Copper and Nickel Alloys Clad with Platinum and Its Alloys

JOINING TECHNIQUES AND MECHANICAL PROPERTIES

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Technical and economic considerations have identified an opportunity for composite materials which combine certain advantageous features of both noble and base metals. During an investigation of some platinum cladding techniques and of the properties of the resulting bimetals, data have been amassed which could have relevance to industrial as well as to decorative applications. Here the effects of deformation on the separate and the combined components are considered. A later paper will indicate how problems that may result from interdiffusion of the metals can be avoided.

In contrast to other ductile precious metals such as gold, silver, palladium and their alloys, the cladding of platinum and platinum alloys onto other metals has until now found only limited technical interest. Platinum electrodeposits from an aqueous solution tend to crack at high thicknesses and only with appropriate intermediate layers can good corrosion protection be obtained (1). However, platinum layers produced from molten cyanide salts are highly ductile and offer good corrosion protection. They are used for coatings on electrodes, and by both the glass and the electronic industries (2).

In recent years there has been increasing interest in platinum and platinum alloys for decorative uses—such as jewellery and spectacle frames. In these applications they compete with gold and gold alloys which are often used in the form of mechanically clad layers on copper- or nickel-based alloys. These layers show excellent wear and ductile behaviour, and in the case of gold can be prepared in a wide range of carat alloys or colours. It therefore seemed appropriate to study the cladding behaviour of platinum and its alloys on the same base materials. Pure platinum is rarely used for jewellery because it is considered to be too soft. To increase its wear resistance up to 5 per cent iridium, ruthenium or copper is generally added, although this causes a change in colour.

About 15 years ago the Forschungsinstitut developed a platinum-5 per cent cobalt alloy for casting and general jewellery applications, for Ch. Bauer, Welzheim, West Germany. This alloy has since taken quite a share of the market due both to its excellent manufacturing properties and its colour, which matches the lustre of diamonds better than any of the other platinum alloys (3). Therefore this alloy was included in our investigations, together with pure platinum and platinum-copper and platinum-iridium alloys.

In mechanical cladding pressure and heat are applied either directly or indirectly to a sandwich of platinum and a base metal or alloy, causing diffusion which ensures very good adhesion between the two layers. As mentioned this coating technique is applicable to a wide range of alloys and also to platinum, and the platiniferous layers show excellent wear and deformation characteristics. The pressure and temperature may be applied in a separate step of the process or directly by giving a high deformation to a sandwich of the metals, with or without the use of external heat (hot or cold cladding). Both processes have their advantages and disadvantages, depending on the application and the scale of production.

The necessary annealing steps not only soften the cladding layer or the base, depending on annealing time and temperature, but may also have disadvantageous effects such as the formation of brittle intermetallic layers or porous zones caused by the different diffusion rates of the elements in the alloys, the so-called Kirkendall effect. It has been shown in our investigations that the Kirkendall effect is very pronounced in nearly all platinum containing systems and demands special process parameters to avoid adhesion problems. These factors will be considered in a second paper.

In principle industry uses two different processes (4, 5):

(i) The cold rolling process, in which base and cladding—in general not preheated—are passed through a rolling mill and a first reduction of more than 70 per cent ensures that the metals are "stuck" together. A following heat treatment causes diffusion and good adhesion between the cladding and base metal or alloy. By further rolling and heating the sandwich is then reduced to the desired dimensions, often, for example, on a reel-to-reel basis for electrical contacts.

(ii) Alternatively cladding and base alloy are welded together, with or without an intermediate layer of solder, at a specified temperature and pressure. This "package" is rolled down in a rolling mill and annealed again; by repeating the rolling and annealing steps the required dimensions are achieved.

In all cases the deformation characteristics at room temperature and at higher temperatures should be known in order to take advantage of the best deformation relationship between the cladding layer and the base metal or alloy. We therefore started our investigations on the cladding of copper- and nickel-based alloys with platinum and platinum alloys by observing the deformation characteristics of the various combinations. While the hardness/deformation and hardness/temperature curves for platinum and platinum alloys had to be determined (6, 7), those for most of the base materials could be obtained from the literature.

Since every mechanical cladding process depends upon the flow stress of the given materials at a particular temperature it is important to know this value fairly accurately. For measuring the flow stress we used the so-called cone-upsetting test.

