

High Purity Palladium Brazing Alloys

MULTI-STAGE JOINTING IN THE MANUFACTURE OF THERMIONIC VALVES

By M.H. Sloboda. Dipl. Ing.
Research Laboratories, Johnson Matthey & Co Limited

The possibility of using palladium as a component of brazing alloys for high temperature service was first explored by Rhodes, working in the laboratories of the Mond Nickel Co Limited, who studied the effect of additions of this metal on the pertinent properties of silver-copper alloys.

This early work was directed towards satisfying the demand for high-temperature brazing alloys suitable for the fabrication of turbine assemblies for jet engines. It resulted in the development of a series of ternary silver-copper-palladium alloys containing between 5 and 25 per cent palladium. All these alloys freeze at temperatures higher than the melting point of the silver-copper eutectic (778 C); they have sufficiently narrow melting ranges, they wet readily nickel-based alloys without causing cracking due to inter-granular penetration and

they meet many requirements imposed by high service temperatures in a large number of industrial applications.

The manufacture of special-purpose thermionic valves, such as magnetrons and klystrons, represents a relatively recent field of application of palladium-bearing brazing alloys.

Since these devices operate at relatively high temperatures and under conditions of high vacuum, the use of standard cadmium- and or zinc-bearing silver brazing alloys is ruled out. Silver-copper eutectic has been widely used in this application, but more satisfactory results can often be obtained with the palladium-bearing alloys because of their better mechanical properties at elevated temperatures, improved wetting characteristics on molybdenum, tungsten, and nickel alloys,

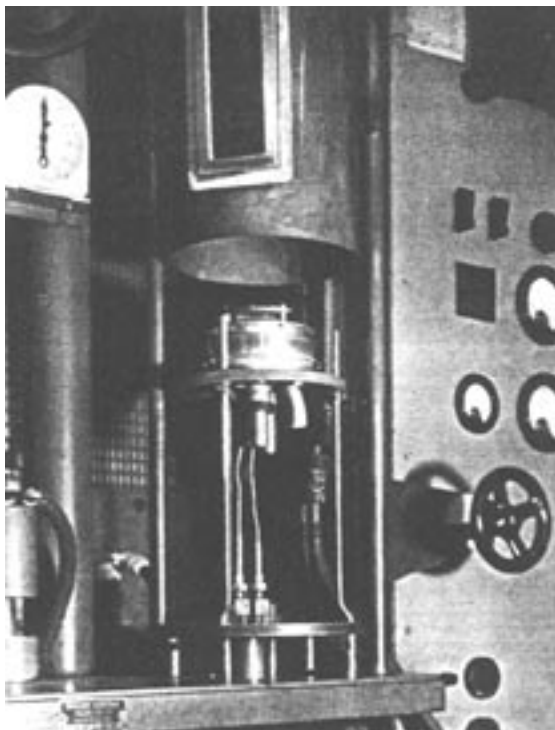
The Pallabrazed Range of High Purity Brazing Alloys		
Alloy	Palladium Percentage and composition	Melting range C
Pallabrazed 810	5 Pd—Ag Cu	807— 810
Pallabrazed 840	10 Pd—Ag Cu	830 — 840
Pallabrazed 850	10 Pd—Ag Cu	824 — 850
Pallabrazed 880	15 Pd—Ag Cu	856— 880
Pallabrazed 900	20 Pd—Ag Cu	876 — 900
Pallabrazed 950	25 Pd—Ag Cu	901 — 950
Pallabrazed 1010	5 Pd—Ag	970 — 1010
Pallabrazed 1090	18 Pd—Cu	1080 — 1090
Pallabrazed 1237	60 Pd-Ni	1237



Components of a power triode header assembly, by English Electric Valve Co Limited, together with the inserts of Pallabrazz S10 wire that are used in the brazing operation. Brazing is carried out induction hearing, and brazing time is about thirty seconds.

and reduced risk of failure due to intergranular penetration. Gold-copper and gold-nickel alloys are also used in this field.

The manufacture of thermionic valves may entail fabrication of components comprising several joints that cannot be brazed in a single operation. A range of brazing alloys is therefore required with the melting points spaced at convenient intervals so that complete assemblies can be fabricated by the step-by-step



The power assembly shown above in position in the induction brazing furnace and ready for the cracked ammonia bell to be lowered. The joints are made between nickel sleeves on the filament posts and Nilo K seals on the ends of the spacers.

