity and, in the case of platinum, cauliflower-like growths occurred in some places, see Figure 3. For the same treatment time, the surfaces of the platinum crystals were more deeply etched than those of rhodium-platinum crystals, as can be seen by comparing Figure 3 with Figures 4 and 5.

The relief developed on each surface corresponded to its symmetry. This is especially evident at the earlier stages of catalytic etching of the platinum crystals, illustrated in Figures 1 and 2. The relief observed on (100) and (111) rhodium-platinum crystals was not as regular as that seen on pure platinum crystals. This results from the partial recrystallisation of the rhodium-platinum single crystals, the crystals having a highly developed mosaic structure.

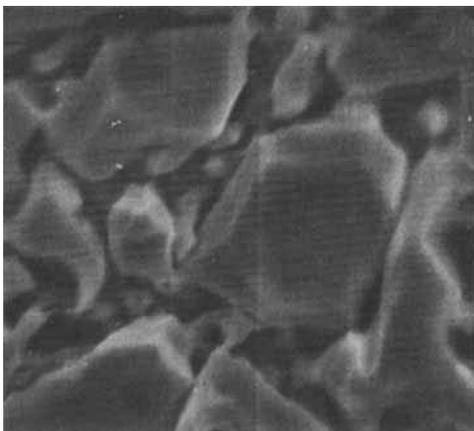


Fig. 5 A 10 per cent rhodium-platinum (111) surface treated for 100 hours ×3400

Both the 5 and 10 per cent rhodium-platinum alloys exhibited the same surface features. Grains with different orientations were etched in different ways, as can be seen in Figure 6, and some preferential etching at grain boundaries took place. Prolonged exposure resulted in very pronounced etching of the interior of the grains, with a distinct relief on different grains. On the surface of some grains, regular square pits occurred (shown in the left hand photomicrograph in Figure 6) similar to those observed on the platinum (100) face at the beginning of the etching process. On the grains of the 5 per cent rhodium-platinum alloy, some cauliflower-like growths were present. It should be noted that these growths were not apparent on the 10 per cent rhodium-platinum alloy after the same 100 hours of treatment.

Discussion and Conclusions

The morphology of the oriented platinum and rhodium-platinum single crystal surfaces exposed to reactant gases during the ammonia oxidation process indicates that catalytic etching takes place along crystallographically defined planes. This explains why pits with four-fold symmetry on (100) surfaces and with three-fold symmetry on (111) surfaces were observed, whereas the pits on the (110) planes exhibited a linear form.

It seems reasonable to assume that the planes exposed during the process of catalytic etching

are the most stable. An analysis of SEM photographs indicates that on platinum (100) crystals the etching takes place with the exposure of (110) planes and to a lesser degree (111) planes. On the (111) oriented surface the pits have edges parallel to the intersection of (100) and (111) or (110) planes, and the exposed planes are probably (100) and (110) because they form more acute angles with respect to the (111) plane than the other (111) planes. For identical treatment conditions the (100) plane is etched more quickly than the (111) plane and this results in the better developed relief observed on the former plane. The 10 per cent rhodium-platinum crystals are more resistant to etching than the platinum crystals.

The relief observed on both the platinum and rhodium-platinum crystals is very regular only over short distances, although its character remains the same all over the surface. This probably results from the highly developed mosaic structure in these crystals and the fact that in some cases the misorientation between subgrains can be as large as several degrees. Figure 7(left) shows Berg-Barrett X-ray topographs of a platinum (100) crystal before annealing, and Figure 7(right) after the third 1 hour anneal. In the case of the rhodium-platinum alloy such an annealing treatment was precluded to avoid segregation of rhodium and recrystallisation. This is why the relief observed on these crystals is more confused and is only roughly similar to that observed on platinum single crystals. As suggested elsewhere the loss of material probably proceeds through the formation of volatile platinum oxide (5, 10, 13,17), and results in the enrichment of the surface layer with rhodium. The volatile component probably condenses on other parts of the crystal and, together with smaller crystallites detached from the bulk of the crystal and carried by the reactant gas stream until randomly deposited elsewhere, forms the observed cauliflower-like growths. These do not have as regular a form on a large scale as the etched crystallites, but in some cases their general shape is parallel to the low index directions of substrate crystals.

The results show that all the examined low-

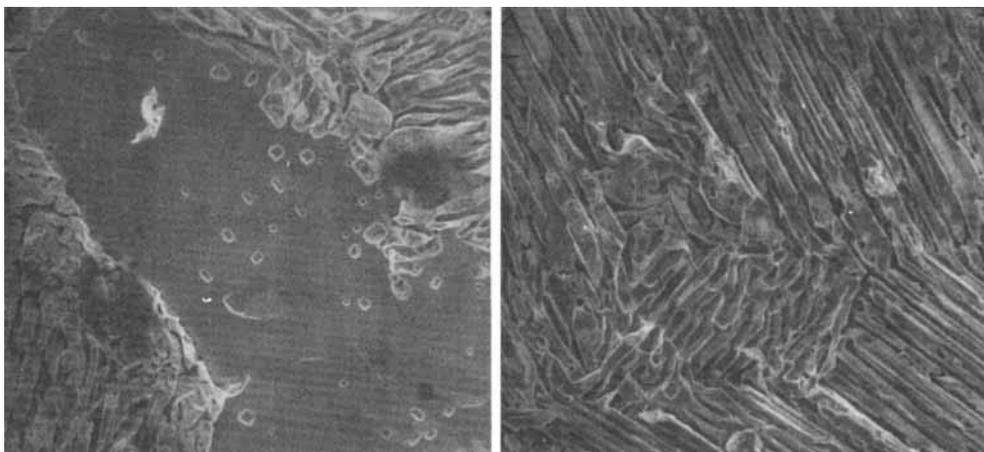


Fig. 6 Two areas on a flat polycrystalline sample of 5 per cent rhodium-platinum after treatment for 100 hours in the reactor. The relief produced by etching depends upon the orientation of the grains. Regular square pits can be observed on one of the grains ×1130

index planes are stable. However their stability depends on the number of points at which the etching process starts.

