THE ROLE OF PALLADIUM IN SILVER-COPPER BRAZE ALLOYS

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This thesis resulted from work in the Department of Materials Science and Engineering of the University of Surrey. It was presented in 1989 in support for an award of the degree of Master of Philosophy.
ABSTRACT.

The research began with a survey of methods used in the brazing of different metals taking 1965 as a 'benchmark' year. The survey took into account types of heating, filler alloys available, design considerations and situations where this method of joining had proved a satisfactory engineering technique.

Following visits to a number of organisations the position of brazing was again reviewed after an interval of c.25 years. The major changes noted related to improvements in vacuum technology as a result of which aluminium is now brazed on a tonnage basis, hydrogen and other gas atmosphere furnaces have largely been superseded for brazing the high nickel alloys and stainless steels, and satisfactory methods have been adopted for titanium, cermets and ceramics to metals. Cleaner and more easily applied filler alloys have also given impetus to many more applications for the technique.

The surveys revealed that one problem which had remained unanswered related to cracking of the low expansion alloys, used in glass-to-metal seals, when high-temperature brazed with filler alloys based on the silver-copper eutectic. Cracks formed as a result of stress which could arise during the brazing cycle but the mechanism was uncertain and a research programme was therefore formulated to establish reasons for the crack formation.

Using a 42% nickel-iron alloy with silver-copper eutectic and three available modifications of this alloy containing nominally 5%, 10% and 25% palladium, a static beam loading technique was devised to assess stress cracking. Specimens were examined by Auger/XPS Spectroscopy, Optical and Scanning Electron Microscopes.

In the case of the silver-copper eutectic braze, molten alloy preferentially dissolved grain boundary nickel atoms leaving vacancies which were replaced by copper. Applied stresses caused propagation of cracks initiated at the weakened boundaries and the mechanism was considered to be a form of stress corrosion cracking. The solidified brazing alloy contained iron and nickel, with the ratio of Fe to Ni increasing as Pd increased. Stress corrosion pits and tunnelling noted with the Pd-free alloy were not found in the 5 or higher % Pd alloys. It was concluded that penetration of grain boundaries in the parent metal reduced as the Pd was increased due to uptake of Fe by the molten brazing alloy.
FOR JO LIANE AND OUR FAMILY.

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G.E.C. Avionics.
Titanium Metal And Alloys.
Inco Europe.
Wall Colmonoy—since retired.
BNF Metals Technology Centre / British Association for Brazing and Soldering.
Culham Laboratory, U.K.A.E.A.
Normalair Garrett (Westland Helicopter Group)
Osprey Metals
Delanair
B.A.J. Vickers
Fry's Metals
British Alcan Sheet
Engelhard.
U.K.A.E.A. Harwell
Neomet
Metals Joining Consultancy
U.K.A.E.A. Springfields
Rolls Royce (1971)
Link Analytical
University of Surrey
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The role of palladium in silver-copper braze alloys

1-Introduction

It can be argued that since the Industrial Revolution the periods of greatest technological advance spanned the two World Wars, when able scientists and engineers from the contestant countries were provided with the resources they required to develop new inventions, aimed at giving their countries advantages over adversaries.

While World War 1 was followed by a prolonged period of depression, with attendant social problems, there was agreement by the majority of British politicians that when World War 2 was concluded there should not be similar national disadvantages upon the return of service personnel to their peace time occupations.

After 1946 the U.K. and the U.S.A. enjoyed the major advantages over the erstwhile Axis Powers and the U.S.S.R., that these countries had not been ravaged to the same extent, leaving them relatively free from major competitors.

There were other factors operating against a continuation of this U.K. state of affairs however:-

(a) From 1946 there was a massive restructuring of the economy leading to nationalisation of industries such as coal, gas, steel, railways and road transport. There were also improved health services and better educational facilities, notable being the introduction of the newer technological universities. These features helped the politicians keep their promises of employment for everyone but at a charge on the national purse which was not appreciated by most at that time.

(b) Two features resulted from the dissolution of the British Empire to the U.K.'s great disadvantage. Firstly there was an upsurge in immigrants, mainly unskilled, who were apprehensive or dissatisfied with undertakings given by the new regimes in the countries of their birth. Together with returning expatriate British nationals, these resulted in a swollen U.K. population, and increased demands on national expenditure. Secondly was the lack of appreciation that the overseas territories gave the U.K. an enormous ready-made market for goods made 'off the shelf' without any real consideration being paid to local conditions; thus a 'take it or leave it attitude' prevailed amongst exporters. This was quickly exploited by market-orientated American sales forces who had not previously been able to go into these territories, due to the protection given by the Empire and who were willing to make to the customers own design requirements.

(c) Very generous American aid programmes enabled Germany and Japan to rebuild their industries using the latest standards of automated machine tools which allied to the intense drive of nationals of both countries helped them become world competitors far earlier than Britain had, if at all, expected.

(d) The formation of the European Economic Community was initially an English concept, but one where we were late in joining the original seven countries. Due to reduced tariff barriers helping the E.E.C. countries with inter-country trade the U.K. found that their European trade was consequently falling away leading to the prospect of losing the major market on our own doorstep.

Once the impact on the British economy of these post war factors was appreciated successive Governments took actions to try and recover the position, as a result of which there were cut-backs in expenditure in endeavours to make budgets balance, and maintain a positive balance of trade. In these efforts
many research and development projects which because of their size-scale were state financed, were cancelled, and there became a trend to buy expensive 'know-how' from America as a prelude to eventually joining collaborative projects with other European countries. Hence Government support to research associations, university departments and ventures too costly for private or nationalised companies to fund themselves were severely curtailed, the most celebrated examples being cancellation of the TSR2 aircraft (forerunner of the Tornado which is now being made by a British-German-Italian consortium) the P1154, (a second generation vertical take-off Harrier-type aircraft), and the most advanced of all civil airliners, the Anglo-French Concorde, of which only 16 production aircraft were completed.

Regrettably the management actions which had been taken were still inadequate to give the required competitiveness to the Nation, and as coupled to this there were increasingly unrealistic demands for improved working conditions, more pay and reduced working hours by organised labour without corresponding productivity, the slide into the mid-1970's depression proved to be inevitable before it became accepted that if living standards were to be regained the country must trade competitively and profitably.

There seemed to be little appreciation of the side effects of cutting back the prime research and development contracts, probably because economists and politicians did not understand how much technological spin-off into other industries devolved from these contracts.

One such area related to the metal joining process known as brazing, which although used for centuries, immediately prior to World War 2 was mainly restricted to garage fitter-type repair work, using oxy-acetylene flame torches. In the immediate post-war period a lot of effort was devoted to this as an engineering technique, and a number of Government contracts had been placed in an attempt to use the method in for examples, aerospace and nuclear applications where other joining methods failed to yield appropriate solutions to specific problems.

The first purpose of this study is to assess the position of brazing as a method of joining as practised prior to 1965. Secondly the present situation will be reviewed in an attempt to assess the changes which have resulted in the intervening years where Government funding has been limited, and any developments in the method have mainly been due to privately funded sources. Thirdly a comparison of situations in 1965 and the present will be used as the basis for suggestions for areas likely to benefit from future research. The final phase of the project will be to take one of these areas and make this the basis of a research programme.
2.1 - Definition

The brazing process is a method of joining together parent metals with an intermediate filler metal of lower melting point. BS499 and BS1723 define it as a process where the filler metal has a melting point above 450°C, and is distributed in the joint by capillary attraction. Unless provision is made in the design to prevent alloy running out however, gravitational effects may cause loss of filler material from the joint if gaps are too wide or filler alloy flows too freely.

The practice of joining metals using a lower temperature filler alloy may be widened from the British Standard Specifications, general trends being to regard soft soldering as the method used up to 450°C, with little or no inter-alloying with the parent metals being detected with the analytical techniques then available. Hard or silver soldering, or low temperature brazing was in the range 450-800°C. The term high temperature brazing was used where the brazing temperature exceeded c.800°C. The mechanism operating for temperatures above 450°C involved inter-alloying of parent and filler materials, and was traced without great difficulty using well-established metallographic techniques.

2.2 - Brazing: Art, Engineering Technique, or Science

Depending on the speaker, brazing may be treated as an art, as an engineering method of joining metals, or as a science.

As an art brazing dates back to antiquity with knowledge of fluxes to be used and manipulative skills of artisans resulting in beautifully fabricated gold and silver artifacts, such as discovered in Tutankhamen's tomb and seen during 1945 in Cairo Museum. Present day silversmiths and manufacturing jewellers techniques basically remain unaltered.

20th century practice is more usually concerned with the use of brazing as an engineering technique. Designers should initially consider the requirements of joints before arriving at the decision to use brazing in preference to bolting, rivetting, adhesing, soldering or welding. In many applications the question of economics finally determines the method of joining to use, although there are countless places where brazing was the only known way of making sound joints.

Scientific considerations relating to brazed joints have resulted in studies of wetting behaviour, spreading method, surface tension effects, interalloying, diffusion effects, and any other reason relating to the retention of molten filler alloy so that it solidifies in the joint to bring about the desired metal fabrication. There is a great deal of overlapping of the engineering and scientific considerations, and as each is dependent on the other, for the purpose of this work they will be treated as synonomous.

