Structure Reconstruction in Palladium Alloy Catchment Gauzes

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The changes of topography and structure in palladium-5 per cent nickel alloy catchment gauzes, which are used to capture the platinum lost from the catalyst gauzes employed in the ammonia oxidation reaction to produce nitric acid, have been studied by scanning electron microscopy, electron probe microarea analysis, X-ray diffraction and other techniques. The structure of the palladium-5 per cent nickel alloy gauze is reconstructed by recrystallisation and this is controlled by vapour deposition (adsorption) and diffusion re-alloying. The initial solid solution of palladium(nickel) changed into palladium(platinum) solid solution, the nickel being gradually oxidised to nickel oxide until no nickel remained. The lattice constants of the palladium(platinum) solid solution increased with the ratio of platinum:palladium. Ladder-like (layered) growth was a main mechanism in the formation of new lattice planes and crystals, while screw-type growth played an important role in the formation of new crystals.

In the preparation of nitric acid by ammonia oxidation platinum-rhodium or platinum-palladium-rhodium alloy gauzes are used as the catalysts. Under typical operating conditions for the process of temperatures from 750 to 950°C and pressures of 1 to 10 atmospheres, platinum oxide, PtO_2, which is volatile, is formed on the catalyst surfaces (1–7) and this can cause a loss in platinum of between 0.05 and 0.5 grammes per ton of nitric acid produced. In order to recover the lost platinum, catchment gauzes made of palladium-gold alloy have been introduced into the ammonia oxidation reaction chamber and installed directly beneath the catalyst gauzes (8–10). In recent years, metals from Groups VIII and IB have been suggested as substitutes for the gold, to economise on its use (11), and as a result, catchment gauzes comprised of a high palladium content alloy containing copper or nickel or other metal have been developed (12, 13).

Changes in the constituents and surface states have been reported for catchment gauzes made of palladium-5 per cent nickel, when used at high pressures of 7 to 9 atmospheres and high temperature of 920 to 940°C, and at medium pressures of 3 to 4 atmospheres and temperatures of 800 to 850°C (13, 14). However, the re-alloying and recrystallisation processes that take place in palladium-gold and palladium-nickel alloy catchment gauzes have been little reported on. In this paper, therefore, the structure reconstruction and recrystallisation processes occurring in palladium-5 per cent nickel catchment gauzes will be discussed, based on the topographic and structural changes observed under conditions of medium pressure and temperature.

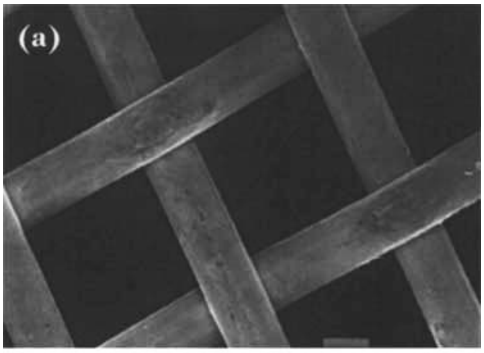
Experimental Procedure

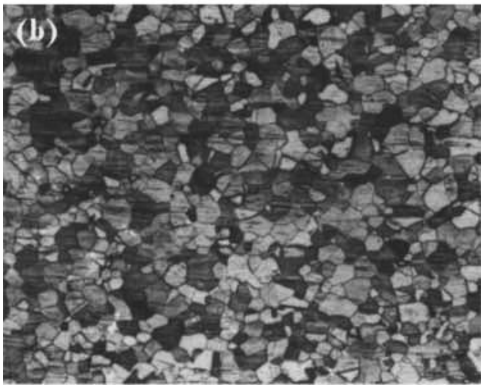
Samples of catchment gauzes were removed from a medium pressure ammonia oxidation apparatus which operated at a pressure of 0.35 MPa and temperature of 850°C. The ammonia concentration in the ammonia-air gas mixture was 10.5 to 11.5 per cent, and the catalyst gauze consisted of three sheets of platinum-4 per cent palladium-3.5 per cent rhodium alloy of 1024 mesh/cm^2.

