Copper and Nickel Alloys Clad with Platinum and Its Alloys

THE IMPORTANT INFLUENCE OF DIFFUSION

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Cladding base metals with platinum or platinum alloys offers certain technical and economic advantages. In an earlier paper the mechanical properties of the metals to be joined were discussed. In this second paper it is shown that interdiffusion of the two materials being joined together must be considered, and that if the partners have different diffusion coefficients difficulties can result during later production stages. This is especially true if voids form in the diffusion zone due to the Kirkendall effect. This effect is particularly pronounced when copper alloys are used as the base metal, however it can be avoided either by using nickel-rich alloys or by incorporating an electrodeposited intermediate nickel layer of suitable thickness.

The mechanical cladding of non-precious metals or their alloys with precious metals, especially gold and gold alloys, is well established. The technology was first developed for jewellery applications, where to some extent it was later replaced by electroplating. However growth in the electronics industry resulted in a revival of mechanical cladding for selectively coating copper- or nickel-based materials with precious metal-containing alloys for contact applications. In the main gold or palladium alloys were used for this application. Mechanical cladding enables a wide range of thicknesses, from 1μm upwards, and a nearly unlimited selection of alloys to be used. Since the process involves alternating mechanical deformation and heat treatment, to improve the adhesion of layers, important parameters are the deformation characteristics and the diffusion behaviour of the metals concerned.

In the first part of this two paper series we discussed and compared the deformation characteristics of base metal alloys with those of platinum and platinum alloys, which are of interest from a cladding point of view. It was shown that it is possible to select combinations that are well suited to this process (1). Now, in this second part we will discuss the diffusion behaviour between the various components, and its importance to the cladding process.

Experimental Work

Initially attempts were made to join platinum sheet, 0.5 to 1mm thick, to the respective base material by cold rolling. To enable the sandwiched materials to be reduced by rolling it was necessary to improve the adhesion of the two layers immediately after cladding, by heat treatment. It was established that if this annealing was carried out at temperatures above 650°C for about 0.5 hours in a vacuum better than 10^{-4} torr the adhesion was very poor, indeed it appeared to be worse than before the heat treatment. On samples annealed at temperatures above 700°C for 0.5 hours it was observed in all cases that the platinum had separated from the copper base. The platinum sheet—at 0.5mm much thinner than the 2.0mm copper base—appeared torn and heavily wrinkled. Scanning electron microscopy showed that the originally contacting surfaces now displayed characteristic features, which are shown in

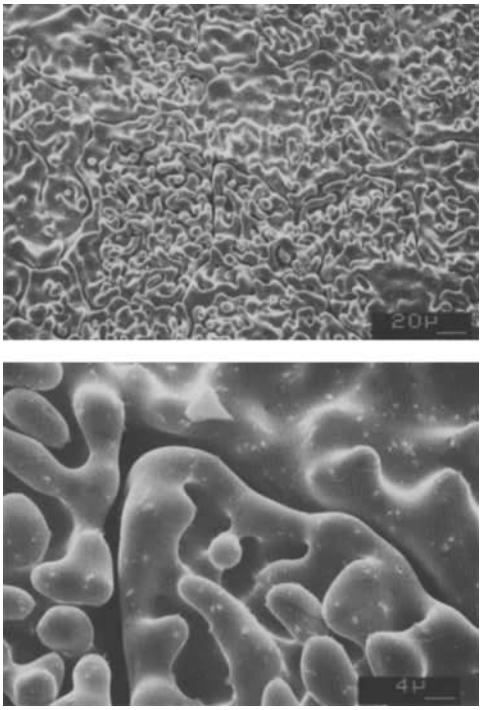


Fig. 1 When a sandwich of platinum-5 per cent iridium/copper, formed by cold rolling, was annealed for 72 hours at 800°C separation occurred. Scanning electron microscopy showed that the two surfaces which were originally in contact had now developed characteristic forms. The copper side of the diffusion zone is shown above in both electron micrographs, the magnification of both being indicated

Figures 1 and 2. It was discovered also that the separation was much less pronounced when nickel was clad with platinum. In order to check the possibility that the poor adhesion was caused by impurities—especially oxides formed during cladding—molten copper was cast onto platinum. When the resulting sandwich was rolled down to 1.2mm the adhesion remained fairly good. Additionally copper and nickel layers 1mm thick were electroplated onto platinum and/or platinum alloys, and a copper sample was platinum plated in a fused salt bath. However after heat treatment for longer than 15 minutes in the temperature range 600 to 800°C poor adhesion or even separation still occurred on all these samples.