2.3 - Design Requirements

With improved filler alloys becoming available for ever increasing ranges of applications excellent mechanical and physical properties are obtainable through careful design and execution. When selecting the parent metal for particular service conditions, there are a number of aspects which equally apply to the filler alloy and the designer-engineer must take into account all the following:
(a) Environment:
The effects of atmospheric conditions in service must be an early consideration in determining whether brazing will be an acceptable joining technique. In certain conditions the combination of parent and filler alloy perform as a cell to bring about erosion in the joint area. A report was received during a visit to the U.S.A. in 1962 that an experimental titanium alloy aircraft had suffered a catastrophic failure. This was due to the use of the 85% silver–15% manganese brazing alloy which resulted in fillet or crevice corrosion. Alternating stresses acting on a notch formed by this type of corrosion at the joint and aggravated by wet air and cryogenic conditions in service, completed the failure cycle. In another sea water application steel coolers brazed with a 50% silver–15.5% copper–16.5% zinc–18% cadmium alloy had suffered from joint failures. It was considered that this was a galvanic failure, although rusting of the steel may also have masked or contributed to the failure mechanism to some degree in that instance.

(b) Bacteriological Effects:
In brazing stainless steels, cobalt- and nickel-based alloys for dairy and medical applications tests proved to be necessary to establish that the combinations of brazing alloys and parent metals did not cause the onset of adverse bacteriological effects in service, for example as in pump components.

(c) Colour Compatibility:
For jewellery and dental applications it is often of great importance that the brazed joint is unnoticeable, calling for care in the selection of an appropriate filler alloy.

(d) Compatible Mechanical Properties:
Parent and filler alloys must be compatible. No engineer would contemplate joining stainless steel with Ag–Cu–Zn–Cd alloy for service at 700°C, since the filler melts at 660°C. On the other hand for a room temperature application with suitable over-lapping joints it can be an acceptable combination in non-corrosive conditions. A widely employed empirically-derived rule was in use, taking as the basis that the liquidus temperature of the filler metal must be at least twice as high as the service temperature of the brazed part, subject to qualifying tests of the component before there was finalisation of the method of brazing specified.

(e) Available Brazing Alloys:
While it is desirable to use fits (clearances) which are as close as possible, the gap between parts being joined must be adequate to allow filler alloy to flow completely through the joint. The gap is therefore largely set by the rate at which inter-alloying between parent and filler occurs, which in most cases was in turn controlled by cleanliness and surface finish of the surfaces and the tenacity of oxides and other films on the metals involved. If tendencies to inter-alloy were relatively slight, brazing alloy filled longer and narrower gaps, as exemplified in copper brazing stainless steels, than if interalloying was rapid, as in the case of flux bath brazing aluminium with the eutectic aluminium-silicon alloy. Clearances rarely exceeded 0.006 ins. (0.15 mm) but if strength was a requirement they could be as low as 0.0005 ins. (0.013 mm) when copper brazing steel.

During the period to 1965 most of the alloys developed as fillers emanated from the U.S.A. laboratories of Dewrance or Wall Colmonoy, and from the English laboratories of Johnson Matthey and Mond Nickel (who had their range made and
Mond's most notable contributions were a range of alloys researched by Edwin Rhodes and David Rhys, who noted the excellent wetting and gap filling properties obtained by adding palladium to the silver-copper and the silver-manganese series, see Fig 1. They also observed that the series was less prone to erode thin foil materials. There were however major criticisms of the cost of these alloys, and before proceeding further a survey of potential British and Overseas customers was arranged in 1958 when the conclusion was reached that at the time price was not a major deterrent if no other alloy would allow fulfilment of the designers requirements. Resulting from this:

(i) a world-wide marketing and publicity programme was initiated to make more users aware of the properties of the range,

(ii) the writer was invited to join the British Standards Committee which was reviewing the brazing specification and as a result the palladium series of alloys was for the first time included, in B.S.S. 1723: 1963 this specification was recently revised, and

(iii) further laboratory work was laid down with the objectives of improving the properties of the series.

Delaney Gallay had been in the forefront of companies using brazing and soldering techniques in the manufacture of car heaters and radiators at lower joining temperatures, and for aircraft secondary surface heat exchangers and oil coolers for higher temperature applications. They concluded that the most satisfactory techniques to meet aircraft industry demands involved high-temperature vacuum brazing of stainless steel and nickel-alloy components and flux-dip brazing of aluminium alloys, they therefore installed the appropriate facilities. As experience showed there was insufficient internal factory demand to keep both vacuum furnace and flux bath fully utilised they took the decision to offer the spare capacity on a commercial basis to other companies. As a result they obtained pre-eminence as experts in the field with customers coming to use their specialist facilities from all over the U.K. and Western Europe. They joined many combinations of parent and filler alloys but as appropriate the preferred filler alloys available on a production basis proved to be those marked with an asterisk in the Table that follows. Delaney Gallay always endeavoured to be leaders, and regular visits were paid to other countries including the U.S.A. to ensure that they were up to date with plant and techniques; their experiences will be given in later sections under the headings 'high frequency brazing', 'car heater production', 'high temperature brazing', and 'aluminium brazing').
Fig. 1.
<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Composition-Wt.%</th>
<th>Brazing Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Mond PN1 (Baker288)</td>
<td>60 Pd-40 Ni</td>
<td>1250</td>
</tr>
<tr>
<td>2-Mond SPM2 (Baker2602)</td>
<td>64 Ag-33 Pd-3 Mn</td>
<td>1220</td>
</tr>
<tr>
<td>3-Standard Nicrobraz</td>
<td>13.5 Cr-4.5 Fe-4.5 Si-3.5 B-0.8 C-Ni Remr.</td>
<td>1180</td>
</tr>
<tr>
<td>4-Nicrobraz LC</td>
<td>13.5 Cr-4.5 Fe-4.5 Si-3.5 B-0.15 max.C-Ni Remr.</td>
<td>1180</td>
</tr>
<tr>
<td>5-Stellite SF6</td>
<td>50 Co-19 Cr-13 Ni-8 W-2.5 B-1.5 Si-1 C</td>
<td>1170</td>
</tr>
<tr>
<td>6-Endewrance 57 (D608)</td>
<td>34 Fe-11 P-7 Co-5 Cr-Ni Remr.</td>
<td>1150</td>
</tr>
<tr>
<td>7-Nicrobraz WG</td>
<td>11.5 Cr-3.5 Si-3.5 Fe-3 B-0.15 max.C-Ni Remr.</td>
<td>1150</td>
</tr>
<tr>
<td>8-Endewrance 56</td>
<td>16-Cr 4.5-Si-4 Fe-3.5 B-Ni Remr.</td>
<td>1140</td>
</tr>
<tr>
<td>9-Mond CPNM2 (Baker279)</td>
<td>55 Cu-20 Pd-15 Ni-10 Mn</td>
<td>1120</td>
</tr>
<tr>
<td>10-Mond NMP1 (Baker318)</td>
<td>48 Ni-31 Mn-21 Pd</td>
<td>1125</td>
</tr>
<tr>
<td>11-Copper</td>
<td>100 Cu</td>
<td>1120</td>
</tr>
<tr>
<td>12-Endewrance 50</td>
<td>3.5 Si-1.9 B-Ni Remr.</td>
<td>1120</td>
</tr>
<tr>
<td>13-Mond SPM1 (Baker2601)</td>
<td>75 Ag-20 Pd-5 Mn</td>
<td>1120</td>
</tr>
<tr>
<td>14-Mond SCP6 (Baker719)</td>
<td>82-Cu 18 Pd</td>
<td>1095</td>
</tr>
<tr>
<td>15/16-Endewrance 52 &amp; Nicrobraz 130</td>
<td>4.5 Si-2.9 B-Ni Remr.</td>
<td>1070</td>
</tr>
<tr>
<td>17-Endewrance 62</td>
<td>16 Co-16 Ni-0.03 B-Mn Remr.</td>
<td>1065</td>
</tr>
<tr>
<td>18-Johnson Matthey Copper-Gold:</td>
<td>70 Cu-30 Au</td>
<td>1050</td>
</tr>
<tr>
<td>19-Nicrobraz LM</td>
<td>6.5 Cr-4.5 Si-3 B-2.5 Fe-0.15 max.C-Ni Remr.</td>
<td>1050</td>
</tr>
<tr>
<td>20-Endewrance 53</td>
<td>7 Cr-4.5 Si-3 Fe-2.9 B-Ni Remr.</td>
<td>1050</td>
</tr>
<tr>
<td>21-Johnson Matthey Copper-Gold:</td>
<td>62.5 Cu-37.5 Au</td>
<td>1030</td>
</tr>
<tr>
<td>22-Johnson Matthey Silver-Manganese:</td>
<td>85 Ag-15 Mn</td>
<td>1020</td>
</tr>
<tr>
<td>23-Electro-plated Nickel:</td>
<td>ca.11 P-Ni Remr.</td>
<td>1020</td>
</tr>
<tr>
<td>24-Johnson Matthey Cu-Mn-Ni alloy:</td>
<td>52.5 Cu-38.5 Mn-9 Ni</td>
<td>1000</td>
</tr>
<tr>
<td>25-Mond SCP5 (Baker718)</td>
<td>95 Ag-5 Pd</td>
<td>1015</td>
</tr>
<tr>
<td>26-Nicrobraz 50</td>
<td>13 Cr-10 P-0.15 C-Ni Remr.</td>
<td>980</td>
</tr>
<tr>
<td>27-Kanigen: Electro-plated nickel:</td>
<td>ca.9.5 P-Ni Remr.</td>
<td>980</td>
</tr>
<tr>
<td>28-Nicrobraz 10</td>
<td>11 P-0.15 max.C-Ni Remr.</td>
<td>980</td>
</tr>
<tr>
<td>29-Baker 441</td>
<td>82 Au-18 Ni</td>
<td>970</td>
</tr>
<tr>
<td>30-Mond SCP4 (Baker725)</td>
<td>54 Ag-25 Pd-21 Cu</td>
<td>955</td>
</tr>
<tr>
<td>31-Baker 429</td>
<td>60 Au-40 Cu</td>
<td>930</td>
</tr>
<tr>
<td>32-Baker 424</td>
<td>80 Au-20 Cu</td>
<td>910</td>
</tr>
<tr>
<td>33-Mond SCP3 (Baker724)</td>
<td>65 Ag-20 Cu-15 Pd</td>
<td>905</td>
</tr>
<tr>
<td>34-Mond SCP7 (Baker748)</td>
<td>52 Ag-28 Cu-20 Pd</td>
<td>905</td>
</tr>
<tr>
<td>34b-Mond Experimental</td>
<td>52 Ag-28 Cu-20 Pd + 0.2 Li</td>
<td>905</td>
</tr>
<tr>
<td>35-Mond SCP2 (Baker723)</td>
<td>58.5 Ag-31.5 Cu-10 Pd</td>
<td>860</td>
</tr>
<tr>
<td>36-Nicrobraz 45</td>
<td>68.4 Ag-26.6 Cu-5 Pd</td>
<td>815</td>
</tr>
</tbody>
</table>
36b-Mond Experimental 68.4 Ag-26.6 Cu-5 Pd-0.2 Li 815
37-Silver-Copper Eutectic 72 Ag-18 Cu 800
38-Johnson Matthey Cu-Ag-Sn alloy: 60 Ag-30 Cu-10 Sn 720
39-Baker 1501 69 Al-30 Ag-1 Ni (or Mn) 680
40-Johnson Matthey Easyflio: 50 Ag-15.5 Cu-16.5 Zn-18 Cd 660
41-BS1475-Type NG21 5.5 Si-Al Remr. 640
42-BS1475-Type NG2 11.7 Si-Al Remr. 600