The platinum recovery packages, which were installed underneath the catalyst gauzes, were made of two sheets of palladium-5 per cent nickel catchment gauze separated and supported by three sheets of iron-22 per cent chromium-5 per cent aluminium alloy gauze.

The recovery packages were operated for 5 months – the (G-5) gauze, and for 8 months – the (G-8) gauze. Samples for study were taken from the top and bottom gauzes. In the downstream direction, the surfaces of the samples were marked as [a] on the front surface of the first gauze through [b] and [c], to [d], on the back surface of the second gauze.

The topography of the samples and a quantitative analysis of the surface constituents were observed by electron probe and also scanning electron microscopy with an energy spectrometer, and the lattice parameters of the gauzes were determined by X-ray diffractometry.





Experimental Results

Topography and Structure of New Catchment Gauzes

New catchment gauzes were woven from clean smooth palladium-5 per cent nickel alloy wire of diameter 0.09 mm which had been previously annealed in an argon atmosphere. Although there were some defects on the surface of the wire, no contrasts in crystallisation were observed on SEM photographs. The alloy had a single-phase solid-solution structure with fine crystal grains, see Figure 1(a) and 1(b). X-ray photoelectron spectroscopic analysis (XPS) indicated that the surface of new catchment gauzes was mainly palladium without any palladium oxide, PdO, being present (14).

Topography of Used Catchment Gauzes

During the ammonia oxidation process the platinum-palladium-rhodium catalyst gauzes produced the volatile oxides: platinum oxide, PtO_2, and palladium oxide, PdO, and the non-volatile rhodium oxide, Rh_2O_3. The weight loss in the catalyst gauzes resulted mainly from volatilisation of platinum as PtO_2, since the concentrations of palladium and rhodium, and thus of PdO and Rh_2O_3, in the catalyst alloy were low. The PtO_2 vapour was transported by the gas stream to the surface of the palladium alloy catchment gauze where it was reduced to plat-

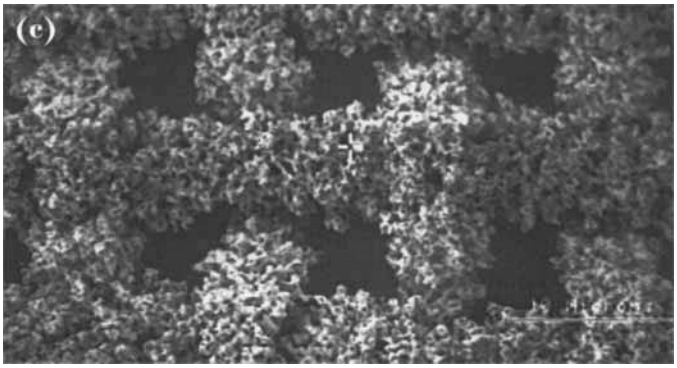


Fig. 1 Fresh palladium-5 per cent nickel catchment gauzes showing: (a) the surface topography, the scale line is 100 μm (b) the crystal structure, and (c) the surface topography of (G-5) gauze, after being used for 5 months; the line is 10 μm long

