

The Structure of Catalyst Gauzes after Hydrogen Cyanide Production

A POSSIBLE EXPLANATION FOR THE FACETED FEATURES

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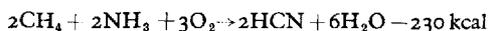
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During hydrogen cyanide production by the Andrussow process considerable redistribution of the surface of the rhodium-platinum gauze catalyst occurs, resulting in the formation of a porous mass of well-faceted metal crystallites. The phenomenon is illustrated in this paper, and some possible mechanisms to account for its formation are discussed.

Rhodium-platinum alloy gauzes feature prominently in two important manufacturing processes, the catalytic oxidation of ammonia to nitric oxide in the production of nitric acid, and the Andrussow process for making hydrogen cyanide from methane and ammonia. Although direct reaction of the latter constituents is possible via:



and has been employed on a large scale (1), the reaction is strongly endothermic, and supplying the heat to maintain the reaction temperature of 1000 to 1200°C makes it inconvenient. In the Andrussow process (2), methane, ammonia and air are reacted by passing the mixture through a pack of 10 per cent rhodium-platinum gauzes woven in similar mesh and wire sizes to those used for ammonia oxidation namely 0.076 mm × 1024 meshes/cm². Under these conditions the self-sustaining reaction:



takes place giving hydrogen cyanide yields of 85 to 90 per cent at about 1200°C.

Consequently both ammonia oxidation and hydrogen cyanide production are high temperature catalytic processes using platinum alloy gauze, and a further common feature is the considerable restructuring of the gauze

surface that occurs during operation. Much has already been written in this journal (3, 4, 5) on the surface effects on gauzes used for ammonia oxidation, but little attention has been paid to gauze packs used in hydrogen cyanide production. At the Johnson Matthey Research Centre we have recently had occasion to examine in detail gauzes that had been used in long campaigns in the Andrussow process. These gauzes showed some unusual features, not found in those from ammonia oxidation and which have not been satisfactorily explained by earlier workers (6, 7, 8, 9) on rhodium-platinum catalysts. This paper presents some new proposals to account for certain of the extreme restructuring effects found in the gauzes now examined.

Gauze Examination

After exposure for about 1200 hours in the hydrogen cyanide reactor, the 10 per cent rhodium-platinum gauzes of the pack had changed from a shiny open mesh, shown in Figure 1, to a matt grey appearance with significantly reduced open area, Figure 2. The upstream gauze of the pack showed these effects most markedly, while less modification of the trailing gauze had occurred, Figure 3. Unlike gauzes used in ammonia oxidation which retain a measure of ductility after the campaign and can usually be separated for

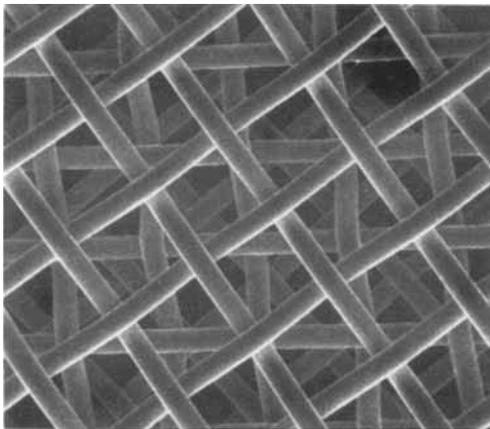


Fig. 1 An unused 10 per cent rhodium-platinum gauze, 0.076 mm diameter wire $\times 1024$ meshes/cm², shows the smooth appearance of the surface of the wire and the open mesh of the gauze $\times 40$