Metallographic examination of diffused samples, heated in the critical diffusion temperature range, showed that voids had formed on or near the original contacting surfaces after only short annealing times. These are illustrated in Figure 3, which is of a sample where the voids formed after an initial diffusion treatment and were sufficient to cause separation of the platinum from the copper base. This microsection shows that both the original contacting surfaces are now rough. Due both to the stresses resulting from heat treatment and to progressive weakening as diffusion alloying caused voids to grow with time, the interface could no longer bear the load and in many places the top separated from the base. However in some areas contact between base

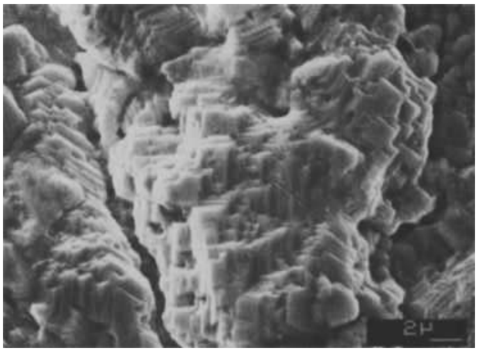


Fig. 2 The surface shown is that of platinum which has parted from the copper, to which it had been roll bonded, following annealing at 900°C for 48 hours

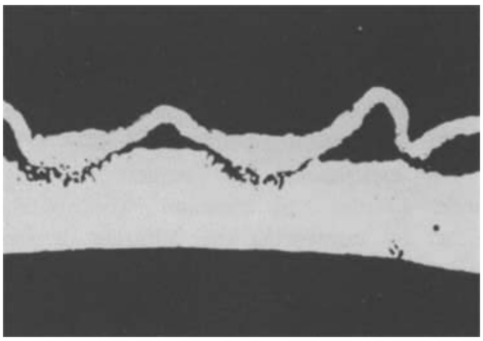


Fig. 3 Different diffusion rates have caused partial separation of the platinum layer from the copper base. The volume of the platinum has been increased and there is a zone of voids within the copper ×55

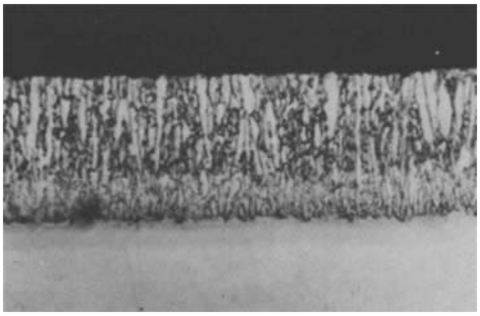


Fig. 4 This interface between platinum and electrodeposited nickel shows no hole formation after annealing for 8 hours at 700°C ×125

and top remained, and here diffusion and hole formation continued. This progressive diffusion and transfer of copper into the platinum shows up as a thickening of the platinum layer at these places, the copper-platinum alloy formed by the diffusion process being more porous than the original platinum foil (2). The separation of platinum from copper and copper based alloys, following heat treatment, is therefore an inherent problem caused by different diffusion rates or mass transfer of metals in contact with one another, the so-called Kirkendall effect (2,3). The metal with the faster diffusion rate diffuses into the other metal and leaves behind voids which are not filled by the slower diffusion of the other metal. Eventually the voids combine along the diffusion interface to produce the type of structure shown in Figure 3, and thus the adhesion gets worse.

This also explains the observation, shown in Figure 4, that the Kirkendall effect is less with a nickel base, since the diffusion coefficient of nickel must be smaller than that of copper due to the higher melting point of nickel.

The experiments also suggest that the order–disorder phenomenon contributes, either by influencing the diffusion or the stresses at the interface. The critical temperatures of ordering, 615°C for $PtCu_3$ and 812°C for PtCu, are a possible reason for the critical temperature range of 600 to 800°C observed during the diffusion experiments. This was not studied in detail as it was outside the scope of the research programme. It would however form a fascinating topic for further work.