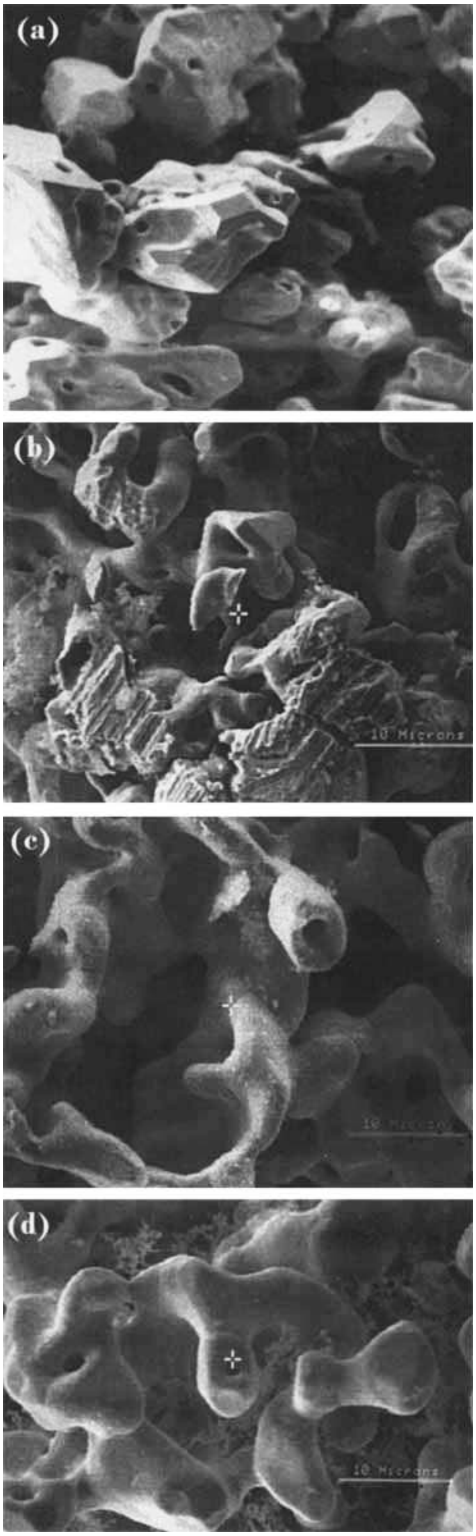


Fig. 2 Topography of (G-5) gauzes:
(a) is the front face, (G-5)[a] and
(b) is the back face, (G-5)[b], of the first gauze;
(c) is the front face, (G-5)[c] and
(d) is the back face, (G-5)[d], of the second gauze

inum and immediately deposited onto the surface of the bright palladium metal (14). The platinum dissolved into the palladium matrix and was alloyed by diffusion, thus causing changes in the structure, topography and constituents of the palladium alloy catchment gauzes.

The process of change is called structure reconstruction or recrystallisation. These structural changes in the catchment gauzes depend upon the position of the gauzes and on how long they are in operation.

The topographies of surfaces [a], [b], [c] and [d] of the (G-5) gauze, are shown in Figures 1(c) and 2. The skeletal construction of the (G-5) [d] surface contains up to 90 per cent palladium, which corresponds to the amount of palladium in molecular PdO. XPS analysis indicated that the (G-5)[d] surface was covered by PdO film. The catkin-like matter around the skeleton was mainly made of nickel oxide, NiO, with additional small amounts of the oxides of palladium, platinum, iron, chromium and aluminium (14). The NiO, which formed on the surface of the catchment gauzes, grew outwards from the surface by nickel diffusion and volatilisation, and accumulated there after transportation by the gas stream. This led to the formation of the catkin-like matter.

On the (G-5)[c] surface, the skeletal construction is obviously swollen, and the NiO catkins have essentially disappeared. On the (G-5)[b] surface the layered structure can be clearly seen and facets of the recrystallised crystals have appeared on the (G-5)[a] surface.

The topographies of various surfaces of (G-8) gauzes, which were used for 8 months, are shown in Figure 3, and some differences can be seen between the (G-8) and (G-5) gauzes.

First, the [d] and [c] surfaces of (G-8) gauze have become porous sponges, evolved from the skeletal construction of the [d] and [c] surfaces of (G-5) gauze. The layered structure which