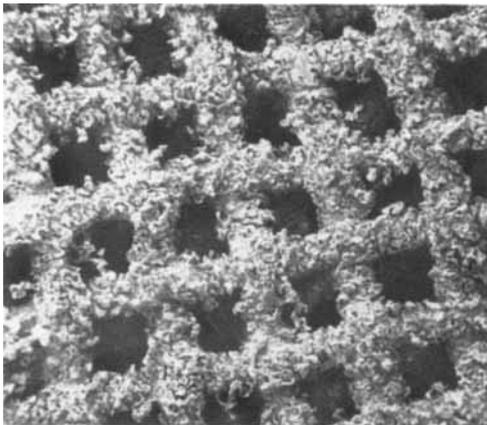
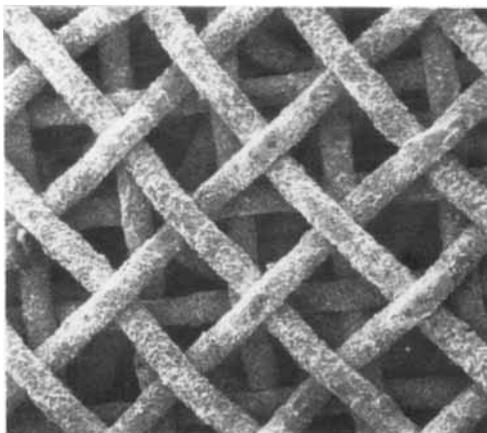


Fig. 2 After prolonged exposure in the Andrussov process the leading gauze in the pack has a matt appearance and the apertures of the gauze have been considerably reduced $\times 40$



reclamation, the gauze pack had effectively sintered into a solid mass and after use behaved in a brittle fashion. Metallographic examination of cross sections of the leading gauze showed that the metal of the wire had been converted into a porous mass, Figure 4, the porosity frequently penetrating the whole cross-section of the wire. As a result the wire had effectively doubled in volume, as is apparent in Figure 2. The degree of penetration of this porosity was reduced towards the trailing side of the pack, the last gauze showing that a substantial core of solid wire was still present with restructuring of the surface layer confined to a depth of about 10 to 20 per cent of the wire diameter, Figure 5.

Scanning electron microscopy at higher magnifications revealed considerable detail of the dramatic changes that had occurred at the wire surface. Views of the leading gauze are shown in Figures 6 (a) to (d). It will be seen that the wire had been converted into a mass of crystallites, many with well-developed pyramidal faces. Crystal sizes are typically 10 to 30 μm , similar to the grain size of the original wire. The extremely open nature of the structure is apparent in Figure 7 (a) taken from a fractured wire end, Figure 7 (b) being a region near the wire centre. As may be seen, the compact metal has been converted into a structure of almost completely separated crystallites.

The gauze at the outlet or downstream side of the pack showed some rearrangement but to a considerably less extent than the leading gauze, Figure 8 (a). The wires had increased in diameter by about 25 per cent, mainly due to deep hole formation near the wire surface, details being shown in Figure 8 (b). In addition,

Fig. 3 The trailing gauze in the pack shows less modification, to both the surface of the rhodium-platinum wire and to the size of the apertures, than the upstream gauzes $\times 40$

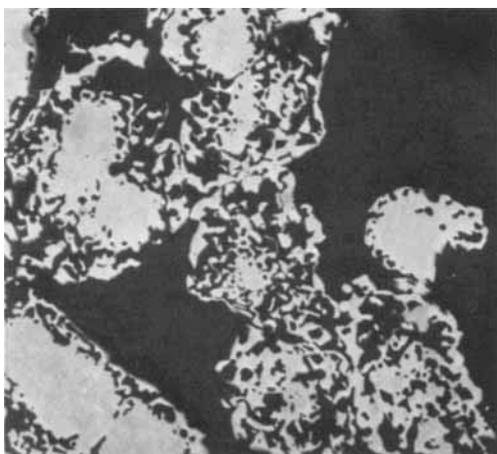


Fig. 4 A metallographic section of the leading gauze reveals extensive porosity, which may penetrate right through the wire ×115



Fig. 5 A section through the trailing gauze of the pack shows the wire to consist of a solid core surrounded by a porous layer ×140

tion to these holes, traces of grain boundaries associated with the holes can be distinguished in the photomicrographs.

Restructuring Mechanisms

The process whereby an essentially homogeneous rhodium-platinum alloy wire is converted into a mass of crystallites is to say the least an unusual phenomenon, and is worthy of detailed consideration. Such discrete crystalline structures are often observed when a metal is deposited from the vapour state, by electrolysis, or from solution, but the formation of a low density agglomerate from the compact material is contrary to normal metallurgical observation.