*The complete English Electric BR 1S9
power triode*

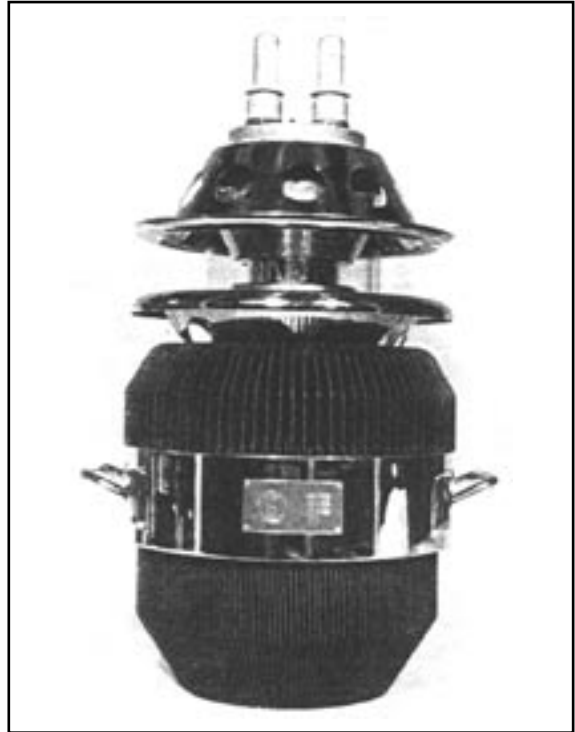
brazing technique. In addition, best results in brazing close-fitting parts are achieved with alloys of the eutectic type — having a single melting point or a narrow melting range — whereas an alloy with a relatively wide melting range may be required to bridge wide joint gaps or to form large fillets.

These requirements are met by a range of palladium-bearing brazing alloys, marketed by Johnson Matthey under the name “Pallabraz”. The range includes six ternary silver-copper-palladium alloys and three binary compositions: ~ per cent palladium-silver, 15 per cent palladium-copper and 40 per cent palladium-nickel, the last of these constituting a useful addition to the range because of its high single melting point of 1237 C. Particulars of these alloys are set out in the table on page 8. In each case the reference number of the alloy is its liquidus temperature.

Importance of High Purity

A feature distinguishing the Pallabraz alloys from similar materials intended for general engineering applications is their extremely high degree of purity. This consideration is of primary importance for several reasons.

First, since the application of brazing fluxes in the fabrication of thermionic valve components is inadmissible, brazing alloys used for this purpose must be virtually free from impurities that might impair their wetting and spreading characteristics; this group of impurities includes metals forming refractory oxides that do not dissociate except at very



high temperatures and low pressures and that can only be reduced in reducing atmospheres of purity difficult to obtain in industrial brazing practice.

Secondly, efficient functioning of thermionic valves and other similar devices depends on maintaining a high vacuum; this means that all the materials of construction, including the brazing alloys, must be free from volatile constituents. These include not only metals that have high vapour pressures at temperatures at which thermionic valves operate, but also carbonaceous surface contaminants (grease, oil, lubricants, etc.) that might affect the vacuum as a result of gradual build-up of carbon monoxide in the valve.

These requirements impose the need both for rigorous control of the purity of the raw materials used in the manufacture of brazing alloys for this application and for special precautions at every stage of the manufacturing process.

Based on the extensive experience of Johnson Matthey in the production and application of ultra-pure materials, very low limits of impurities for Pallabrazo alloys have been established. These are set out in the table. All the JMC Pallabrazo alloys listed in the table on page 8 are made to this specification, and every batch of wire is checked to ensure that these limits are not exceeded.

Brazing Technique

Although palladium-bearing alloys can, in principle, be used for torch brazing, this method is not applicable in the manufacture of thermionic valves because of the complications caused by the necessity of using a brazing flux. For this reason brazing must be carried out either in vacuum or in a neutral or reducing atmosphere. Depending on the nature of the parent metals, a vacuum of to mm Hg, or a protective atmosphere with a dew point lower than -50 C, may be required. Hydrogen and cracked ammonia are both suitable as protective atmospheres, provided that their moisture content is sufficiently low.