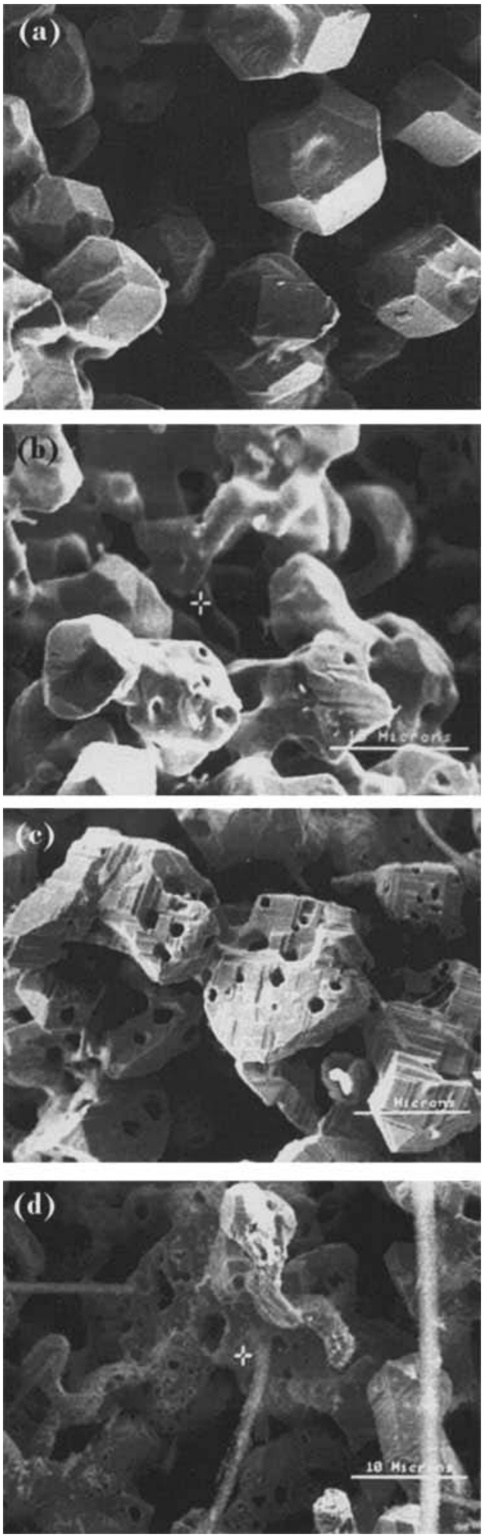


Fig. 3 Topography of (G-8) gauzes:
(a) is the front face, (G-8)[a] and
(b) is the back face, (G-8)[b], of the first gauze;
(c) is the front face, (G-8)[c] and
(d) is the back face, (G-8)[d] of the second gauze

occurred in the sponge of [d] surface has developed further on the [c] surface of (G-8) gauze. The formation of the holes may be linked to the oxygen that is released during the reduction of PtO_2 on the surface of the catchment gauzes. The wiry substance seen on the (G-8) [d] surface, in Figure 3(d), is the remnants of wire of the iron-22 per cent chromium-5 per cent aluminium alloy support gauze. Facets of the recrystallised crystals have developed on the (G-8) [b] surface, and whole recrystallised crystals have formed, or are forming, on the (G-8) [a] surface, as shown in Figure 3(a).

Careful observation has indicated that the whole crystals are of tetrakaidecahedron structure, (a 14-faced body) made up of quadrilaterals and hexagons, and are grains ranging in size from several micrometres to tens of micrometres, which are visible to the naked eye.

Second, no NiO catkins were visible on the various surfaces of the (G-8) gauzes. Chemical analysis has indicated that the content of the nickel in used (G-5) catchment gauzes is 0.18 weight per cent in the first sheet and 1.17 weight per cent in the second sheet, but only 20 to 40 ppm in the two sheets of (G-8) gauzes. During operation, the nickel solute in the catchment gauzes is gradually oxidised until it is all reacted.

Structure of Used Catchment Gauze

Palladium-5 per cent nickel alloy exists as a single-phase solid solution with lattice parameter $a = 0.3858$ nm, which is smaller than the lattice parameter of palladium, $a = 0.3890$ nm. This results from the atomic radius of nickel, 0.125 nm, being smaller than that of palladium, 0.137 nm.