In the field of catalysis it has been abundantly demonstrated that reactions taking place on metals can cause enhanced migration of surface atoms, but the precise mechanism by which this occurs is still a matter of debate. Exposing the surface to the reactant gases singly causes only very little diffusional movement, giving rise to effects akin to thermal etching such as grain boundary grooving and step formation. When, however, a reaction is being catalysed in particular at platinum surfaces, massive transfer of material may take place, and indeed one of the major aspects of supported noble metal catalyst

design is aimed at preventing movement of this type which gives rise to particle agglomeration and thence loss of active surface area.

The synthesis of hydrogen cyanide over rhodium-platinum gauze catalysts has been the subject of a detailed investigation by Pan (6). Morphological changes similar to those described in the present paper were observed, but no explanation was given of their origin. Pan also reports face-centred tetragonal and face-centred orthorhombic phases in used gauzes. Such structures have not previously been found in the rhodium-platinum alloy system, and from the fact that the axial ratios given for these phases are near unity, it is more likely that some changes in rhodium concentration had occurred during the surface restructuring. The resultant X-ray diffraction pattern from face-centred cubic phases of different lattice spacings could then be erroneously interpreted as orthorhombic or tetragonal. It is interesting to note that unlike ammonia oxidation, in the production of nitric acid, the losses of rhodium and platinum from the gauze during hydrogen cyanide synthesis are very small.

Schmidt and co-workers (7, 8, 9) have reported several recent studies of surface effects on platinum or platinum alloys during catalytic reactions, including a study of

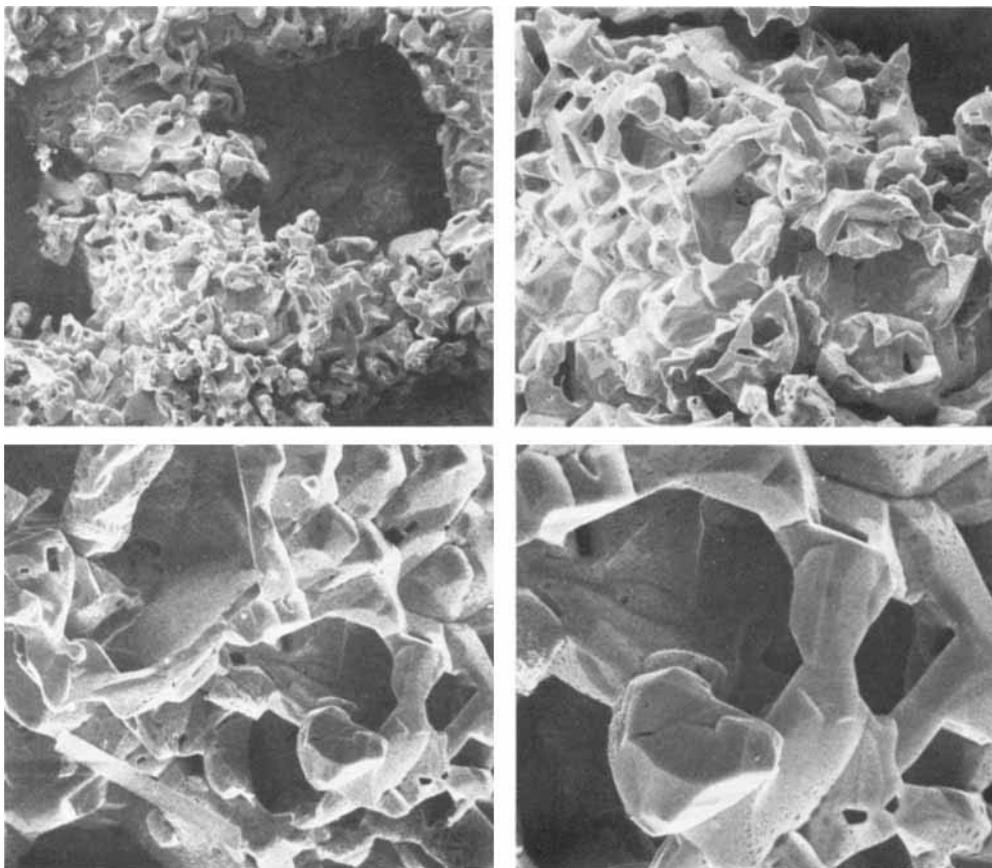


Fig. 6 Scanning electron micrographs of the leading gauze of the pack show that the formerly solid wire has been transformed into a mass of crystallites, many with well-developed pyramidal faces (a) top left $\times 150$, (b) top right $\times 375$, (c) bottom left $\times 750$, (d) bottom right $\times 1500$

hydrogen cyanide gauzes. Various mechanisms are proposed for the enhanced mobility of the surface atoms. The platinum oxide, PtO_2 , entering the vapour phase is a probable source of metal loss in ammonia oxidation over rhodium-platinum gauze, but in view of the very small losses normally encountered in hydrogen cyanide production vapour transfer via this oxide phase appears unlikely. Normal bulk diffusion or surface diffusion processes are also known to be too slow to account for the rapid transport.