Impurity Limits in Pallabrazo Alloy	
Impurity	Parts per Million, Maximum
Aluminium	5*
Beryllium	5
Chromium	10
Manganese	10
Titanium	10
Zirconium	5
Antimony	30
Bismuth	10
Cadmium	10
Calcium	30
Lead	20
Lithium	30
Magnesium	30
Tin	30
Zinc	10
Phosphorus	100

Total
of
these
impurities
90 ppm



The brazing alloys are supplied ready for use in the form of wire. They can, however, become contaminated during any forming operation or in handling, in which case they should be vapour-phase degreased immediately before brazing. Similar steps should, of course, be taken to ensure cleanliness of the work pieces.

Difficulties encountered in fluxless brazing of components made from alloys containing metals which form refractory oxides can sometimes be overcome by raising the brazing temperature. If this expedient fails, recourse may be taken to nickel plating the components before brazing, and all the alloys tested expanded 16 to 18 suggest. The proportional changes in length to inch per inch over the range 0 to 1500 C C.

Part of an assembly of an English Electric power klystron being prepared for furnace brazing. <All the components shown are copper and the joints are made with wire in ring of Pallabrazo SS0

of the alloys tested over the temperature range 0 to 1500 C are summarised in the somewhat

less than its composition might table on the preceding page.

References

- 1 H. Ebert *Phys. Zeit.*, 1938, **39**, 6
- 2 L. Holborn, K. Scheel and F. Henning Warmetabellen, Braunschweig, 1919, p. 54

High Temperature Brazing of Heat-resisting Materials

INVESTIGATION OF NICKEL-PALLADIUM ALLOYS

The many problems in the design and construction of gas turbines and other equipment operating at high temperatures include the need for brazing alloys capable of giving strong sound joints resistant to oxidation in service. The parent metals to be joined are the range of heat-resisting alloys most of them based upon nickel-chromium compositions with additions of cobalt, iron, aluminium and titanium, and for many applications a number of nickel-base brazing alloys have been developed containing chromium, silicon, boron or phosphorus.

The major disadvantage of these nickel-base alloys is that the additions designed to promote flow and to reduce melting temperatures always tend to produce severe penetration or undercutting of the parent metal when used in conditions conducive to the achievement of ductile joints, and they must therefore be used with great caution—if at all—on thin sections.

For moderate strength combined with good wetting properties without appreciable diffusion, alloys based on palladium have for some time been accepted as useful brazing media in such assemblies as thin-wall tubular heat exchangers and sandwich panels, particularly as they are ductile alloys capable of being produced as thin foil and wire. One alloy of this type, 40 per cent nickel-palladium, the lowest melting in the Ni-Pd system, has been used successfully but its melting point of 1238 CC is inconveniently high.

An investigation to develop a ductile brazing alloy of this type having a lower melting range together with good wettability has recently been reported by W. Feduska, of the Materials Engineering Department of Westinghouse Electric Corporation, and presented as a paper

to the American Welding Society conference in Los Angeles . *Welding*., 1960, 39, 292-s). As a basis for achieving a new low-melting solid-solution alloy free from embrittling intermetallic compounds, the nickel-palladium system was considered to be attractive, and the investigation was concentrated on additions of beryllium and silicon to this base alloy. The most promising composition was found to be the 40 per cent nickel-palladium alloy with additions of 0.5 per cent silicon and 0.2~ per cent beryllium. this alloy having a melting range of 1115 to 1160 C and satisfactory ability to wet heat-resisting alloys containing aluminium and titanium. It was also found to cause little penetration or erosion of the parent metal during the brazing of thin-walled structures, to possess adequate shear strength up to 800C and to show ductility at room temperature in brazed joints on various materials.

It is a little unfortunate, however, that the results given for shear strength of joints both at room and at elevated temperatures cannot be considered of very great value, as the tests were evidently conducted under conditions of rapid loading—conditions of considerably less interest to designers of high-temperature equipment than are creep studies.

The author also reports observing an apparent reduction in the flow temperature of the new brazing alloy when used on parent metals containing manganese, and infers this to be due to pick-up from the parent metal. No extension of the work into brazing alloys containing additions of manganese is, however, reported, nor is reference made to the known palladium-manganese-nickel brazing alloys that have been developed by other workers. H. R. B.