The (G-5) and (G-8) gauzes also exist as single-phase solid solutions. Figure 4 shows the X-ray diffraction pattern of (G-8) gauze and Figure 5 shows the lattice parameters for (G-5) and (G-8) gauzes and the platinum:palladium ratios on the gauze surfaces. The lattice parameters

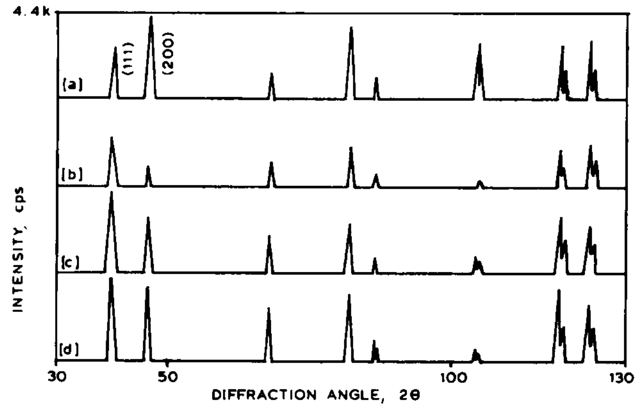


Fig. 4 The X-ray diffraction patterns for the [a], [b], [c] and [d] surfaces of (G-8) gauze

of (G-5) and (G-8) gauzes are larger than those of palladium-5 per cent nickel alloy and pure palladium. Thus, the solid solubility of platinum, which has a larger atomic radius (0.139 nm) than palladium (0.137 nm), increased in the palladium matrix, while the solid solubility of nickel in palladium decreased. That is to say, the initial solid solution of palladium(nickel) has transformed gradually into a palladium(platinum) solid solution, while the catchment gauzes were in use.

The trends in the changes of the lattice parameters on various surfaces of (G-5) and (G-8) gauzes are the same as for the values of their respective platinum:palladium ratios, which are found from weight per cent measurements, see Figure 5. For (G-5) gauzes, the lattice parameters and the values of the platinum:palladium ratio decrease from the [a] to the [d] surface. For (G-8) gauzes, both the lattice parameters and the size of the platinum:palladium ratios are generally higher than for the (G-5) gauzes, and for both measurements the values of the front faces of the gauzes, namely the [a] and [c] surfaces, are higher than for the back faces, the [b] and [d] surfaces, respectively. This indicates that more platinum is dissolved in the (G-8) gauzes, which were used for 8 months, than in the (G-5) gauzes, used for 5 months, and that more platinum dissolved in the front faces of the gauzes than in the back faces.

On the other hand, it can be seen in Figure 4,

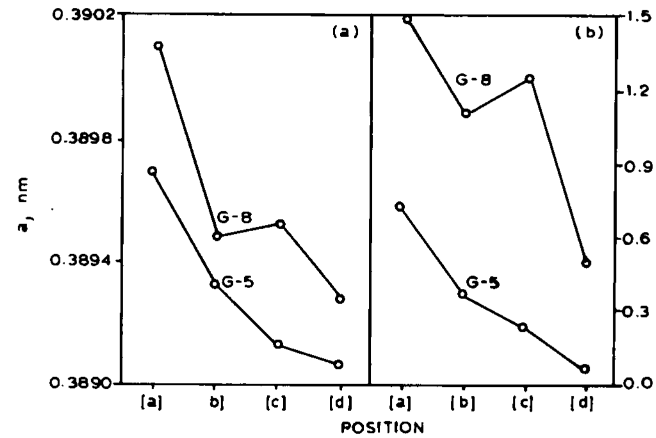


Fig. 5 (a) Lattice parameters for (G-8) and (G-5) gauzes and (b) values of platinum:palladium ratios, found by weight per cent, on various surfaces of (G-8) and (G-5) gauzes