Work Hardening and Annealing Characteristics

During these experiments samples were soft-annealed at 900°C for 1 hour and after hardness testing they were rolled down by specific amounts and their hardnesses remeasured. The work hardening behaviour at room temperature should be known as accurately as possible since

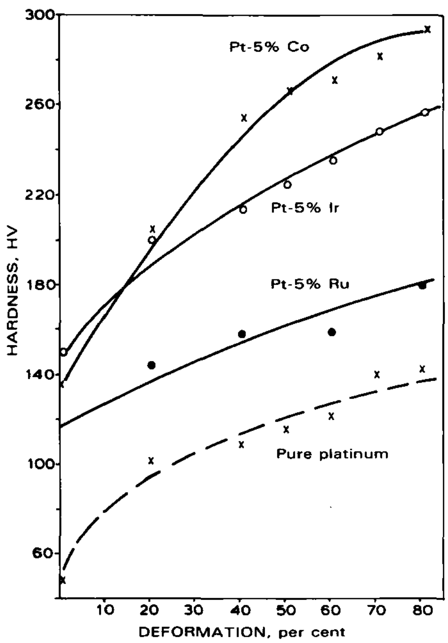


Fig. 1 The hardness of platinum and its alloys is related to the degree of deformation that has taken place. From about 20 per cent deformation the rate of increase in hardness is similar for platinum and platinum-50%ruthenium. Of the alloys examined platinum-5%cobalt shows both the greatest hardness and the greatest rate of hardening

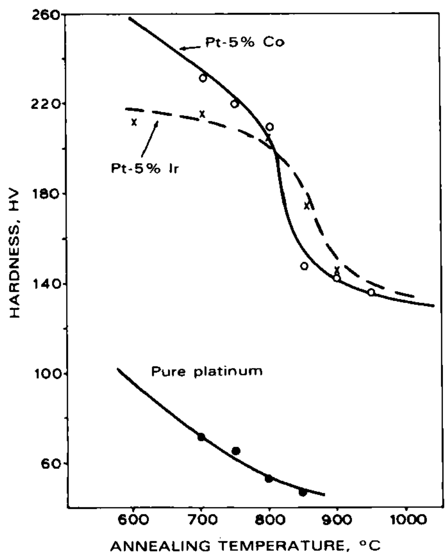


Fig. 2 The dependence of hardness upon annealing temperature is shown for platinum, platinum-5%cobalt and platinum-5%iridium, after annealing for 1 hour. The platinum-5%cobalt alloy shows a relatively steep decline in hardness when annealed at about 750°C

it determines the necessary annealing procedures. On the other hand, during annealing treatments both the cladding and the base alloys should soften in a comparable way. Therefore the hardness of deformed samples was determined in relation to the annealing temperature and time.

The results of measurements on platinum and various platinum alloys are shown in Figures 1 and 2. The work hardening curves of platinum-5 per cent cobalt, platinum-5 per cent iridium, platinum-5 per cent ruthenium and pure platinum are given in Figure 1. Platinum-5 per cent cobalt shows the greatest work hardening of all the alloys investigated. From about 20 per cent deformation platinum-5 per cent ruthenium exhibits nearly the same rate of hardness increase with deformation as pure platinum. The increase for platinum-5 per cent iridium is slightly higher than that for platinum-5 per cent ruthenium but lower than that of platinum-5 per cent cobalt. This suggests that a base which is to be clad with platinum-5 per cent cobalt should be one which has a rapid rate of deformation hardening.

The effects of annealing for 1 hour at various temperatures on 60 per cent deformed samples of platinum-5 per cent cobalt, platinum-5 per cent iridium and pure platinum are shown in Figure 2. The behaviour of the two alloys is rather similar. The greatest drop in hardness occurs at about 850°C. After annealing for 1 hour at 950°C the hardness of both alloys is nearly identical at about 140 HV. Of importance for cladding, however, is a rather steep decline in hardness, from more than 280 HV to 220 HV, which occurs if platinum-5 per cent cobalt is annealed at about 750°C, a temperature quite often used in industrial annealing furnaces.

The results confirm the observation that platinum-5 per cent cobalt alloy has good properties for jewellery fabrication, since a rather high degree of work hardening is asked for in certain applications, for example where excellent resistance to wear is required, or for diamond setting.