(f) Heating Methods:
In evaluating the design, the method of heating available to the engineer must be considered, and BS.499 listed as acceptable techniques depending on the type of application and metals to be joined:
- Resistance Brazing
- Dip Brazing
- Flame (or torch) Brazing
- Furnace Brazing
- Induction Brazing
- Salt Bath (Flux-Dip) Brazing

From comments already made it will be appreciated that while some methods are suitable for many combinations of metals they are quite unacceptable for others, e.g. high frequency electric induction brazing is suitable for simple joints and quick evaluation of brazing alloys capabilities to wet parent metals which require to be joined; as a method it is however totally unsuited to the manufacture of a secondary surface aluminium alloy heat exchanger.

(g) Atmosphere Versus Chemical Flux:
While some alloys can be used in air with fluxes such as those based on 65% potassium pentaborate and 35% potassium hydrogen fluoride or 33% potassium metaborate, 33% boric acid and 34% potassium hydrogen fluoride, these may be wholly inadequate where fine tubes are to be brazed, and there is difficulty in eliminating flux residues which may run into the tubes during the brazing process. In such instances recourse was made to brazing in reducing atmospheres, depending on the nature of the parent/filler metals involved in joining. Atmospheres used were cracked ammonia (75% nitrogen 25% hydrogen) forming gas (90% nitrogen 10% hydrogen) and hydrogen. The gas, notably hydrogen, was dried by passing over P₂O₅, thence heated copper followed by reactivated alumina and a liquid air trap before introduction at a dewpoint of -60°F (-50°C) to the furnace in which the braze was to take place. An alternative which was being employed to an increasing extent was the use of vacuum at c.10⁻³mm mercury pressure, sometimes back-filled to ca.40 mm Hg pressure with the inert gases, argon, helium or nitrogen.
The method of atmosphere control available had to be considered at the drawing board stage of component design.

(h) Heating And Cooling During Brazing Cycle:
The effect of the brazing cycle may be expected to affect the physical properties of the parent metal. During heating tensile properties of cold-worked wrought materials will give way to the lower strength properties of annealed metals. Further, with the highest-temperature brazing alloys grain growth may result in deterioration of properties, these effects understandably
being less pronounced with cast structures.
Where higher strengths than given by an annealed wrought structure were necessary, heat treatable metals such as FV520 stainless steel, and the Nimonic range of nickel-base alloys could be used. However to develop optimum properties it then became necessary to follow the brazing cycle with solution and age-hardening heat treatments, although there were a number of occasions when by selection of a suitable filler, brazing and solution treatments could be combined.

(i) Stress Relief:
A major problem encountered was a change of dimensions in the specified clearances, due to the internal relief of stress, especially in the case of wrought metal components. In the case of machineable wrought stock, good practice was to leave stock 0.02 to 0.04 ins.(0.5-1.0 mm) oversize and anneal it before final machining prior to brazing. In the case of sheet or foil brazements, where it is not possible to anneal at an over-size intermediate stage it was found desirable to shape the component as required, anneal, and in many cases to re-size before brazing the components together.

(j) Dissimilar Sections:
When these required joining, heating and cooling methods needed careful consideration due to the ability of thin sections to both heat and cool more quickly than thick sections. The resultant distortion due to those effects could result in joint clearances being affected. Good practice was to arrest the heating cycle some 40-50°C below brazing temperature to allow temperature equalisation, since an important consideration is the joint clearance at brazing temperature.

(k) Machining After Brazing:
In cases of a brazed fabrication requiring a machining operation after joining, attention must be paid to ductility in the joint area as some high temperature fillers are hard and difficult to machine, notably the nickel-chromium-cobalt-silicon-boron series. It was found that in certain cases a prolonged soak at brazing temperature brought about diffusion in the joint area, as a result of which brittle compounds could be dispersed.

(l) Inherent Properties Of Certain Parent Metals Calling For Special Consideration:
Thought must be paid to weld decay if unstabilised stainless steels are slowly cooled through the 800-850°C temperature range. Season-cracking had been found to arise in 60/40 brass which had not been stress relief annealed before H.F. induction brazing. Stress corrosion could arise when low expansion nickel-iron alloys were brazed with certain copper and silver containing brazing alloys. Certain elements such as boron may have detrimental effects in service and brazing alloy constituents had to be carefully considered to ensure that these elements were kept within specification, notably for nuclear applications.

(m) Electrical Properties:
Electrical conductivity is a particularly important consideration when using H.F. brazing. The input of heat if endeavouring to join copper to mild steel, because of the different rates of heat absorption by these two metals, could effect joint clearances so that all the molten filler alloy ran out of the joint.
(n) Thermal Conductivity:
It is important in heat exchanger production that sound joints are made between fins and tubes, calling for combinations of fillers and parent metals which are suitable in effecting removal of heat from the tubes containing the hot fluid in service.

(o) Thermal Expansion:
This property can dictate materials to be used for components and jigs. It had earlier proved a major stumbling block to brazing metals to glasses and ceramic materials but limited success had been achieved by first "metallising" the ceramics for sparking plug and radio valves.

(p) Joint Configuration:
Experiences showed that the configurations displayed in figs. (2) to (9) answered most engineering problems to be anticipated in general use, with systems preferable for joints to be made in aluminium illustrated by figs. (10) to (12).
Joints have to take into account the availability of brazing alloy as wire, foil, shim, powders, plating or as clad on to parent metal. Problems have arisen as to where to locate the filler. In the case of a stack of thin silicon-iron alloy laminations to be used in a small gyroscope operating at 25,000 R.P.M. for a guided missile application, the method in this case was adopted of holding the laminations in position by a squirrel-cage. This was made from 60/40 brass where constituent parts were all silver-plated. The assembly was suitably jigged before heating to the copper-silver eutectic melting temperature in dried hydrogen.

(q) Sequential Joints:
It became the practice to use two or more brazing or soldering operations in the production of a component, and the designers had to ensure that the alloys selected could be used in the required production sequence, to make what were known as graded or 'step-by-step' joints. In the sequence the highest melting brazing alloy would be used for the first joint to be made, with the final joint using the lowest melting alloy in the sequence. The electronic industry was a major user of joints made by this approach.

(r) Jigging:
The ideal was to use self-jigging and self-aligning designs with the intention of minimising distortion effects during the heating and cooling cycles. The many ways of making designs self-jigging included spot-welding, rivetting, knurling, twisted-tagging (so-called 'tinker toy' method). Where external jigs were used the designers tried to match expansion characteristics of jig materials with parts being joined, and it was therefore essential that thermal expansion characteristics of parent metal, filler metal and jigs were not markedly dissimilar.