In order to study the diffusion behaviour without the formation of voids produced during the initial cladding stage, the apparatus described in the earlier paper for high temperature tensile testing was used. Sandwiches of platinum and platinum alloys with base materials (each in the form of squares with sides of about 10mm) were annealed to the cladding temperature—which in most cases corresponded to the later annealing temperature—and held for 15 minutes at a pressure of 1 to 8kN. After the pressure was released and the sample cooled, the adhesion was good in all cases. Typical microstructures of the diffusion zones produced in this way are shown in Figure 5. These "pressed" samples were generally annealed without pressure so that the hole formation could be observed, and so that the conditions approximated to those likely to be met with in service. They could, however, have been carried out under pressure in the tensile testing machine.

During pressing a nitrogen/2 per cent hydrogen atmosphere was used, and later annealing was carried out in a vacuum better than 10^{-5} torr. All samples were cold rolled after the diffusion processes, and in general the reduction prior to an annealing step was at least 50 per cent.

In a series of experiments we established the best conditions for obtaining good adhesion of pressed samples. For the alloys under consideration annealing at 700°C for 20 minutes while pressurised at 5kN was found to produce the best results. At lower loads or for shorter times the adhesion between the platinum component and the base metal could be poor.

Good joining, that is where there were few or no pores, occurred with the following systems: (i) copper/platinum, (ii) copper-25 per cent nickel/platinum, (iii) copper-25 per cent nickel/platinum-5 per cent cobalt, and (iv) copper-25 per cent nickel/platinum-5 per cent iridium.

Difficulties occurred with platinum-5 per cent cobalt/copper or copper-tin (6 or 8 per cent).

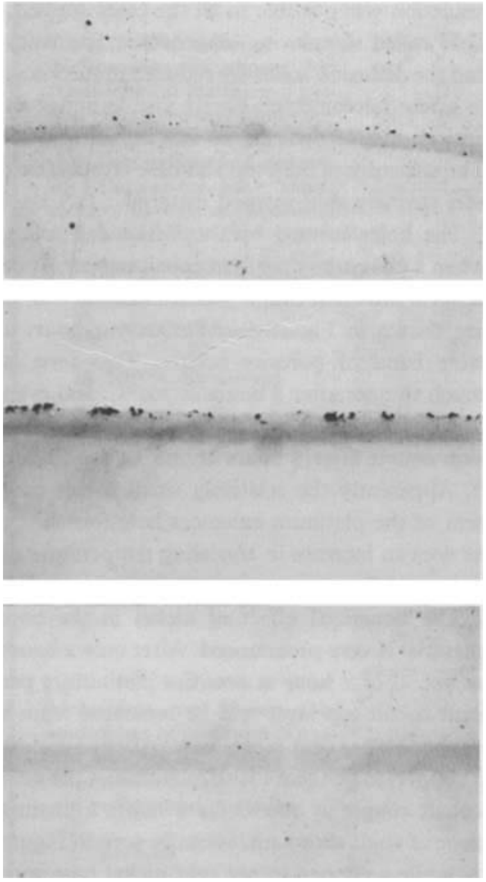


Fig. 5 **Unetched microsections showing the diffusion zones produced when sandwiches of noble metal and base have been annealed at 700°C for 20 minutes under 5kN pressure, followed by cooling to normal pressure. The platinum-rich layers are on top in each case ×275**
(a) Platinum/copper
(b) Platinum-5 per cent cobalt/copper
(c) Platinum-5 per cent iridium/copper-25 per cent nickel

In order to show the various degrees of void formation that occurred during diffusion or pressure welding, microsections of diffused sandwiches were photographed in the unetched condition. Furthermore, etching revealed the characteristic diffusion tails caused by the increased diffusion rates along grain boundaries, compared to the slower rates within the lattice. This is shown in Figures 6 to 8.