If one uses the as-cast condition as a comparison among all platinum alloys investigated a slight deformation will cause the highest hardness increase in platinum-5 per cent cobalt. Thus after a diffusion treatment only a slight deformation of platinum-5 per cent cobalt will be necessary to attain a hardness of 180 to 200 HV, which is most suitable for jewellery fabrication.

Deformation Characteristics at Elevated Temperatures

The quantity which best describes the characteristics of a material used for cladding is its flow stress at a given temperature. This critical hot welding temperature is between 600 and 900°C for platinum and its alloys. The flow stress may be defined as:

$$k_f = \frac{L}{A}$$

where L is the load applied and A is the cross-sectional area under consideration.

For measuring k_f we used the so-called cone-upsetting test as this is used to determine the deformation characteristics of copper-based alloys. In this test a cylinder of the material to be tested (dimensions: diameter 5 mm, height 7 mm) with conical indentations in its two plane surfaces, is compressively deformed at a given temperature and its compression is measured. In our case the sample was compressed by about 50 per cent of its original height.

The conical shape of the indentations in the base planes of the column is necessary to keep the sample cylindrical during pressing. The angle of the cone is 5° and depends on friction.

The equipment developed is shown in Figure 3. The whole apparatus can be inserted into an electronic tensile tester and can be heated in a furnace under various atmospheres. All parts of the equipment were made from heat-resistant steel. This equipment was also used to prepare clad test samples at various temperatures and pressures, after the conical plates had been replaced with flat ones.

Figures 4 and 5 show the dependence of the flow stress upon the degree of deformation, determined according to $h/h_0.100$ per cent, where h is the actual height of the sample after deformation and h_0 is the height of the sample before testing. Copper and copper-6 per cent tin show no influence of the degree of deformation upon the flow stress. The slight increase at the beginning is probably due to the experimental technique.

Above 700°C both metals are in a hot working regime. At 800°C the flow stress decreases, the decrease for copper-6 per cent tin being greater than that for copper, as shown in Figure 4. In contrast copper-25 per cent nickel shows a different behaviour. At up to 10 per cent deformation a sharp increase in the flow stress is measured, due to the effect of cold working. If this critical deformation is passed recrystallisation occurs, and the flow stress is fairly constant or even slightly decreased.

At 700°C platinum shows a flow stress/deformation dependence which is typical for cold working, where deformation takes place without recrystallisation, see Figure 5. At 800°C the k_f value remains constant after a higher degree of deformation—more than 30 per cent—due to the effect of recrystallisation.

The behaviour of platinum-5 per cent cobalt at 800°C is identical to that of pure platinum. However, at 700°C the flow stress increases markedly to a high value at a low degree of deformation; this is followed by a slight decrease, reaching a constant value at deformations greater than 30 per cent, as is evident in Figure 5.

The k_f values of the various metals and their alloys at selected deformation levels are summarised in Table I.

Technically, cladding is a process which is influenced by temperature and deformation. In

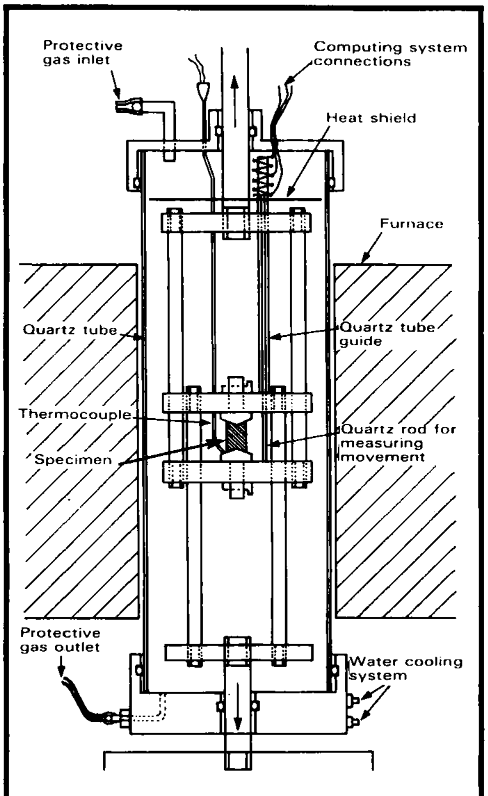


Fig. 3 Apparatus has been developed to enable the deformation characteristics of the separate and combined materials to be established under various conditions. The main components are indicated here