(s) Cleaning Procedures:
It was important that when preparing his specification the designer took into account the needs for both pre-brazing and post-brazing cleaning treatments. Pre-cleaning treatments were generally satisfied by using metals which were not heavily contaminated by oxides, such as newly machined metal parts. These were de-greased with carbon tetrachloride or trichloroethylene vapour and/or acetone before applying the brazing alloys to the prepared and, as necessary, jigged parts. After de-greasing it was essential to observe clean-room procedures.
Fig. 2 . . . Lap joint designs for low and high stresses. Unless an abnormally strong brazing alloy is used in A, failure is to be expected. In B, failure will occur in the parent metal. Flexure of the right-hand member in C and D will distribute the load throughout the parent metal, offsetting the stress-raising effects at changes in section brought about with A and B type joints.

Fig. 3 . . . Butt joint designs and modifications to increase load carrying capacity of joints under static stress and dynamic loading are illustrated. It should be noted that C has both butt and lap joints. The broken arrowed lines indicate unsuitable load distributions.

Fig. 4 . . . Designs for use with sheet metal assemblies are given here. Loading is symmetrical in B and C, unsymmetrical in A and D.

Fig. 5 . . . These joint designs for sheet metal assemblies give increasing ability to carry high static and dynamic loads.

Fig. 6 . . . Plate to plate, or hub to shaft, designs for similar applications to the designs illustrated in Fig. 7. On rotation, centrifugal loading will put this joint in tension, whereas in Fig. 7 the joint will be in shear.
The grooves shown in B and C apparently weaken the members, but in fact they increase the overall strength compared with A by removing the stress region from the joint. Strength improves proportionately as the design progresses from A to E.

Fig. 8... Reducing the tube diameter as in A will produce a satisfactory assembly for low stresses. However, expanded tubes as shown in D produce best overall strength.

Fig. 9... Designs for tube and header joints in heat exchangers where there is a high pressure gradient across the tubes. In A and B maximum stress is at the header and the tubes may fail in fatigue where they enter the header. In C, D and E, stresses are distributed more widely, thereby increasing resistance to failure.

Fig. 10... Jigging—methods of self location

Fig. 11... Lap joints for high strength

Fig. 12... Flux entrapment prevented by venting.
with only cotton-gloved operators handling the parts, and for transitory periods all parts were retained in polythene bags wherever practicable. Ultrasonic cleaning was also used for aluminium parts immediately before fitting the components together prior to brazing.

After-brazing cleaning: This treatment was necessary if chemical fluxes had been used, as residues were usually corrosive to the system, particularly in the case of aluminium alloys. In this instance examination of areas away from the brazed joints was also important to ensure that flux residues had not been trapped in blind areas.

(t) Inspection Techniques:
It was usual to include with the work pieces being brazed a test coupon. This could take the form of a simple lap joint, one end of which, after brazing, would be retained in a vice before the other end was struck with a hammer. The expectancy was that failure would occur outside the joint area if the brazing cycle had been correctly followed. On occasion it was possible for complete destruction of a percentage of the components made to be specified, with full metallographic inspection of all joints. In all cases of aircraft, avionic components, or atomic energy parts, a full inspection was carried out to ensure that a 'witness' of the brazing alloy fillet was continuous at every exposed joint. In the case of 'blind' joints a visual inspection method was developed using intrascopes. With heat exchangers another test involved a pressure test using air, sometimes under water. Occasionally radiography was specified.

(u) Proving Tests:
A number of tests have been used. There was no universal test. Engineers designed their components, and if heat exchangers, these were subjected to wind tunnel tests; if pressure soundness was concerned, air under-water testing at pressures well in excess of those encountered in service were carried out. Again if the brazed component was to be subjected to thermal cycling, fatigue or creep stresses in service the designer invariably introduced a final proving test to establish that the brazed joints could withstand the conditions. Usually a tensile test piece would be made and tested to destruction to determine the amount of overlap required if lap joints were used. Attempts were made to test for impact if shock resistance was a requirement. Metallographic examinations were carried out to note effects of intermetallic compounds. Experience using sintered Vitallium and tracing hardnesses of different compounds with a Reichert micro-hardness tester had proved that normal polishing techniques could mask differences between phases, and an electro polishing technique had been employed to note differences previously undetected when surfaces had been prepared by hand polishing specimens.\(^{12}\)

Wettability and spreading tests usually took the form of loading a metal specimen with a controlled weight of flux and putting into an air muffle furnace. Effectiveness of the flux was initially established by noting the visible spread of flux over the metal and the cleanliness of the metal.\(^{13}\) Next, having selected the most appropriate flux, different brazing alloys of the same weight were loaded into the furnace with flux, and wetting of the parent metal noted using the contact angle procedure developed by G.L.J.Bailey's team at B.N.F.M.R.A.\(^{(23-25)}\) in which the specimens were sectioned for metallurgical examination with low powered microscope. The angle between the base plate and the tangent of the bead of brazing alloy was determined as a contact angle, utmost spreading occurring if for example contact angle was 1°, and zero capability for brazing if 89°.

The same approach was used to determine the cleaning method to be used for
aluminium. In that case different samples had controlled amounts of Al-Si eutectic added. They were first cleaned by treating in trichloroethylene vapour alone; vapour followed by a pickle in 10% aqueous HNO₃; 10% HNO₃ alone; carbon tetrachloride alone and acetone followed by 10% HNO₃. After treating in vacuum there was little difference in brazeability but after loading into the flux bath it was concluded that trichloroethylene followed by 10% HNO₃ resulted in superior contact angles for brazing aluminium alloy.¹⁵³

2.4.- High Frequency Brazing

This heating method¹⁶,²⁰,²¹ was used for the quick assessment of filler alloys, where expensive time would otherwise be spent on setting up furnace equipment normally used in the manufacture of company products. As a method it had also gradually evolved from the mid-1930's as a very satisfactory system in mass production runs, when continuous supervision became unnecessary after brazing conditions had been established.

2.4.1.- Equipment

It was concluded that of the plant available a 12kVA Delapena E14 450kc/s brazing unit would give excellent flexibility for alloy assessment. This unit was used in conjunction with a clear, vertically held, siliceous tube which contained the test specimens and was centred inside a heating coil. It could be used with air and a chemical flux; purified gas could be introduced to pass over the metals being joined throughout the heating cycle, or as provided commercially pure gases could be used in conjunction with a flux. The parent metals to be united took the form of tubes of different diameters located so as to create an eccentric gap (in plan form); hence where tubes touched clearances were zero, with the gap a maximum at the opposite side of the tubes. Subsequent sectioning and metallographic examination established the ability of the filler alloy to wet, spread, and fill the space between the parent metal tubes.

In other series tubes were arranged concentrically within each other to ensure constant gap clearances before brazing. Following joining the addition of suitable securing equipment allowed the brazed composite to be loaded into a tensile machine when load-to-rupture in shear could be determined for different brazing alloys for comparison purposes.

2.4.2.- Method Of Heating

When electric current passes through a conductor, heat is generated within it which is proportional to I²R (I = current; R = resistance). This is resistance heating, and the heat so generated can be transmitted to other objects by conduction, radiation and convection. In the case of induction heating this is effected by placing the parts to be heated inside a suitable high frequency coil in which there is no contact between parts and coil. The HF current sets up a rapidly changing magnetic field at the coil. Therefore the faster the field is changed, the higher the voltage developed, and the greater the heat induced in the skin of the parts to be brazed. In fact the induction coil and the parts within it act in a similar manner to a transformer where the induction coil is equivalent to the primary winding, and the conductor performs as a short-circuited secondary winding carrying a heavy current. When a conductor cuts through lines of magnetic force, an electric current flows in the conductor i.e. the lines of force from the induction coil cut through the component being
brazed. The number of lines of force cutting the component will depend:

(a) on the cross-sectional shape of the coil (square sectioned tubing was used in preference to round sectioned tubing for the induction coil as it created a larger magnetic field over the component), and

(b) upon the proximity of the coil to the component, the closer the coil being in relation to the component, the more lines of force cut the component, thus creating larger electrical currents, and therefore more heat. In practice it was found that if coil distance exceeded circa. 0.25 ins. (6.35 mm) it was difficult to induce enough heat in the component for brazing to take place. In the case of the ferro-magnetic materials, iron, nickel, and cobalt, heating rate is faster than with non-magnetic or weakly magnetic materials. The reason is that hysteresis enhances skin effects up to the temperatures at which they become non-magnetic.

The following table lists the resistivities of various metals and assesses their coupling factors, where coupling factor is used as a rating to indicate the ability of the induction coil to heat different metals to their brazing temperatures:

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity (microhms-cm)</th>
<th>Coupling Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At Room Temp:</td>
<td>At 800°C.</td>
</tr>
<tr>
<td>Carbon</td>
<td>1400</td>
<td>-</td>
</tr>
<tr>
<td>Mild Steel</td>
<td>16</td>
<td>109</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>69</td>
<td>114</td>
</tr>
<tr>
<td>Titanium</td>
<td>55</td>
<td>165</td>
</tr>
<tr>
<td>Brass</td>
<td>6.9</td>
<td>-</td>
</tr>
<tr>
<td>Aluminium</td>
<td>2.7</td>
<td>-</td>
</tr>
<tr>
<td>Copper</td>
<td>1.7</td>
<td>-</td>
</tr>
</tbody>
</table>

From the quoted resistivities, for example copper, applying the $I^2R$ rule, takes longer to heat than titanium and in practice, whereas the former metal took several minutes to reach brazing temperature, titanium required only a few seconds, using identical weights of metals, currents and time settings.