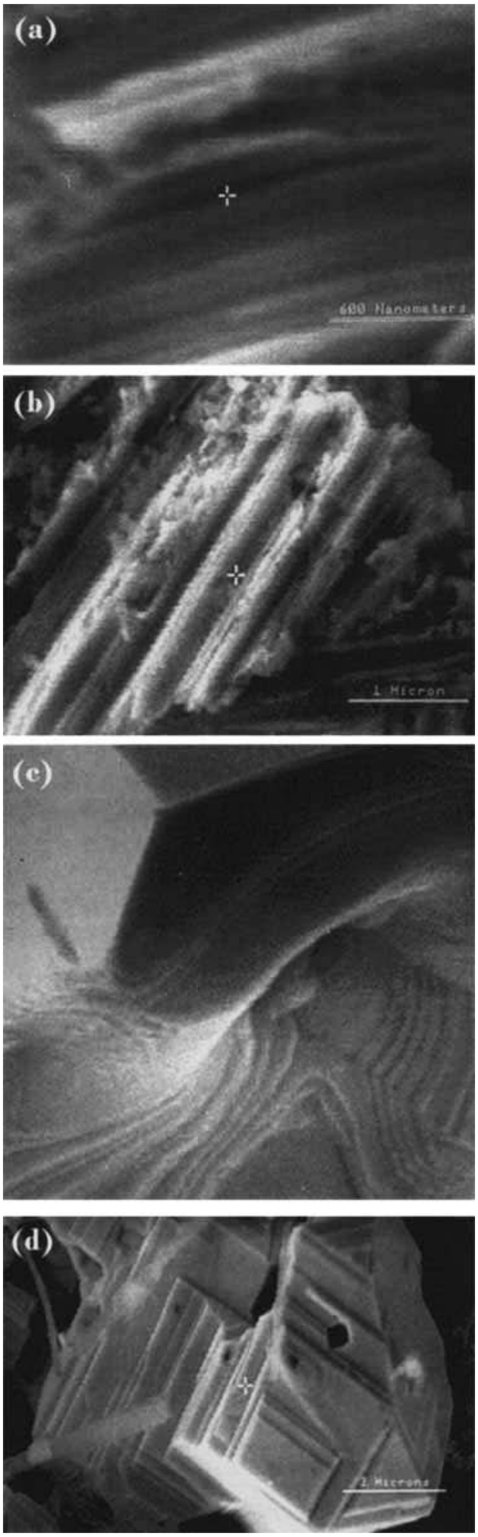


Fig. 6 The layered structure that is observed during recrystallisation is controlled by a ladder-like growth process: (a), (b) and (c) are surfaces of (G-5)[c], (G-5)[b] and (G-5)[a] of (G-5) gauze, respectively, and (d) is the [c] surface of (G-8) gauze

that the X-ray diffraction intensity on the (200) crystal plane of the [a] surface of (G-8) gauze is clearly higher than on the (111) crystal plane, but the intensities of the diffraction on the (111) and (200) crystal planes are reversed for other surfaces of (G-8) gauze, and this is also true for various surfaces of (G-5) and new gauzes. This is because the [a] surface of (G-8) gauze is the most completely recrystallised surface, which indicates that the orientations of the crystals must have changed during the recrystallisation process in the gauzes.

The Growth Pattern of Recrystallised Crystals

The key to the recrystallisation process in the palladium-nickel alloy catchment gauze is the substitution of palladium(platinum) solid solution for palladium(nickel) solid solution. This process can be divided into two stages: the formation and the growth of recrystallised crystals, namely new palladium(platinum) solid solution crystals.

The structures of the [c], [b] and [a] surfaces of (G-5) gauzes and the [c] surface of (G-8) gauze, shown in Figure 6, illustrate to a certain extent the formation process of crystal recrystallisation. This process includes the deposition of platinum and the alloying of platinum with palladium Figure 6(a), ladder-like growth Figures 6(b) and 6(c) and the formation of the layered structure, and new facets and crystals Figure 6(d).

In other words, the ladder-like growth mechanism controls the formation of recrystallised crystals. The structures of the [c], [b] and [a] surfaces of (G-8) gauze, shown in Figure 7, illustrate the growth process of the recrystallised crystals. On the [c] surface, Figure 7(a), new facets and small crystal nuclei can be seen. On the [b] and [a] surfaces of the (G-8) gauze, screw-type growth and screw cones are visible on the faces and crystal planes in addition to the