Table I

Flow Stress Dependence on the Degree of Deformation

Material	Degree of deformation, per cent			
	5	10	20	40
	Flow stress, N/mm²			
At 700°C				
Copper	~24	~24	~24	~24
Copper-6% tin	41	44	47	47
Copper-25% nickel	109	117	120	118
Platinum	43	56	79	80
Platinum-5% cobalt	108	103	97	94
At 800°C				
Copper	~18	~18	~18	~18
Copper-6% tin	~30	~30	~30	~30
Copper-25% nickel	51	60	61	59
Platinum	36	46	57	62
Platinum-5% cobalt	21	42	52	62

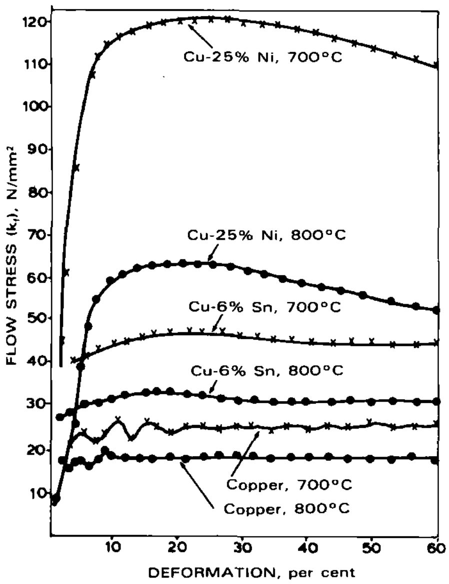


Fig. 4 The flow stresses of copper and copper-6%tin are little influenced by the degree of deformation, however for copper-25%nickel a 10 per cent deformation results in a sharp increase in the flow stress. At higher deformations this strength is maintained, or slightly decreased by recrystallisation

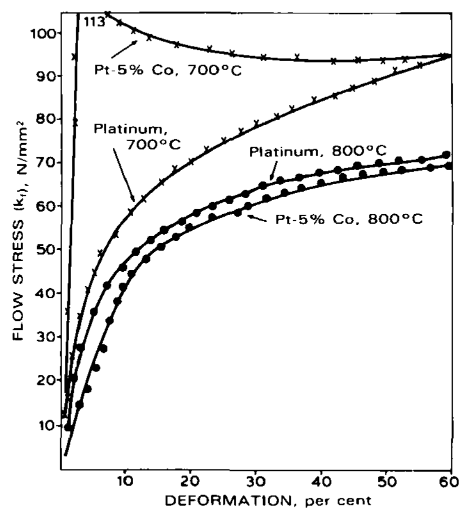


Fig. 5 The relationship between deformation and the flow stress shows platinum and platinum-5% cobalt to behave identically at 800°C. At 700°C the flow stress of platinum-5% cobalt increases very rapidly to a value of 113, at around a 5 per cent deformation, and it then decreases to a constant value at deformations greater than 30 per cent

cases where there is a significant difference between the k_f values of the two metals or alloys, to be joined, the degree of deformation will be distributed inhomogeneously between the two layers, resulting in a shift of the cladding relative to the base material.

The k_f values of copper are the lowest determined and do not differ much in the range 700 to 800°C, thus small variations in temperature should not affect the deformation behaviour significantly.

Copper-6 per cent tin shows almost the same strength as platinum at small degrees of deformation. At higher deformations platinum possesses the higher strength and in a platinum/copper composite platinum should be deformed less than the copper.