Induction heating results in the skin of the part being heated before the interior. This effect can be offset and uniformity of temperature in the joint area gained, by inserting a graphite susceptor between coil and parts being brazed. In this way the work is heated by radiation from the susceptor (a disadvantage is that susceptors obscure the view of the braze).

While in the simplest form the prepared joint is introduced into the coil, it was found possible to heat the inside of tubular joints by inserting a coil within the assembly.

2.4.3-Advantages of HF Heating

These may be regarded as follows:

(a) Rapid Heating:

With precise temperature control this is available, particularly important when liquidus temperatures rise rapidly as a result of interalloying between certain parent and filler alloys.
(b) Distortion Small:
During the heating cycle distortion is minimal.

(c) High Temperatures:
Depending on materials being heated, high temperatures can be reached in a relatively short time e.g. 1250°C.

(d) Adaptability:
The method is readily adapted to production line methods, and once the conditions have been established, semi-skilled workers are capable of operating HF units for long runs.

(e) Fluxing:
While in many cases heating can be used in conjunction with a controlled atmosphere to prevent oxidation, there were other instances where contaminants from air were not particularly harmful to joint properties, and heating could be performed in air with a chemical flux added with the brazing alloy to ensure removal of those contaminants from the joint at the time of melting of the filler alloy.

2.4.4—Disadvantages of Method

The following list disadvantages of this heating method:

(a) Non-Portable Equipment:
Unlike torch heating which it was coming to replace on flow production lines the equipment is not portable (but can be made somewhat more flexible by fitting extension leads to the HF coil).

(b) Simple Joints Only:
Usually only simple joints such as tube-to-tube are satisfactory, with one joint being made at a time.

(c) Skin Effects:
Heating commences at the skin of the joint and progresses inwards. The frequency of the generator controls the depth of skin which is heated, and very high frequencies can lead to a shallow region of heated metal. When selecting a generator it is advisable to use a frequency which results in deep skin heating.

(d) Preferential Heating At Edges:
When establishing conditions for brazing, care is essential to control temperatures so that edges of parent metal do not overheat to the extent that edges melt before the rest of the joint area reaches the brazing temperature.

(e) Flow Line-Control:
In HF brazing a most important consideration is not to exceed a time which has been selected by experiment for a given joint assembly. This calls for an accurate timing device for, if temperature is not closely controlled, the work may be ruined. Such control is particularly important for flow lines, for which the process is most suited.

(f) Clearances Control:
Unless self-jigging designs are employed it is difficult to control clearances...
such that if a designer has laid down that gap clearance must be 0.006 in. (0.15 mm), it is not unknown for the 2 parent metals being joined to be in contact at one side and have a 0.012 in. (0.3 mm) gap at the other side of the joint. Capillary forces would be unlikely to retain the majority of molten brazing alloys in a gap of the latter size.

(g) Electrical Efficiency:
Efficiency can be low, and depending on coil design and application will rarely exceed 50% of the electrical input applied to the workpiece.

(h) Maintenance:
Expensive maintenance calls for specialised equipment and personnel.

(i) Capital Cost:
Initial capital cost of equipment was relatively high.

2.4.5-Brazing Various Components

Having considered the basic approach to be followed, attention will now be turned to considering specific items which used this technique.

(a) Protection During Brazing:
While stable oxides on 18/8 stainless steel parent metals acted as a barrier to wetting of parts by brazing alloy in undried commercial-purity argon, no problem was experienced for a room temperature application if a proprietary flux, based on mixed fluorides and borates was applied to the joint before brazing with Johnson Mattheys 'Easyflo' (BS1845 Type 3) in the same gas. Argon had the beneficial effect when compared to air, of not permitting further tarnishing of parent metals during the brazing process.

(b) Brazing Alloys For Stainless Steels:
When 18/8 stainless steel joints were required to withstand high temperatures and/or pressures, success was achieved using a nickel-chromium-silicon-boron brazing alloy (Endewrance 53) with a borate-type flux in a stream of 90% argon 10% hydrogen gas to prevent discolouration. Ideal joint clearances at room temperature were found to be 0.004 in. (0.1 mm) One assembly comprised a 0.01 in. (0.25 mm) thick bellows to be joined to a 0.25 in. (6.35 mm) flange and the total brazing cycle from switching on the current to completion of cooling of the brazement was circa 30 seconds.

Other brazing alloys successfully used to join stainless steels included alternative BS1845 types (since revised) copper-silver-eutectic, copper-silver-eutectic plus 0.2% lithium (lithium was thought to improve the wetting properties of the copper-silver alloy) and copper-silver-palladium alloys with and without 0.2% lithium (Mond SCP7 and Mond SCP1).

(c) Copper to Stainless Steel:
A 0.5 in. (12.7 mm) thick copper flange was joined to a 18/8 stainless steel pipe, 6 ft. (1.83 m) long, where the clearance between flange and steel was 0.004 in. (0.1 mm). Johnson Matthey's 'Easyflo' alloy was used with argon as a gas cover. The brazing alloy penetrated completely through the joint to appear on the reverse side to which it was applied; in the presence of the large amount of copper the brazing cycle in this case took 10 minutes.
(d) Glass Industry Application:
To obtain a joint for a glass industry application, where it was to operate at prolonged periods at 900°C, stainless steel had to be joined to molybdenum rods. Mond PN1 alloy (60% Pd 40% Ni) was used under protective covers of both argon and 90% argon 10% hydrogen mixed gases on different occasions. The additional use of borate-type flux was essential.

(e) Platinum To Steel Contacts:
Platinum electrical contacts were brazed to steel contact breakers with 82% Au-18% Ni alloy, after failure resulted from an earlier attempt in a vacuum furnace, which took 45 minutes to reach brazing temperature. In that case the failure was attributed to a progressive increase in solidus temperature of the gold-nickel alloy due to inter-alloying between platinum and gold/nickel alloy, and even though the recommended brazing temperature was exceeded by 150°C the brazing alloy still failed to melt. Using HF the complete brazing cycle took only 10 seconds. These experiments with the induction heating unit were repeated in vacuo at 10^-2 mm Hg pressure; also with mixed gases, both with and without flux. The type of atmosphere did not affect the results, and the heating rate appeared to be the only factor affecting joint soundness.

(f) Commercially Pure Titanium:
This was brazed to stainless steel on one occasion with the Johnson Matthey 'Easyflo' alloy, and on another with the copper-silver eutectic under a commercial argon cover. Although brazing times were minimal, and both alloys wetted and flowed throughout, sectioning, metallographic and micro-hardness examinations revealed the presence of a brittle intermetallic constituent(s) between silver from the brazing alloy, and the titanium. It was concluded that the method would probably be adequate for lightly loaded structures, but not for stressed applications.

(g) Nimonic 90 Lacing Wire:
Aero-engine turbine blades called for lacing wires; in this requirement Nimonic 90 was brazed to Nimonic 90 using copper as the filler alloy under a 90% argon-10% hydrogen cover. The braze took 60 seconds, and many joints were successfully made using this approach, although, in another application the slow heating experienced in a vacuum furnace with the same combination of parent and filler metals resulted in intergranular penetration of parent by copper, and was regarded for this reason as unsatisfactory.

(h) Medical Research Council:
Their Laboratory of Molecular Biology had developed a 5kW X-ray tube for investigating the structure of haemoglobin. The large rotating anode assembly, approx 5 ins.(127 mm) diam. x 2 ins.(51 mm) deep involved HF brazing copper inserts into a 70/30 brass component. The complete assembly was heated to 600-700°C, and brazed with 'Easyflo' alloy. The brazing alloy was a pre-positioned ring and flux was used. Heating took 10 minutes. This was a case where no gas cover was used, and the completed component was pickled in acid to remove oxide products caused during the heating cycle.

(i) Electronics Industry:
This industry was using HF brazing to an increasing extent for components used in high frequency valves, magnetrons and thytrons. There was particular interest in the Mond 60% Pd-40% Ni alloy and their silver-copper-palladium series, especially where two joints could be made at different stages of
manufacture of the component e.g. using the SCP3 alloy at brazing temperature 850°C and SCP1 at 807°C in a later operation.

Another interesting application was the use of SCP3 to braze beryllium to Monel in the production of 'windows' for the Raymax 50 X-ray tube.

Pd-containing brazing alloy was again used where nickel-iron parts were brazed with the PN1 alloy to ceramics in the manufacture of a copper-free ceramic-to-metal seal for high temperature neutron detection equipment (in this case to counter adverse thermal expansion effects, the metal was arranged to be the outer member of the joint).

Before the advent of the palladium-containing series the electronics industry was using the Easyflo-type alloys for Monel and the low expansion Ni-Fe alloy Nilo-K. However, users were finding deterioration of electrical properties in service due to evaporation of cadmium or zinc from the brazed joint. Further they were experiencing cracking when Nilo-K was brazed with the alternative copper–silver eutectic. This did not arise when the palladium-containing alloys were used.

Other combinations successfully HF brazed as routine included tungsten rods brazed to molybdenum anodes with PN1 alloy and copper rings brazed to Monel diaphragms using the silver-copper-palladium alloys.