The results confirm that the problems which arise when attempting to obtain good adhesion

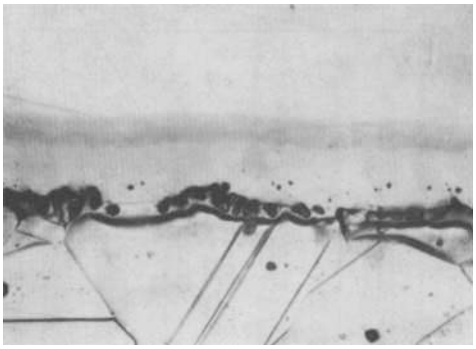


Fig. 6 **After 50 per cent cold deformation followed by annealing for 4 hours at 800°C a porous zone, resulting from the Kirkendall effect, is shown in a platinum-5 per cent cobalt/copper-8 per cent tin diffusion couple ×275**

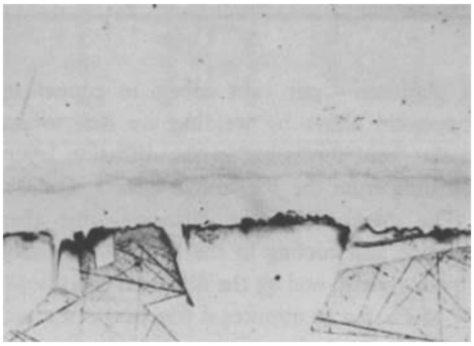


Fig. 7 **After 50 per cent cold rolling followed by annealing at 700°C for 8 hours the porous zone in this platinum/copper-8 per cent tin diffusion couple is thinner than that shown above in Figure 6 ×275**

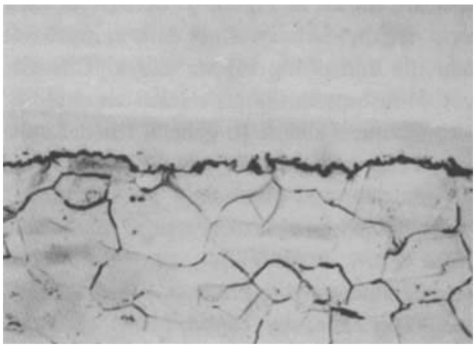


Fig. 8 **Following 50 per cent cold deformation and annealing for 8 hours at 700°C the diffusion zone of this copper-20 per cent nickel base and platinum-5 per cent cobalt top layer contains a zone of porosity, but this is narrower than those shown in Figure 6 and 7 ×275**

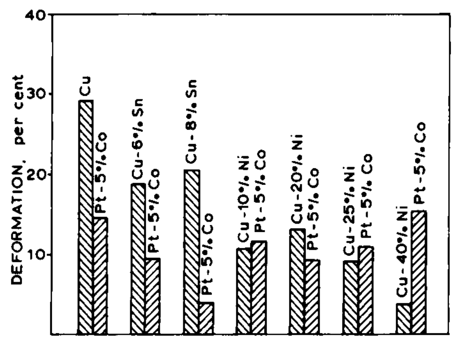


Fig. 9 Deformation ratios observed in diffused sandwiches with platinum-5 per cent cobalt as the top layer on copper and copper alloy bases, after annealing for 20 minutes at a temperature of 700°C under 7kN pressure

of platinum-5 per cent cobalt to copper or copper-tin alloys by welding are due to excessive void formation in the diffusion layer, resulting from the Kirkendall effect.

The thickness of the diffusion zone after pressing and cooling in the furnace depended on the system, and on the diffusion conditions. At 700°C for 20 minutes it was between 2 and 9μm. During the hot welding stage the different metals in the diffusion couples are compressed differently, depending on their hot strengths (1). The deformations observed in the diffusion pairs with platinum-5 per cent cobalt as the top layer are shown in Figure 9. Because of their hot strength, platinum alloys deform much less than the underlying copper alloys. This also may contribute to the poor adhesion observed with platinum alloys. In general the deformation of copper-nickel alloys is similar to that of the platinum and platinum-5 per cent cobalt top layers. When a pressure welded sandwich is rolled down, a platinum-5 per cent iridium alloy exhibits only 50 per cent of the deformation experienced by copper-nickel alloys. A platinum/copper sandwich pressed at 700°C for 20 minutes with 7kN showed a 60 per cent reduction in thickness of the copper but only 10 per cent for the platinum. After diffusion welding, cold rolling to at least 50 per cent reduction was possible in all the cases studied. Cold rolled samples no longer show any voids and the diffusion zones are reduced in thickness to a few micrometres; barely visible under an optical microscope at ×1000 magnification. The structure of both top and base layers is that of a strongly cold worked material.