In the range 700 to 800°C the strengths of copper-25 per cent nickel and platinum-5 per cent cobalt are influenced considerably by temperature. Thus small differences in temperature may cause larger differences in the deformation ratio and in the cladding properties. Cladding copper-25 per cent nickel with

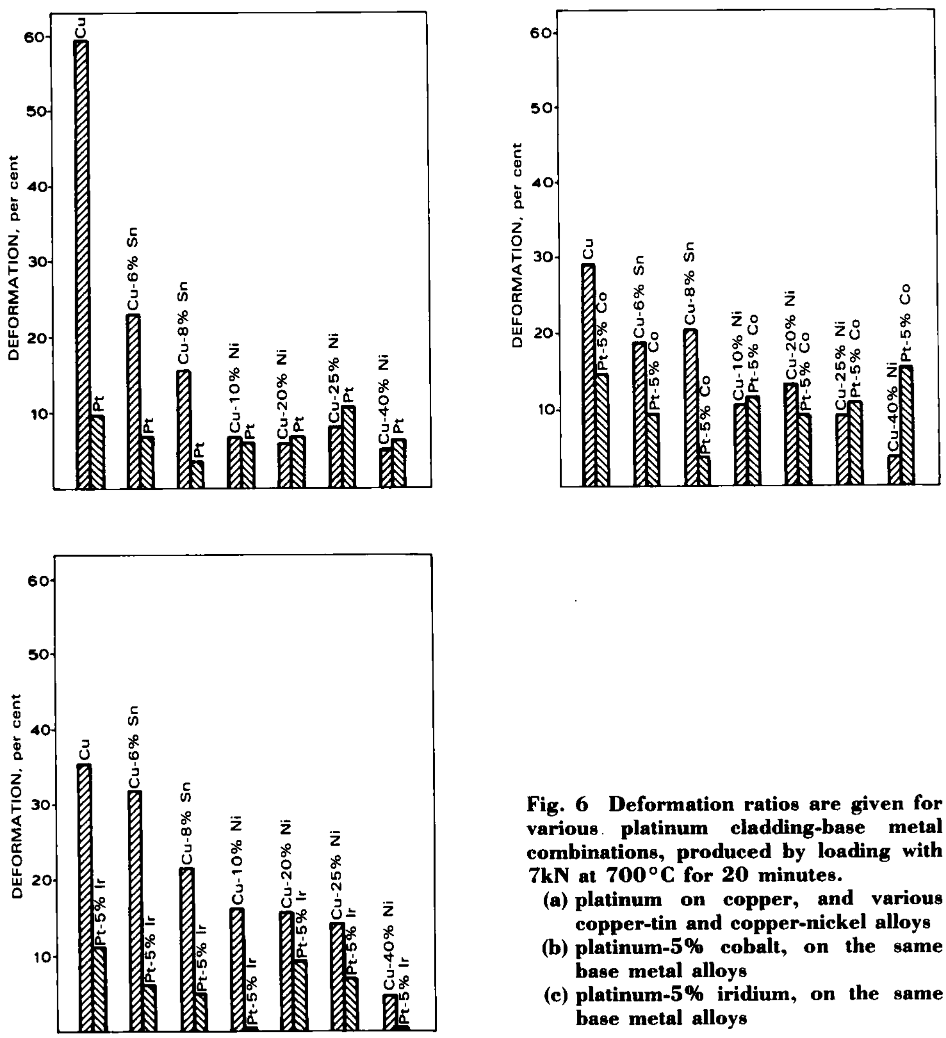


Fig. 6 Deformation ratios are given for various platinum cladding-base metal combinations, produced by loading with 7kN at 700°C for 20 minutes.
(a) platinum on copper, and various copper-tin and copper-nickel alloys
(b) platinum-5% cobalt, on the same base metal alloys
(c) platinum-5% iridium, on the same base metal alloys

platinum-5 per cent cobalt results in uniform deformation of the two component materials; combining copper-25 per cent nickel with platinum at 700°C may cause heterogeneous deformation, whereas at 800°C the deformation ratio is more uniform.

These preliminary conclusions, which were obtained by examining the k_f values, were tested by measuring the deformation ratios of the two components of the clad samples.

Cladding Experiments

At the beginning of the present investigations various cladding methods were examined.

The most generally used methods are either cold or hot rolling. However, for the purpose of this research project these were found to be unsuitable. The results were not reproducible and the adhesion of the cladding differed considerably when the trials were repeated. This was due to the following reasons: (a) The small samples cooled down quickly during rolling; thus a constant, well defined temperature could not be maintained. Additionally it was difficult to get a high deformation rate step to start with, especially when cold rolling. (b) Oxidation of the base metal or alloy could not be prevented completely, even though the samples were wrapped in thin copper sheet.

To overcome these disadvantages, the sample size should be increased to a production scale.