2.5-Car Heater Production

The advent of both motor car and aeroplane at the turn of the century lead to requirements to cool essential moving engine components to prevent their seizure. Such requirements resulted in the development of heat exchangers viz. radiators and oil coolers. In each the principle involved was to pass hot liquids arising from work carried out by the moving parts of the engine, through an arrangement of tubes and fins making up the radiator surface. The radiator surface was exposed to a mass of moving air in service, and on the basis of heat being removed faster from thin sheet material 'fins', than from the heavy sections of the engine, a state of balance could be calculated to tell the designer the number of fins required to enable the liquid to be cooled to a sufficient temperature, hence permitting its re-introduction to the engine.

Designers calculations also took into account thermal conductivities of the different metals used in production of these components, as a result of which copper or aluminium were the preferred materials for the heat exchanger "block", as the core of the radiator was called.

A development of this approach was to insert a second, smaller block into the water cooling circuit, immediately after the engine, but before the water was re-circulated through the radiator. This provided the basis for the car heater (16.33) which was progressively introduced into automobiles from around the 1950’s. Because the heater came immediately after the engine with water at its hottest, external fresh air, capable of blower assistance from a fan, was arranged to pass over the block to be introduced via appropriate venting into the car to provide warmth for the passengers. Initially car heaters were made and marketed as expensive extras, but by going to mass production techniques, where the adoption of soldering and brazing processes played an essential part in manufacture, car heaters had by 1965 become an integral part of the vehicle.

A discussion of the manufacture of car heaters, where one production line was producing 2,000 units per day, appears to be appropriate, as this was probably the largest single user of brazing and soldering techniques, providing good examples of how 'graded' joints could be made at different stages in the production of a component, ready for installation into the motor car, where all
the assembler was involved in was connection of the inlet and outlet water pipes into the engine-cooling water circuit.

2.5.1-The Heat Exchanger Block

The heat exchanger block is the heart of the car heater as performance largely depends on adequate heat dissipation from this part. In arriving at a suitable design of heater, factors to be considered ranged from size of the block to power of the fan blower. Copper was the preferred fin metal, but as trace elements adversely affected conductivity phosphorus had to be controlled not to exceed 0.1%, as any amount above this resulted in excessive deterioration of heater performance. Once the decision had been reached on the basic material to be used in the construction of the heat exchanger, the standard of jointing to be expected was considered, bearing in mind that the maximum service temperature was 110°C. Badly made joints would lead to losses in thermal efficiency, quite apart from the obvious hazards of leakage of hot water into the engine mechanism and car interior. Type and shape of joint design brought forward the conclusion that to ensure maximum contact between copper fins and the alpha brass tubing used to carry the hot water should be lap joints; with adequate clearances to permit the solder to fill the gap between the two metals. The target for the gap was 0.003 in. (0.076 mm) (although BS1723:1963 allowed a maximum clearance of 0.006 in. (0.015 mm) for this combination of parent/filler). The length of overlap was equally important to ensure both joint soundness and maximum contact between brass and copper after joining. In practice the overlap had to equal between 4 and 5 times the thickness of the thinner of two members to be joined, and if this rule was followed a sound joint, having superior tensile properties to the parent metals, was always to be expected. The block after manufacture was joined to header tanks, each with baffles inserted to ensure water was directed through the required tubes in the correct direction. One header tank had 70/30 brass inlet and outlet tubes brazed to it (header tanks were made from stress relief heat treated 60/40 brass, season cracking having been experienced when tanks were used in the 'as pressed' state).

2.5.2-Joining Sequence

The sequence of making the assembled heater involved the production of sub-assemblies made with different melting filler alloys before bringing these together in a final lower melting joining operation and installation into the car heater case.

(i) Sub-Assembly 'A':

The first joint involved the use of a high frequency coil to braze the water pipes to one header tank using flux and 'Easyflo' (50 Ag-15.5 Cu-16.8 Zn-18 Cd) at 620°C, i.e. mid-way between the solidus and liquidus temperatures given in makers literature.

The second joint involved an air-gas torch, and an aqueous-type flux based on killed spirits (HCl) to braze in the baffle separating water flows into each header tank using a proprietary low temperature silver-cadmium-zinc alloy which joined at 350°C.

(ii) Sub-Assembly 'B':

Fins, tubes and collector plates (which lock the fins and tubes at each end) before joining to the header tanks of sub-assemblies of 'A'.
The first joint was involved in the manufacture of the brass tubing. Flat 70/30, 0.005 in. (0.127 mm) strip was passed through a 60 lead-40 tin solder bath at 205°C, which "tinned" both surfaces. The tinned strip then passed through forming rollers over a mandrel to form a double lock-seam. Afterwards the tubing was re-heated when solder ran to fill the lock-seam. Lengths were then cut at appropriate sizes and fitted into the two collector plates with the heat dispersing-fins stacked between. The sub-assembly was then passed on a conveyor belt, to make the second series of joints, through a bath of the same aqueous-type flux as per 'A' second joint, and thence into a muffle furnace with a solder melting at 200°C. The blocks often suffered minor "misses" and these had to be filled, particularly where tubes joined collector plates. The third joint therefore involved tinning collector plates, and filling wide gaps in a dip process in which the block ends were manually immersed in another of the lead-tin solder alloys melting at 185°C.

(iii) Joining the Sub-Assemblies Together:
The last joints were made by using HF coils in two operations, one at each end of the block, to re-melt the solder on the tinned collector plates to the sub-assembly of water pipes, fin and collector plates, and also to the brazed sub-assembly of water pipe, baffle and header tanks.

2.5.3-Quality Control

The final operation before installing the block and blower into the car heater casing was to clean all surfaces, to be free from flux residues. Quality control of all incoming materials played an important part in ensuring a uniform product. Similarly, testing on a routine basis of all features of the production line was essential. While final inspection may have met all visual standards, and all water containing joints were shown to be pressure tight, it was still necessary to ensure that performance figures stipulated by the designer were met. For this purpose blocks were selected at random every day and subjected to wind tunnel evaluation; this gave a measure of assurance that all joints were being properly constructed.

In conclusion: at that time it was felt that car heaters typified components which could not be produced without the use of these joining methods if complete reliability was essential. The methods used resulted in an end product both technically sound and economical as a result of the mass production methods employed in manufacture.

2.6-High Temperature Brazing

Developments in the sphere of brazing stemmed from an awareness that latest requirements for heat exchangers by aero-engine manufacturers called for first-class corrosion-resistant joints under arduous conditions of service. It was concluded that for high temperature usage having given thought to various atmospheres for brazing, ultimately the best prospects were to be obtained with vacuum for consistent joints where stainless steel stabilised with titanium was the parent metal. Long term it was foreseen that requirements would call for brazing of the wide range of high temperature alloys which were undergoing development, notably the Nimonic nickel-based range, and the Stellite cobalt-based series.

While the company had long been approved by the Ministry of Supply's Aeronautical Inspection Directorate, the latter Department advised that getting the laboratory manager, and his deputy, individually qualified to their Harefield...
laboratory requirements, should also prove beneficial in obtaining direct contracts from the Ministry, as there was no commercial vacuum furnace in production elsewhere in the U.K. at that time. Ministry contracts were regarded as valuable, as they gave access to classified work done by other laboratories, and the AID recommendation was therefore followed up, bearing in mind that this was an era when many workers were exploring different ways of achieving the same aim. For example, whereas Nimonic 90 could be used as appropriate as stator and compressor blade materials for service at up to 900°C, higher temperature materials were required in the development of engines of greater power. Ivor Jenkin's team at G.E.C. Wembley worked on powder metallurgy approaches using titanium for lower temperature stages of compressors, and Vitallium (64% Co-30% Cr-6% W alloy) for higher temperatures, of the order of 1200°C. The approach followed for Vitallium was to compact powders around pre-positioned cadmium wires. During a pre-sintering operation at 650°C. in vacuum (0.1 mm Hg) the cadmium was vapourised so that passages suitable for cooling were left in the block. After sintering at 1300°C in H₂, the block was machined to give a turbine 'bucket' through which cooling air was introduced, to enable the material to be used in higher engine temperatures than had been envisaged by the makers of this high temperature alloy. (At the Reutte Seminar in 1955 a paper given by the G.E.C.team was reported as 'perhaps being the most important contribution to this conference'). A second approach at introducing cooling into blades was followed by Bristol Siddeley Engines, in which machined half-section buckets were copper-brazed in the vacuum furnace later installed by D.G. at Cricklewood. A third laboratory was engaged on casting in cooling vents using the lost wax process, and yet another approach considered the use of molybdenum disilicide wires, which could subsequently be leached away, after casting the chosen high temperature alloy around them. However, the multiplicity of approaches being followed were severely curtailed by the Government, who cancelled many Ministry sponsored contracts in the late 1950's, leaving the aero-engine manufacturers to make their own arrangements when the brazed approach became favoured by the Rolls Royce Group who had by now taken over B.S.E.

2.6.1-Parent Metals

While a wide range of alloys had been brazed in controlled atmospheres and in vacuo, the most important were the stainless steels, the heat resisting alloys and the refractory metals, these being of prime interest to the aircraft, nuclear and electronic industries.