The explanation therefore appears to lie in the exothermic reaction occurring at the catalyst surface between an adsorbed oxygen atom and ammonia or methane. During this reaction some of the heat liberated results in

energetic or activated platinum atoms at the surface. These atoms lose energy by collision and come to rest at some low energy state on the surface, usually as a low energy crystal plane. In face-centred cubic metals the plane of lowest energy is the (111) plane, but the presence of adsorbed species on the surface may modify the situation so that a wide range of higher index planes may be revealed. For example recent work on single crystal platinum spheres has shown that under certain conditions in ammonia oxidation (421) planes may predominate (8).

We may now consider what features of the initial metallurgical structure of the wire lead to the formation of the final configurations observed. From a metallurgical viewpoint

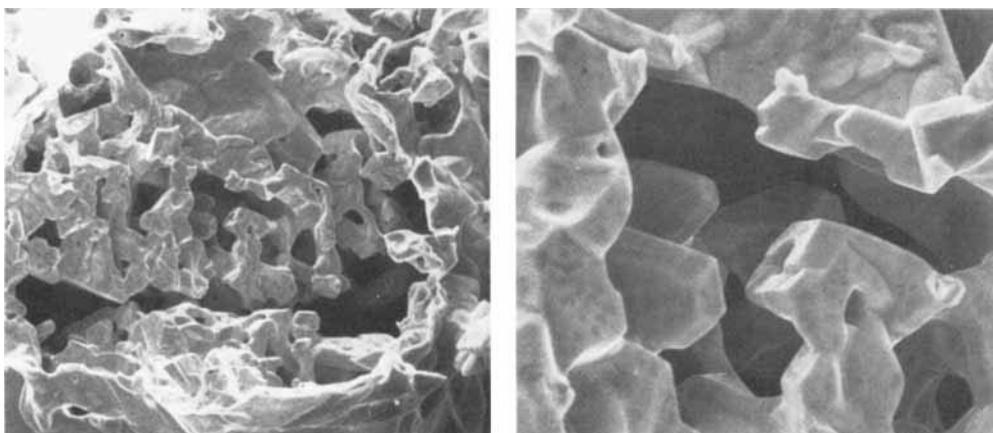


Fig. 7 Scanning electron micrographs of the cross-section of a fractured wire show the extremely porous nature of the wire, a small area at the wire centre being shown at the higher magnification (a) left $\times 425$, (b) right $\times 1750$

the 10 per cent rhodium-platinum alloy wire is essentially a homogeneous material, having a single phase face-centred cubic structure with only a small impurity content. Explanations of faceting and step formation during thermal etching and similar processes have been based on minimum energy considerations with the growth of low energy planes. Similarly etch pit formation has been associated with dislocations at the surface, but no satisfactory explanation has been given to account for the very deep channelling found in gauzes used in the Andrussow process. To do this it is necessary to recognise some structural irregularity which penetrates to a considerable depth into the metal and is likely to be attacked during the catalytic process. Two such features are known to exist, they are dislocations and grain boundaries. Typical dislocation densities in annealed metals are 10^7 to 10^8 lines/cm² and if dislocations were responsible, channels much more closely spaced than those observed would be formed.