The holes formed by the Kirkendall effect when a platinum-5 per cent cobalt/copper-8 per cent tin diffusion couple was annealed at 800°C are shown in Figure 6. After only 4 hours a wide band of porosity occurs. This zone is much thinner after 8 hours at 700°C, and even less in a copper-8 per cent tin/platinum diffusion couple after 8 hours at 700°C, see Figure 7. Apparently the relatively small cobalt content of the platinum enhances hole formation, as does an increase in annealing temperature of only 100°C.

The beneficial effect of nickel in the base material is very pronounced. After only 2 hours at 700°C or 1 hour at 800°C a platinum-5 per cent cobalt top layer will be separated from a copper-10 per cent nickel base. After annealing a copper-20 per cent nickel/platinum-5 per cent cobalt couple at 700°C for 8 hours a distinct zone of voids shows up, as can be seen in Figure 8, while a copper-40 per cent nickel base with a platinum or platinum-5 per cent cobalt top layer shows practically no hole formation after annealing at 700 or 800°C for 6 and 8 hours.

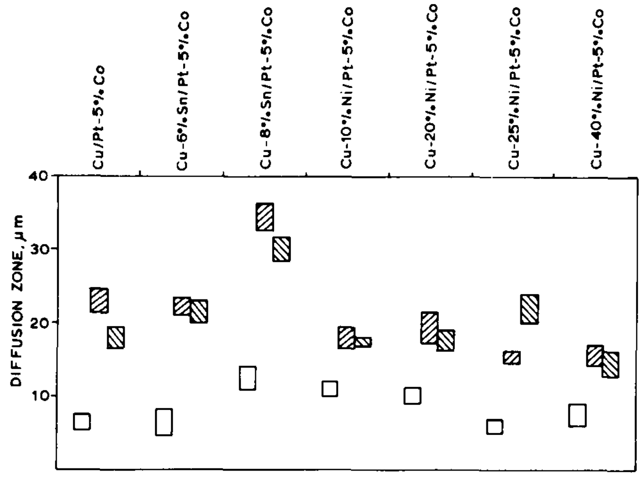
The growth rates of the diffusion layers between various copper-based materials and platinum-5 per cent cobalt and platinum-5 per cent iridium, after annealing 50 per cent cold worked samples at 700°C for 8 hours and 800°C for 4 hours, are shown in Figures 10 and 11, respectively. In general the results are widely scattered, due to the non-uniform formation of the layers caused by holes. Nevertheless it can be stated that in general copper-tin alloys exhibit the widest diffusion zones and that the width of the zone increases with tin concentration. The copper-nickel alloys generally have the narrowest diffusion zones. Apparently the growth of the diffusion zone decreases at higher nickel concentrations; this confirms the observation that there is reduced porosity at the

Fig. 10 The diffusion zone thicknesses are shown for sandwiches of platinum-5 per cent cobalt top layers on copper and copper-based alloys after cold rolling and annealing. Copper-tin base sandwiches have the broadest diffusion zones

□ **pressed**

▨ **800°C 4h anneal**

▧ **700°C 8h anneal**



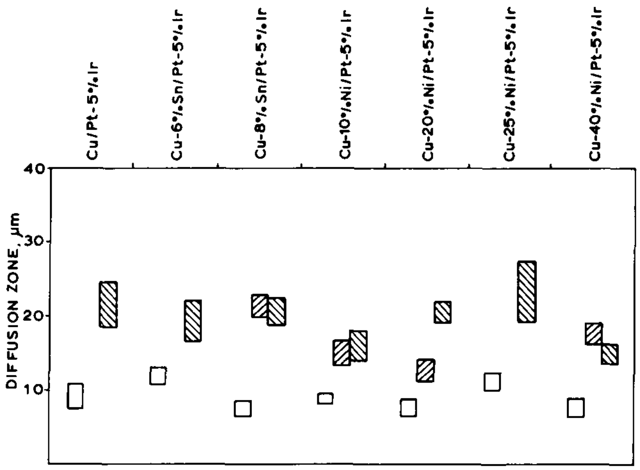


Fig. 11 Diffusion zone thicknesses are shown for sandwiches of platinum-5 per cent iridium on copper and copper-based alloys after cold rolling and annealing

□ **pressed**

▨ **800°C 4h anneal**

▧ **700°C 8h anneal**

higher nickel concentrations. In general there is less diffusion after 8 hours at 700°C than after 4 hours at 800°C.