(a) Stainless Steels:
During the 1950's to 1960's there had been an increasing demand for complex heat exchangers to operate under arduous conditions of temperature and pressure. To meet these requirements stainless steels had been used, and typical oil coolers were made from 0.008 in. (0.2 mm) wall thickness tube x 0.125 in. (3.175 mm) outside diameter brazed with Endewrance 53 to 0.125 in. (3.175 mm) collector plates at either end. Another heat exchanger involving air to liquid used 3/32 in. (2.38 mm) diameter tubes of 0.008 ins. (0.2 mm) wall thickness to 0.028 ins. (0.71 mm) collector plates, brazed with Endewrance 52 alloy. In an unrelated application involving master dies produced for a gramophone company (E.M.I.) stainless steel was plated with copper prior to vacuum brazing. Stainless steels were brazed in both hydrogen atmosphere furnaces and vacuum furnaces. While capital cost of the hydrogen installation was substantially lower than costs for vacuo, and the hydrogen approach allowed higher output,
effectiveness of the $H_2$ depends upon its ability to reduce the oxides, nitrides, carbides, or a combination of these which form on stainless steel. The $H_2$ must be virtually free from water vapour, oxygen and other contaminants. It had been found in practice that to braze stainless steels the water vapour content of the $H_2$ going into the furnace should not exceed 0.04% (equivalent dewpoint of $-60^\circ F (-51^\circ C)$). Additionally the flow must be sufficient to flush out any water vapour produced by reduction of oxides at high temperatures. However, experience had proved that many heat exchangers with their complex matrices were difficult to purge and keep flushed with fresh $H_2$, and in such structures it had been found that gas entrapment inhibited wetting and spreading of the filler leading to 'misses' when final inspection was carried out. Many structures which would not give total success when $H_2$ brazed, have on the other hand due to the technical advantage held over $H_2$ by vacuum furnaces, been most successful for such complex parts.

(b) Heat Resisting Alloys:
Commercially available alloys contained appreciable quantities of titanium and aluminium which formed tenacious oxides, incapable of reduction in dried hydrogen. Because of the wide use of such alloys for aero-engine components, special techniques had been devised to braze them. One commonly used method was to pre-plate the surfaces to be brazed with Ni, Cr, or Cu and then to braze in $H_2$.

A second approach was to braze in $H_2$ with the addition of borax to the filler metal, however, this called for a post-brazing cleaning treatment to remove flux residues and often joints were unsound.

A third method involved pickling the parts in a pre-treatment operation in a nitric acid-hydrofluoric acid mixture with the intention of removing surface oxide films containing titanium and aluminium oxides. The alloys were subsequently brazed in $H_2$ of dewpoint $-80^\circ F (-62^\circ C)$.

All three methods had been successful albeit inconsistent results were obtained after brazing. On the other hand brazing the same alloys in vacuo avoided such problems as long as the degree of vacuum was controlled, although various workers differed on the degree of vacuum required for a particular alloy. This apparent divergence of opinion seemed to relate to the type of measuring gauge, the type of vacuum furnace and the vacuum pumping system employed.

Although heat resisting alloys had been successfully brazed the mechanism by which wetting took place was obscure. The dissociation pressure of the oxides of chromium, titanium and aluminium are many orders lower than the vacuo obtained in commercial furnaces, making it extremely unlikely that such oxides would be decomposed by heating in vacuo. Work by Wall and Milner with aluminium alloys appeared also to be applicable to the heat resisting alloys. In their work they found that on heating Ni and Cu containing small percentages of Al in vacuo, a surface film formed of aluminium oxide. This type of film was capable of penetration by molten filler metals, which then spread over the surface of the alloy along the metal-oxide interface to flush the oxide film away from the joint. For penetration of the oxide film to occur the base metal should be soluble in the liquid filler, also some solubility was required for spreading to occur along the metal-oxide interface. However wide solubility favoured erosion of the parent metal rather than spreading. There appeared to be a critical pressure below which a penetratable oxide formed; above this pressure no wetting took place.

Nickel-chromium-boron alloys, and palladium containing brazing alloys appeared most suitable for Nimonic alloys as intergranular penetration of Nimonic 90 had been experienced when copper brazed.
Because of its reactivity in air at elevated temperatures, titanium, and similarly zirconium, could only be brazed in purified argon or vacuum. The main problem was that this metal forms brittle intermetallic compounds in the presence of most other elements. A vacuum of $10^{-5}$ mm Hg had proved satisfactory, but to prevent any contamination of work it was the practice to enclose the titanium charge in a titanium box which in turn "gettered" contaminating gases. The brazing time had to be kept as short as possible. Success had been achieved in brazing a commercial purity Ti tube to a stainless steel tube with a 60 Ag-30 Cu-10 Sn alloy.

2.6.2-Brazing Alloys

In addition to the properties required of a brazing alloy given earlier, (wet parent metals, fluidity at brazing temperature, joints to possess mechanical and chemical properties satisfactory for the intended service application, etc.), if brazing is to be carried out in vacuum the filler should not contain constituents having a high vapour pressure at the process temperature, otherwise compositional changes can arise at the time of brazing such that the furnace operator is chasing increasing liquidus and/or solidus temperatures before the filler is seen to flow (by which time damage can arise to the inherent properties of the parent metal due to grain growth, or at worst melting). Vapours so produced also contaminate the furnace retort which would then be out of action while a costly cleaning operation took place, otherwise on reheating in a later furnace run the constituent(s) could be re-deposited on the work piece as a harmful contaminant.

For brazing to occur it had long been concluded that the liquid filler metal must alloy with the base metal. Subsequent wetting and spreading is influenced both by melting range of the filler alloy, and also by type and extent of alloying that took place. A filler with a narrow melting range tended to flow freely and was preferred for joints having small clearances. A filler metal of wide melting range tended to be viscous, and subject to liquation. To inhibit liquation occurring the latter types of filler should be heated quickly through the melting range.

The type of alloying taking place between filler and parent metals had a pronounced effect upon the filling and strength of the joint. If an intermetallic compound were formed the liquid filler could even de-wet and separate as beads on the surface of the parent metal. On the other hand if the parent metal had wide solubility in the liquid filler, considerable compositional changes could take place, which could alter the melting point of the liquid metal. If the melting point is lowered as a result of compositional changes considerable erosion could occur if heating was prolonged. Alternatively if compositional changes resulted in raising the melting point of the brazing alloy the liquid may become pasty and not flow unless the temperature is raised - under these circumstances long capillary paths would not completely fill. Non-uniform heating should be avoided since the hotter parts of a joint will be the first to alloy, solidify, then leave un-brazed pockets in the cooler parts. In an alloy system of this type a wider joint gap should be used to prevent choking by premature solidification.

Another metallurgical process frequently taking place during brazing is the diffusion of certain constituents of the brazing alloy into parent metals. While excessive diffusion may be harmful to thin sections, many alloys depended upon the alloying and inter-diffusion that occurs during brazing for high joint strength. The amount of diffusion can be regulated by controlling gap width,
time and temperature of brazing.

Section 2.3 para (e) listed the compositions and melting points of the most commonly used filler alloys. The selection of alloys for a particular application is mainly determined by service conditions of the brazed component. Some of the important alloys will be considered in more detail in the following paragraphs, particularly with respect to vacuum brazing.

(a) Copper:
This was widely used as a filler alloy, with a lot of experience gained by brazing in dry hydrogen. It was conveniently applied as plating, foil, wire or powder. It was also extensively used as a filler in vacuum. Because there is limited solubility between Cu and Fe, Cu flows freely on plain carbon steels, and the optimum joint clearance derived was 0.001 in. (0.025 mm). The solubility for Cu in Ni is much higher, and as a result when brazing Ni alloys with Cu, considerable diffusion (and counter-diffusion) takes place, and this could take the form of undesirable intergranular penetration. Joints brazed with Cu have only moderate strength compared with joints made using alternative alloys, and Cu should not be used for service conditions over 400°C.

The vapour pressure of Cu is quite high at its melting point, and when used in the vacuum furnace the brazing time should be as short as possible to prevent excessive volatilization and deposition on cooler furnace parts.

(b) Silver-Copper Eutectic Alloy:
Although silver has a high vapour pressure at its melting point, (2.5 x 10⁻⁹ mm Hg at 960°C) the 72% Ag-28% Cu alloy, melting at 780°C had been used in the vacuum furnace to join Cu to Cu and Cu to steel. When joining Cu to steel the brazing alloy could be applied as foil etc. or by plating, the steel component being Cu-plated and the Cu-part, silver plated. The assembly was then heated to 800°C, for a short time to allow alloying and melting to take place, and cooled to room temperature.

(c) Copper-Gold Alloys:
Several alloys in the Cu-Au series have been used for vacuum brazing copper to copper, or copper to stainless steel. They have good corrosion resistance and low vapour pressure. However, because of their high cost their use had been limited almost exclusively to the electronics industry for the fabrication of high power valves.

(d) Gold-Nickel Alloys:
This was another expensive alloy having greater strength and corrosion resistance than the Cu-Au alloys, but its use was similarly restricted as (c) above.

(e) Nickel-Base Alloys:
Since 1948 a wide range of Ni-based alloys had been developed for brazing stainless steels and heat-resisting alloys. Many had high stress-to-rupture properties, and excellent resistance to oxidation and corrosion. Compared to other high temperature brazing alloys they were inexpensive. Although there were considerable variations in composition they could be divided into two broad classes, those containing boron and/or silicon, and those containing phosphorous.