Table II

The Combinations of Noble and Base Metals Studied

Cladding material	Base material
Platinum (99.99% pure)	Copper (99.9% pure)
Platinum-5% cobalt	Copper-6% tin
Platinum-5% iridium	Copper-8% tin
	Copper-10% nickel
	Copper-20% nickel
	Copper-25% nickel
	Copper-40% nickel
	Copper electroplated with nickel

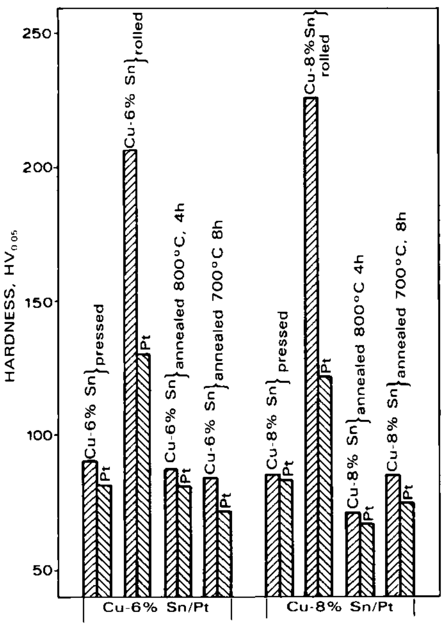
Another cladding technique is to cast the lower melting point base metal onto the surface of the platinum metal. This process can take place in vacuum or in a protective atmosphere, in order to prevent oxidation, but a predetermined cladding temperature and time could not be achieved. None the less this cladding technique was used for preliminary investigations into the diffusion process and the origin of microporosity, which will be considered in a later paper.

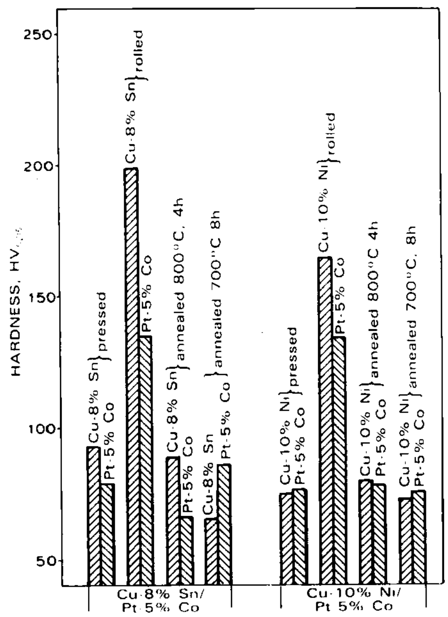
The most convenient cladding method was found to be hot pressing. Small samples could be clad at a selected temperature and pressure, both of which could be maintained for a given time. Furthermore a protective atmosphere could be used. For these experiments the equipment developed for the cone-upsetting test was used.

The cladding-base combinations studied are listed in Table II, they were produced under constant conditions of 7 kN load at 700°C for 20 minutes. The properties investigated were: adhesion of the two layers, porosity in the critical diffusion zone, thickness of the diffusion zone, distribution of the deformation on the two parts of a clad sample and Vickers hardness. The effect of annealing at 700°C and 800°C after cold rolling to a 50 per cent reduction was also examined.

The deformation ratios of the various combinations, after the pressing stage had resulted in adhesion, are shown in Figures 6 and 7. The values are scattered and hardly reproducible, but some general conclusions can be drawn. In all cases pure copper with the lowest flow stress is the most deformed part of the cladded combinations. When the base is either copper-6 per cent tin or copper-8 per cent tin, this layer is again deformed the most.

As expected, the absolute values of deformation decrease when using tin bronzes. The deformation of the platinum cladding whether platinum, platinum-5 per cent cobalt or platinum-5 per cent iridium also decreases progressively when applied to copper, copper-6 per cent tin and copper-8 per cent tin. Results indicated that the cladding process and the