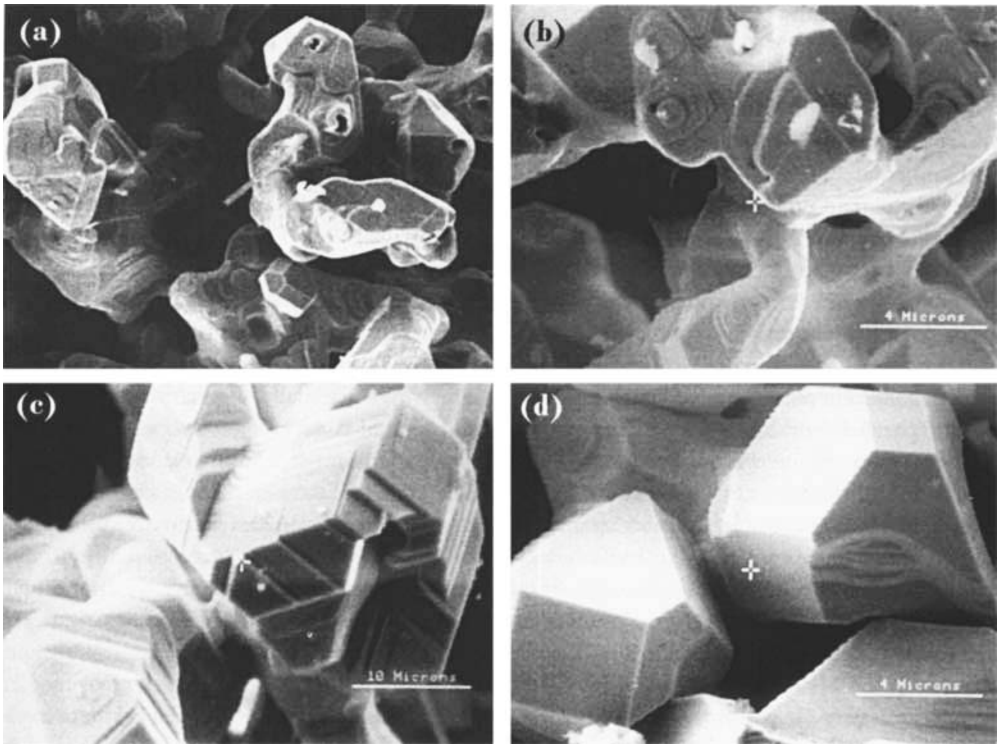


Fig. 7 Screw growth and screw cones occurring during recrystallised crystal growth: (a) the (G-8)[c] surface; (b) the (G-8)[b] surface, showing screw-type growth and screw cones; (c) the (G-8)[b] surface, showing ladder-like structure and small screw cones on the crystal face, and (d) the (G-8)[a] surface for (G-8) gauzes

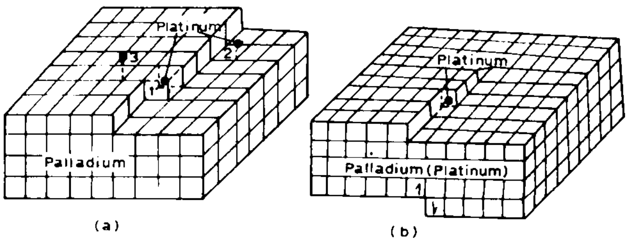
layered structure. This indicates that the screw growth mechanism plays an important part in the growth process of recrystallised crystals.

Discussion and Conclusions

The basis of the structure reconstruction in palladium-5 per cent nickel alloy catchment gauzes during the platinum recovery process is that the initial palladium(nickel) solid solution is replaced by new palladium(platinum) solid solution. It is a re-alloying or recrystallisation process in the palladium-nickel alloy. The recrystallisation process can be divided into two stages: the formation of new crystals controlled by a ladder-like growth mechanism and further growth controlled by both a ladder-like and a screw growth mechanism. A simple discussion is given here, based on Figure 8.

When a platinum atom is absorbed onto the lattice of the palladium matrix, it deposits preferentially into position '1' where there is a tri-rectangular "concave" structure, Figure 8(a).