Grain boundaries on the other hand possess the properties required. By definition a grain boundary is the meeting of two metal crystals of different orientation, and is a high energy or strained region of the structure where the atoms do not have the normal number, arrangement or separation of nearest neigh-

bours. The considerable contribution of the grain boundaries to the total energy of the structure is apparent from measurements that have been made on the heat evolved during grain growth of fine grained samples. No data is available for platinum or rhodium-platinum alloys but by comparison with other high melting point metals, a grain boundary free energy of about 700 ergs/cm² may be expected (10). This represents the excess energy associated with the two dimensional regions between individual metal crystals, but it seems a reasonable extrapolation to consider that the grain edge, where three grains meet and which is a linear discontinuity in the metal, represents an even higher energy region of the structure. It is therefore postulated that attack commences along grain edges, in particular at edges where large orientation differences exist and where the grains are favourably aligned to the surface. This is illustrated as an idealised metallographic structure in Figure 9. In the original structure (a) grain edges intersect the surface at points, and attack starts (b) at some of these. The metal removed accumulates on low energy planes of the crystal and the process continues until ultimately essentially separated crystals are formed as shown in (c). This proposed mechanism is compatible with

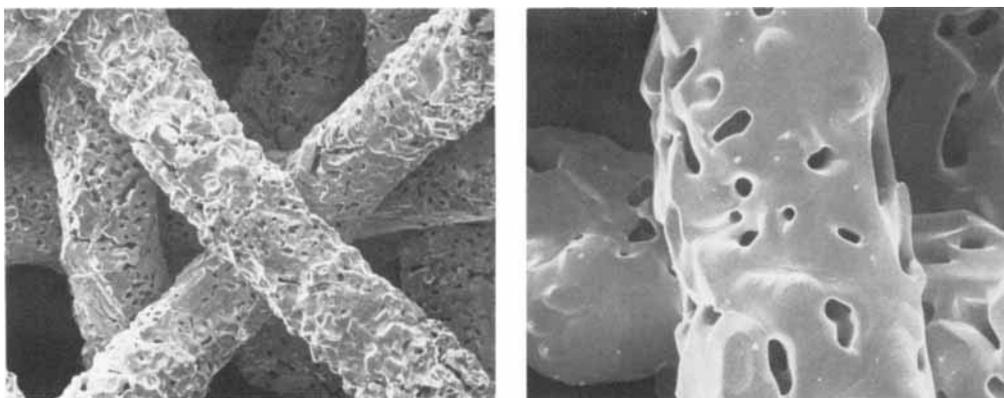


Fig. 8 The gauze on the downstream side of the pack shows some rearrangement, although this is considerably less than on the leading gauze. The diameter of the wires has increased due to the formation of deep holes, which can be seen in greater detail in the right-hand scanning electron micrograph, and traces of grain boundaries associated with these holes may also be distinguished (a) left $\times 125$, (b) right $\times 300$

the sample shown in Figure 8 (b), in which the channels formed can be seen to be associated in many cases with grain boundaries.

The postulated mechanism may therefore be summarised as a redistribution of metal by the catalytic process which occurs most rapidly at grain edges, and continues with the formation of stable crystal faces with the almost complete elimination of grain boundaries. This suggests that the specific surface energy of the grains with well-developed crystal facets is less than the grain boundary energy, an unusual state of affairs when it is

generally found that the grain boundary free energy is about $0.3 \times$ mean surface free energy of the metal (10). However this may be rationalised by assuming that these relationships are grossly modified in the presence of adsorbed species and catalytic reactions taking place at the surface and that under these conditions the crystal faces are particularly stable. This is supported by the sharp corners and edges found on the crystals, see Figure 7 (b) for example. Although perturbation of the metal atoms during reaction occurs on these faces by the mechanisms already mentioned,

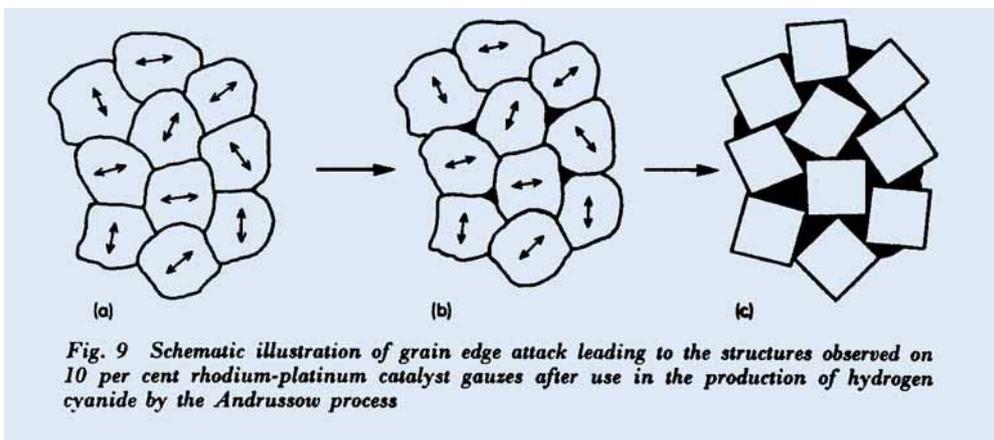


Fig. 9 Schematic illustration of grain edge attack leading to the structures observed on 10 per cent rhodium-platinum catalyst gauzes after use in the production of hydrogen cyanide by the Andrussov process