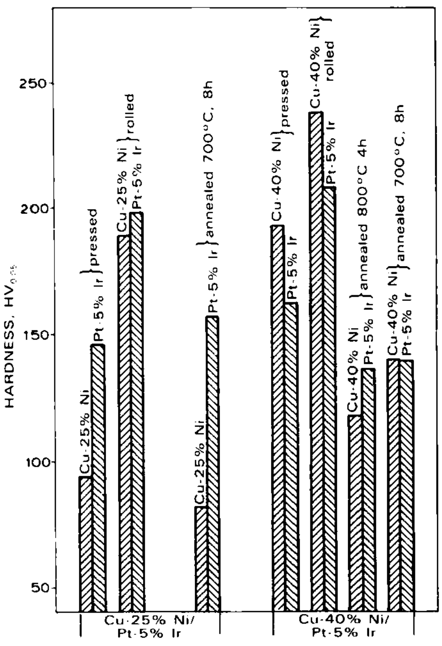


Fig. 7 The effect is shown of various annealing treatments and conditions upon the hardness of clad components:
(a) platinum cladding upon copper-tin bronzes
(b) platinum-5% cobalt alloy cladding upon copper-8% tin and also upon copper-10% nickel
(c) platinum-5% iridium cladding upon two copper-nickel alloys

formation of a diffusion zone are completed within a short time and after relatively little deformation. Then the two joined materials act as one, with a mean flow stress (k_f).

The flow stress of the copper-nickel alloys is about the same, or higher, than that of platinum or platinum-5 per cent cobalt. The deformation is distributed almost equally between the two components. Only in the case of copper-40 per cent nickel/platinum-5 per cent cobalt is the base material deformed significantly less than the cladding.

The deformation of platinum-5 per cent iridium in clad compounds varies widely. This might cause adhesion difficulties.

The influence of various treatments on the hardness of cladded materials is shown in Figure 7. Values measured both on the base metal and on the platinum cladding are given. The scatter is considerable and this may be due to inhomogeneity of the material and to the small testing load (0.5 N), which was necessary because of the thinness of the sheets. No relationship could be established between hardness and the quality of the cladding.

In this first part of our investigations on cladding with platinum and platinum alloys, it has been shown that certain base materials, such as copper-nickel alloys, are more suitable than others, such as pure copper. A later paper will report the second part of our investigations, which are concerned with the diffusion of the clad and base metal constituents into each other, and the occurrence of very pronounced hole-formation in the diffusion zone. This Kirkendall effect causes severe adhesion problems and may result in separation of the cladding and the base during later annealing steps. Therefore special precautions have to be taken to overcome this disadvantage.

Acknowledgement

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Barium Ruthenate Thin Film Resistor

ADVANTAGES FOR HIGH SPEED THERMAL PRINTING

Thermal printing is widely used for terminal outputs, facsimile receivers, and other applications in office equipment, as well as for laboratory and industrial recording instruments. Thermal printers are small, relatively simple, and quiet by comparison with impact devices. The working components of these thermal dot matrix printers are their heads which must have long life and be capable of rapid heating and cooling, so as to allow fast operation. High resolution is required to yield a dense dot pattern, of say 16 dots per millimetre, that is necessary for the printed lines to appear continuous. The heads are made of an alumina substrate on which several patterned layers are physically deposited. These consist of a glaze, the resistor element, an electrical conductor, and an abrasion resistant overcoat. The layers have a total thickness of less than 100μm. Driver circuits apply current pulses to the resistors, which in turn apply the desired pattern to the recording paper with which the head is in continuous contact.

A barium ruthenate thin film resistor has been developed by O. Takikawa, H. Hiraki, M. Harata, and T. Saito of the Toshiba Corporation, Research and Development Centre, Kanagawa, Japan, and a report of their work was presented at the IEEE 36th Electronic Components Conference on 5th–7th May 1986, in Seattle, Washington. The resistor was deposited by r.f. sputtering using a barium ruthenate ceramic target, followed by thermal annealing. Prototype printing heads were fabricated with a barium ruthenate film thickness of 50nm and a 2μm alumina abrasion resistant layer.

An advantage of barium ruthenate is its high resistivity, which results in a resistance of 1,000 ohms per dot and allows the necessary printing temperatures of about 370°C to be achieved with little power, that is 0.25 watt per dot. In addition it has high oxidation stability, thereby permitting the wear resistant alumina layer used on the barium ruthenate to be thin, which in turn facilitates the conduction of heat. Life tests with 2 ms pulses showed the resistor to have nearly constant electrical properties for at least 10^8 operations, which is a practical life requirement. The authors believe that this new material will be used commercially in thermal printing.

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