It is reasonable to assume, as in the case of chemical etching, that the sites of preferential etching are places of high stress concentration, grain boundaries, impurity segregation and other kinds of defects. Once activated, catalytic etching proceeds to expose the nearest low-index planes. This process spreads until new points of preferential etching develop on the newly exposed planes. New low-index planes are

then exposed at these points. In this way the etching process proceeds not only at right angles to the crystal surface, but also in other directions. Some parts of a crystal may be etched from all sides and the crystallites formed in this way will be moved away from the bulk of the crystal by the stream of reactant gases. This model should also be valid for polycrystalline material, where every crystal grain is behaving in the same manner. For such polycrystalline material the existence of grain boundaries makes the number of sites of preferential

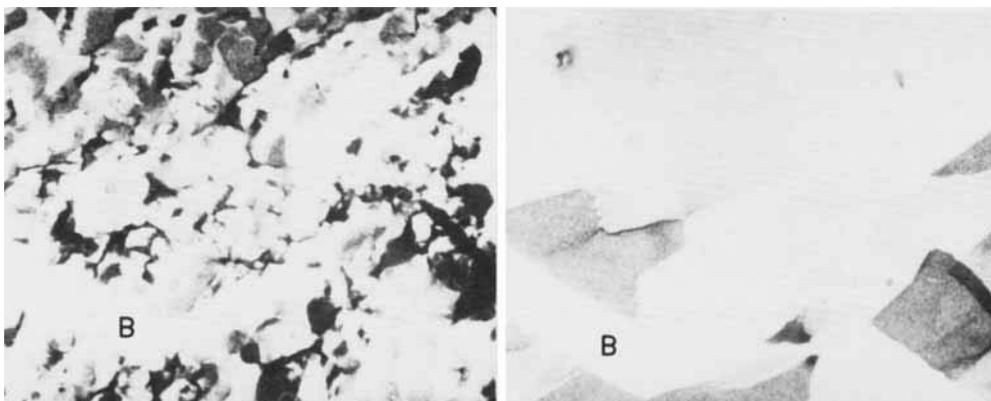


Fig. 7 Berg-Barrett X-ray topographs of a (100) oriented platinum crystal showing, on the left, the sample after annealing for 1 hour at 1200°C, and on the right after the third period of 1 hour annealing at 1200°C. (Reflex (311), CuK_α radiation). The same low-angle boundary is marked B on both topographs. The increase in size of the micromosaic blocks after repeated annealing is clearly shown approx. ×85

etching much higher and the random orientation of grains causes more non-stable high-index planes to be exposed at the surface of the sample.

The rhodium-platinum wires have a high degree of longitudinal texture of the (100) type in their surface layers. This means that a higher than average number of grains have the $\langle 100 \rangle$ direction parallel to the wire axis. The $\langle 100 \rangle$ planes are stable. Thus, etching on these planes will be much slower than on any other adjacent plane, and etching along the $\langle 100 \rangle$ planes perpendicular to the wire axis will be even slower. As a result, grains with a longitudinal texture close to $\langle 100 \rangle$ will be more stable. The other grains will be attacked more readily and some of them will be separated from the matrix and removed by the stream of reactant gases. The SEM studies (18) of post-reaction dusts revealed crystallites with the dimension of a few μm and with habit planes looking very similar to the crystallites developed on oriented single crystal planes, as shown in Figure 3. As a result, the relative number of grains in the surface layer with an orientation of the (100) type is increased. This was actually observed.

The etching processes observed on platinum and rhodium-platinum wires and single crystals, presented above, can explain the crystallographic features observed on catalytic gauzes used in ammonia oxidation. It can also explain why well developed crystallites are found in post-reaction dust (18). However, it does not account for the way the loss of material takes place, although it seems that the most effective way for the described model to operate will be through the formation of volatile products.

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Palladium-Nickel Plating

The economic advantages of palladium-nickel as a replacement for electrodeposited gold in the electronics industry have been demonstrated many times during recent years and an extended study of their relative performance recently reported by K. J. Whitlaw of LeaRonald U.K. (*Trans. Inst. Met. Finish.*, 1984, **62**, (1), 9-12) serves to substantiate the potential value of these deposits.

The experimental work shows that a duplex layer of 2.5 to 3.0 μm 70 palladium-30 nickel followed by 0.1 to 0.25 μm of acid hard gold is to be recommended as a replacement for 2.5 μm gold deposited on a copper substrate such as a printed circuit board. This combination offers freedom from porosity, stability of contact resistance, excellent resistance to wear and to corrosion, and also resistance to copper diffusion at elevated temperatures.

These properties, while being identical to those secured with a conventional gold deposit, offer savings in cost of as much as 65 per cent.