Fig. 8 (a) Ladder-like growth and (b) screw growth in the early and late stages of the recrystallisation process for palladium-nickel catchment gauzes



This position has the strongest attractive force for platinum atoms, which deposit there until the line containing position '1' is fully filled. Then a platinum atom deposits on position '2', where there are two-rectangular "concaves", and immediately forms a tri-rectangular "concave", similar to position '1'. The deposition process of position '1' is repeated until the plane is fully filled. When a platinum atom deposits onto position '3', it immediately creates two-rectangular and then tri-rectangular "concaves", and the above deposition processes are repeated until the adjacent plane is fully filled. This gradual and parallel deposition and evolution results in the formation of a layered structure.

The palladium(platinum) solid solution lattice, facets and crystals are formed by mutual diffusion and alloying. The completely recrystallised crystals are tetrakaidecahedron, each made up of quadrilaterals and hexagons. During the formation of new facets and crystals, ladder-like growth is the main mechanism, while screw-type growth is hardly observed. The increasing solid solubility of platinum in the palladium matrix expands the palladium lattice and produces internal stress. Through the action of the internal and thermal stress, a relative shear displacement can easily occur along some crystal planes, thereby forming a screw dislocation, and creating the tri-rectangular "concave" shown in Figure 8(b). The tri-rectangular "concaves", are the preferred places for the deposition of platinum atoms. The deposition along the screw dislocations produces the screw-type growth and the formation of screw cones. Thus, in the growth process for crystals of palladium(platinum) solid solution, the screw-type growth mechanism plays an important role.

In summary, the recovery of platinum by palladium-nickel catchment gauzes is a re-alloying and recrystallisation process of the palladium-nickel alloy. The reduced platinum atoms deposit on the surfaces of the catchment gauzes and are alloyed with the palladium matrix, changing the topography and structure of the gauzes. The bright smooth palladium-nickel alloy wires gradually acquire a porous sponge and layered structure, and faces and crystals of new palladium(platinum) solid solution form. The growth of the new crystals finally produces a tetrakaidecahedron structure and the initial solid solution of palladium(nickel) with lattice parameter a = 0.3858 nm turns gradually into palladium(platinum) solid solution. The lattice parameters of the palladium(platinum) solid solution increase with the increasing platinum:palladium ratio. The nickel solute in the initial palladium(nickel) solid solution is completely oxidised to NiO. In the early stages of recrystallisation, that is during the formation of new crystals of palladium(platinum) solid solution, ladder-like growth is the main mechanism; while in the later stages, during the growth of new crystals, screw-type growth plays an important role.

Acknowledgement

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References

1 J. E. Philpott, *Platinum Metals Rev.*, 1971, **15**, (2), 52
2 J. P. Contour, G. Mouvier, M. Hoogewys and C. Leclere, *J. Catal.*, 1977, **48**, 417
3 J. Pielaczek, *Platinum Metals Rev.*, 1984, **28**, (3), 109
4 A. R. McCabe and G. D. W. Smith, *Platinum Metals Rev.*, 1988, **32**, (1), 11
5 T. L. G. Fierro, J. M. Palacios and F. Tomas, *Surf. Interface Anal.*, 1988, **13**, 25
6 M. Rubel, M. Pszonicka and W. Palczewska, *J. Mater. Sci.*, 1985, **20**, 3639
7 M. Rubel and M. Pszonicka, *J. Mater. Sci.*, 1986, **21**, 241
8 H. Holzmann, *Platinum Metals Rev.*, 1969, **13**, (1), 2
9 A. E. Heywood, *Platinum Metals Rev.*, 1973, **17**, (4), 118
10 A. E. Heywood, *Platinum Metals Rev.*, 1982, **26**, (1), 28
11 R. W. Hatfield, B. S. Beshty, H. C. Lee, R. M. Heek and T. S. Hsing, *European Patent* 77,121A; 1982
12 J. L. G. Fierro, J. M. Palacios and F. Tomás, *Platinum Metals Rev.*, 1990, **34**, (2), 62
13 J. L. G. Fierro, J. M. Palacios and F. Tomás, *Surf. Interface Anal.*, 1989, **14**, 529
14 Z. Yang, Y. Ning and H. Zhao, Research to be published on constituent and surface state of palladium catchment gauze in ammonia oxidation apparatus