these atoms essentially come to rest on the same low energy planes. There is hence little tendency to the formation of other configurations, and after the perturbation the crystal face is virtually unchanged.

A further curious feature from a metallurgical viewpoint is the absence of any marked grain growth—that is increase in crystal dimensions—during the restructuring process. In metals it is usual to observe grains increasing in size under conditions of high atomic mobility, as occurs for example during annealing at elevated temperatures. The driving force for this grain coarsening is normally considered to be the reduction of grain boundary area, with the consequent reduction in total free energy of the structure. Similarly in systems consisting of isolated particles, such as the precipitated phase from a metallic solid solution, growth will occur in the larger particles at the expense of smaller ones, also due to the reduction in particle

surface area and thence of the surface energy contribution. The absence of any significant crystal growth in the gauze samples is perhaps further evidence of the low surface energy or remarkable stability exhibited by the crystal facets in the catalytically reacting environment.

From this qualitative discussion it will be apparent that considerable scope exists for further investigation of the detailed mechanism of restructuring of the rhodium-platinum catalyst in hydrogen cyanide production, and for quantifying the energy relationships between grain boundaries, various crystal planes, and so forth, in the alloy. If the ideas outlined prove to be correct, it would be possible in principle to produce a dimensionally stable Andrussow catalyst from a collection of suitably faceted crystallites. However the economic practical realisation of such a material may be difficult to achieve, except perhaps in a fluidised bed.

References

- 1 F. Endter, *Platinum Metals Rev.*, 1962, **6**, (1), 9
- 2 J. M. Pirie, *Platinum Metals Rev.*, 1958, **2**, (1), 7
- 3 J. E. Philpott, *Platinum Metals Rev.*, 1971, **15**, (2), 52
- 4 N. H. Harbord, *Platinum Metals Rev.*, 1974, **18**, (3), 97
- 5 R. T. K. Baker, R. B. Thomas and J. H. F. Notton, *Platinum Metals Rev.*, 1974, **18**, (4), 130
- 6 B. Y. K. Pan, *J. Catalysis*, 1971, **21**, (1), 27
- 7 L. D. Schmidt and D. Luss, *J. Catalysis*, 1971, **22**, (2), 269
- 8 M. Flytzani-Stephanopoulos, S. Wong and L. D. Schmidt, *J. Catalysis*, 1977, **49**, (1), 51
- 9 R. W. McCabe, T. Pignet and L. D. Schmidt, *J. Catalysis*, 1974, **32**, (1), 114
- 10 M. C. Inman and H. R. Tipler, *Metall. Rev.*, 1963, **8**, (30), 105

Platinum Silicide Fuses Provide Rapid Response

The electronics industry has produced another significant advance in the technology of semiconductor devices. Recently reported work by Advanced Micro Devices, Sunnyvale, California, has produced programmable read only memory (PROM) fuses which utilise platinum silicide fuse links on low power Schottky chips (*Electronic Design*, 1978, **26**, (7), 23).

Nickel-chrome fuses are most commonly used, together with titanium-tungsten or phosphorus-doped polysilicon materials, but the advantages of platinum silicide have been shown by life tests extending to two billion fuse hours without a single fuse oriented failure. Such fuses are, of course, blown when

the surface tension of the molten fuse material divides the fuse link and draws the material back. In the case of platinum silicide the gap formed may be 1 to 3 microns, some ten times longer than that formed by nickel-chrome materials.

The physical properties of platinum silicide—it is considerably harder, less ductile and has greater chemical inertness than the other metal systems—together with the width of the gap formed, retard the regrowth of the fuse link.

With a recommended programming time of only 50 microseconds, compared to 2 milliseconds for typical nickel-chrome PROMs, the fuses have obvious advantages.