The widest diffusion zone, 35μm, occurs in the system platinum-5 per cent cobalt/copper-8 per cent tin after 4 hours at 800°C. The narrowest zone was 13μm, which was observed in copper-40 per cent nickel with platinum and platinum alloys forming the top layer, after 8 hours at 700°C. If one assumes parabolic growth rates according to the equation: $X = \sqrt{2Dt}$ (where X is the thickness of the diffusion zone, t the annealing temperature and D the diffusion coefficient) then the values obtained for D are 4×10^{-10} cm²/s at 800°C and 3×10^{-11} cm²/s at 700°C. These figures are remarkably close to the ones given elsewhere for the platinum/copper system, which were about 3.5×10^{-11} cm²/s at 850°C and 1.5×10^{-11} cm²/s at 700°C (2).

The concentration/distance curves, as determined by electron microprobe analysis for copper-8 per cent tin/platinum, copper-25 per cent nickel/platinum-5 per cent cobalt and copper/6μm electroplated nickel/platinum are shown in Figures 12, 13 and 14. Across the diffusion layer the concentration gradient for copper is much flatter than that of the platinum, showing that copper diffuses faster into platinum or nickel than vice versa. On the other

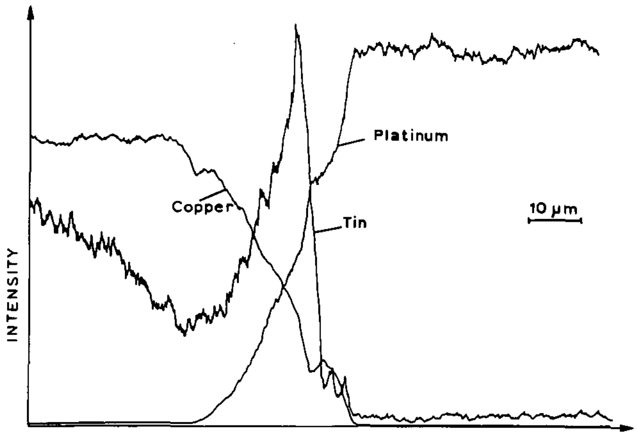


Fig. 12 Shown here are the three concentration/distance profiles across a diffusion zone of a pressure welded 50 per cent cold rolled platinum/copper-8 per cent tin sandwich after annealing at 800°C for 4 hours

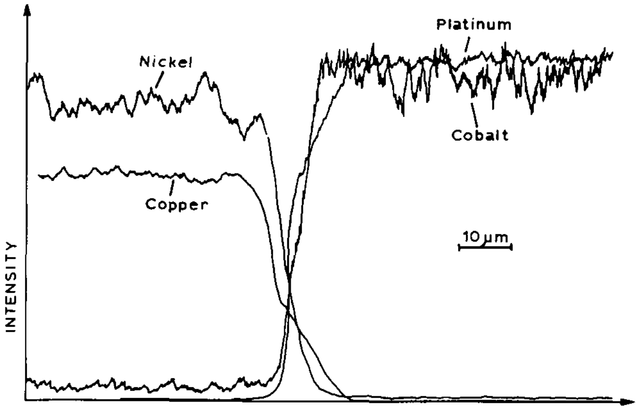


Fig. 13 These are the concentration profiles across the diffusion zone of a pressure welded platinum-5 per cent cobalt/copper-25 per cent nickel sandwich 50 per cent cold rolled after annealing at 700°C for 4 hours. The concentration gradient for copper is much flatter than that of platinum

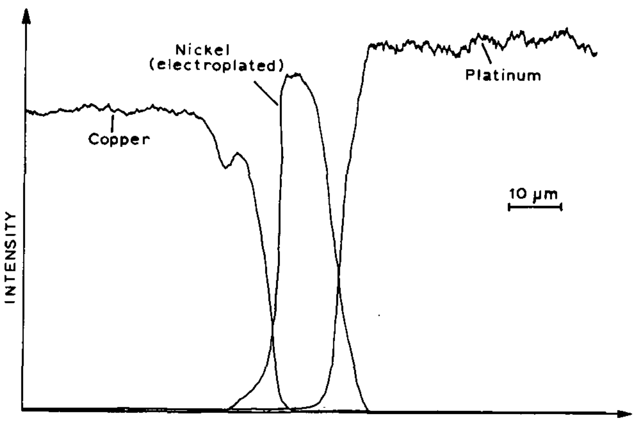


Fig. 14 The concentration/distance profiles of a diffusion zone for a pressure welded copper/electroplated nickel/platinum sandwich are shown after 50 per cent cold rolling and annealing at 700°C for 8 hours. The dip in the copper curve is due to the porous zone

hand cobalt seems to have diffused even less than platinum. The irregularities on the copper curves are explained by the hole formation. From similar measurements made on platinum top layer diffusion couples it is concluded that platinum and also cobalt form a tin-rich intermediate phase on diffusion with copper-tin alloys. Apparently the cobalt "getters" some of the tin away, forming a platinum-(cobalt-copper)-tin phase faster than platinum does on its own. As yet it is not known if this platinum-(cobalt-copper)-tin layer is a true separate intermediate phase, but it will be studied later.

The Vickers microhardness of these ternary platinum-cobalt-tin or quarternary platinum-(cobalt-copper)-tin phases is about 380 HV, significantly higher than those of the starting metals. It is surprising that this high hardness of the diffusion layer did not show up as an adhesion problem during cold rolling of the diffused sandwiches.

From the gradients of the relevant elements, shown in Figure 13, platinum and cobalt seem to diffuse differently, as do copper and nickel. Apparently there is a relationship between the changing slope of the copper and of the cobalt curves near the top layer, since the platinum and nickel curves show no change in the gradient of their concentration/distance curves. From Figure 14 one can deduce that nickel and platinum diffuse evenly into each other. But during copper/nickel diffusion the well known Kirkendall holes form within the copper, as is shown in the dip of the copper curve on the concentration/distance graph, see Figure 14.

Conclusions

Investigations of the diffusion behaviour of various copper- and nickel-based components in contact with layers of platinum, platinum-5 per cent cobalt and platinum-5 per cent iridium have been made by various methods, and have shown a consistent picture of pronounced diffusion of copper into platinum. This causes voids to form on the copper side of the interface due to the Kirkendall effect and results in adhesion problems. However these can be overcome by using nickel as the base metal, by incorporating an electrodeposited nickel layer or by using a nickel-rich copper-nickel alloy.

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Hydrogen Permeability at Elevated Temperatures

The study of the reactivity of minerals in fluid media under conditions of high temperature and pressure has important implications for their industrial utilisation. In such hydrothermal experiments the precious metals are commonly used as containment materials; platinum and silver-palladium being employed as semi-permeable membranes for hydrogen while gold and silver serve as hydrogen barriers. To date the lack of reliable data on the permeation rates of hydrogen has caused difficulties in the selection of materials and experimental conditions.

Now, however, a study by I-Ming Chou of the U.S. Geological Survey has remedied this deficiency *(Am. J. Sci.*, 1986, **286**, 638–658). Using an oxygen-buffered, double capsule technique, Chou has measured the permeation of hydrogen through platinum, two silver-palladium alloys, gold, and silver at a pressure of 2 kilobar (29,000 psi, 200 MN/m^2) in the temperature range 450 to 812°C. He showed that the permeabilities lie in the order:

$$Pd_{30}Ag_{70} > Pd_{20}Ag_{80} > Pt > Ag > Au$$

The activation energies increase in this order.

This study shows that the addition of palladium to silver increases its hydrogen permeability exponentially, and extends the data on the silver-palladium system, where the palladium-rich alloys are used commercially as diffusion membranes for the purification of hydrogen. C.W.C.