(d) Ni-Si-B Alloys:
These were the largest group, and in addition they could contain chromium and
iron with brazing temperatures ranging from 1050°C to 1190°C. A feature of this class of alloy was that they readily alloyed with the parent metals, and if held at brazing temperature for any time, diffused into them. The diffusion of B, C and Si takes place both along the grain boundaries, and into crystals of the base metal. Where these elements diffused they reacted with base metal elements as appropriate to form borides, carbides and silicides.

The importance of diffusion depends on the cross section of the parts being brazed, and the use to which the parts are to be put. Diffusion increases strength, high temperature properties, and ductility of a joint. The compositional changes which took place increased the remelt temperature of the brazing alloy. Where an assembly was constructed of very thin gauge material, extensive penetration was undesirable, but in applications requiring strong joints for high temperature service some penetration could be tolerated, and may be necessary for maximum strength. As well as penetrating into the parent metal by diffusion, this class of alloy would cause erosion, if present in excess. For this reason the amount of alloy applied and the brazing cycle was carefully controlled, particularly when joining thin material. For maximum strength from the Ni-Si-B alloys joint clearance was kept to 0.004 in.(0.1 mm). With wider clearances brittle mixtures of eutectic phases and intermetallic compounds formed which lowered the impact strength of the joint. A programme of work was carried out for the Ministry of Supply through 1960-65 when impact strengths of a number of brazing alloy and parent metal combinations were explored, together with other properties. Micro-hardness checks were carried out across metallographically prepared specimens, and these highlighted the variations between the different compounds which could exist across brazed joints.

There were a number of occasions when tight clearances could not be maintained, and where maximum strength was not necessary. In these cases a special wide gap filling alloy, such as Microbraz WG could be employed. All of the Ni-Si-B brazing alloys were hard, and only readily available as powders. The powders were mixed to a slurry with an acrylic resin cement and applied with a paint brush or eye dropper.

(ii) Phosphorous Containing Nickel-Based Alloys:
Nickel based alloys containing P were mainly developed for the nuclear industry where the presence of B could not be tolerated. While this type alloy is brittle it does not erode stainless steel, and proved suitable for joining thin gauge material. Most alloys were only available as powders, an exception being the 40% Ni-10% P eutectic alloy applied by Albright and Wilson's Kanigen electroless plating technique. The strongest phosphorous containing alloy available was Endewrance 57, which in addition contained Fe, Cr & Co.

(f) Cobalt Based Alloys:
An alloy holding promise for both stainless steels and Nimonic alloys was Stellite SF6. In addition to excellent corrosion resistance BNFMRA proved this to be one of the strongest fillers available.

(g) Palladium Containing Alloys:
Although 12 alloys were being marketed by Engelhard at this time, with melting temperatures ranging from 810°C to 1240°C, four were particularly suitable for brazing in vacuum, namely the 60 Pd-40 Ni; 82 Cu-18 Pd; 55 Cu-20 Pd-15 Ni-10 Mn alloys, available as wire or foil, and the 48 Ni-31 Mn-21 Pd alloy as a powder. The latter alloy held future promise with a limited number of stress-to-rupture tests at 450°C. on brazed Cr/Mo steel showing it to offer
improvement of this property over the established hydrogen brazed silver-
palladium-manganese alloys. The palladium containing alloys otherwise had
moderate high temperature strength and corrosion resistance.
The main virtues of the palladium containing alloys were in their abilities to
join a wide range of parent metals with a minimum of erosion, to wet and spread
on most metals and to fill gaps consistently up to 0.01 in. (0.254 mm) wide.
They were also softer and more ductile than the higher strength Ni-and Co-based
alloys, permitting machining of joints after brazing. While not as costly as the
gold-containing alloys they were still more expensive than the nickel-and
cobalt-based alloys, which acted as a deterrent to their use in many places.
Other systems undergoing evaluation at that time by Mond were the Pd-Ag-Al: Pd-
Ni-Ag; Pd-Ni-Cu; Pd-Ni-Cr; Pd-Ni-Ti and Pd-Cu-Au series.

2.6.3-The Vacuum Furnace

GEC designed a cold retort type vacuum furnace specifically for brazing to
the Delaney Gallay requirement. When it was installed in 1959 it was one of
the largest furnaces in Europe designed for brazing. The unit had a working
area which was 2ft. (60.96 cm) diameter x 3ft. (91.44 cm) high. The furnace was
rated at 200 kVA. Heating employed graphite resistance elements where the
heating element took the form of a cylindrical assembly of graphite rods fed
with low voltage from a 3-phase transformer having a steplessly variable
output. Surrounding the elements were concentric stainless steel radiation
screens which provided thermal insulation. The whole was contained in a water-
cooled, mild steel, internally clad with stainless steel, vertical cylindrical
tank, dished at the bottom and closed at the top with a water-cooled domed
cover which was raised/lowered by an electric hoist. Water cooling was effected
by soldering mild steel pipes to the 'tinned' outer casing of the retort.
Temperatures of 1250°C +/- 5°C were attained within the charge space. The
ultimate vacuum pressure obtained with the system was 10^-4 mm Hg and was
achieved with a 16 inch (40.64 cm) Vacuum Industrial Applications Ltd. oil
diffusion pump, having a capacity of 5,500 litres per second. This pump was
backed by a General Engineering Ltd. gas ballasted 110 cu.ft./min. (3134 dm³/min)
Kinney rotary pump. Interesting features of the equipment included the
provision for multiple thermocouples (Pt-Pt/13%Rh 'Fibro' thermocouple Pt*35
preferred) to measure temperature distribution throughout the charge. Ports
were also arranged to enable the work to be visually inspected through the lid
and side throughout the brazing cycle. The power output to the heating
elements could be manually or automatically regulated. Using the manual
control, heating rate was capable of being controlled to suit a particular heat
treatment being carried out - this useful facility was appreciated when
comparing vacuum sintering with brazing thin sheet. In vacuum sintering
considerable out-gassing occurs during heating, and to maintain high vacuum the
temperature had to be slowly raised over several hours. On the other hand when
brazing thin sheet, heating rate should be as rapid as possible, and time at
temperature kept to a minimum to prevent erosion of parent by the molten filler
metal.

(a) The Vacuum Brazing Process:
Care had to be taken in the pre-treatment of the work pieces. Oxidised metal
was acid pickled or cleaned by scratch-brushing prior to de-greasing. Heavily
cold worked components or parts which had been severely machined, had to be
stress relief annealed before assembly for brazing. As far as possible the
assembly should be designed to be self-jigging, and many parts could be held
together by rivetting, spot welding or knurling, thereby simplifying final assembly and saving furnace space. However, many components, particularly those made from light gauge material, having low creep strengths at elevated temperatures, required support to prevent distortion. In such instances a separate jig made from a heat resistant material was used. This was designed so that in its turn it did not induce stresses into the joint. It also had to be as light as possible, and preferably not shield the work piece from the heat radiated from the elements during the heating cycle. Often a stop-off agent, such as magnesia or alumina suspended in an aqueous solution, was applied to the jig to prevent the work becoming attached. Filler alloys were applied as powder, foil, wire and plating. For small very thin secondary surface heat exchangers involving the joining of corrugated 0.005 in. (0.127 mm) thick 18/8 stainless steel to 0.006 in. (0.152) separator plates, applying powders uniformly was overcome in one method by electro-phoresis. In this method resin was applied followed by shaking fine powdered brazing alloy over the surfaces, and tapping off the excess before assembly into the brazing jig.

Amounts of filler required varied widely, depending on such factors as the base metal, joint clearance, length of capillary, and mechanism of alloying between base metal and filler. The prepared work was loaded into the furnace. The furnace was then evacuated before heating to the appropriate temperature. The order of vacuum required depended on the base metal being joined; generally for stainless steels a vacuum of 10^-2 mm of Hg was satisfactory, while for the Nimonic, containing aluminium and titanium, a vacuum better than 10^-3 mm Hg was required. Once temperature reached 700°C, the charge could be observed through the windows, and this, together with thermo-couples attached to the charge gave close control over the brazing temperature. Since the vacuum gauges gave a continuous indication of the degree of vacuum within the furnace it was considered that a very closely controlled method was available throughout the brazing cycle.

A typical brazing cycle for a 1001b. (45.36 kg) weight stainless steel component was to heat to 1085°C, in one hour, hold at 1085°C, for 5 minutes, and cool to 200°C in 3½ hours. The cooling time was substantially reduced in certain circumstances by admitting H2 into the furnace to a pressure of 100 mm Hg once the charge had cooled to 800°C. The effect of the H2 was to increase the rate of heat transfer by convection between the work and the walls of the furnace, resulting in improved furnace capacity (i.e. the furnace could be used for a greater number of runs each week).
configuration.
The special requirements of the nuclear process stipulated that the brazed joints must:
(i) withstand service conditions of 650°C in CO/CO₂ atmospheres,
(ii) the filler alloy chosen should not erode the stainless steels, nor should it diffuse into it to any appreciable extent,
(iii) the grain size of the can material had been carefully controlled during manufacture to achieve optimum creep ductility and corrosion resistance; because of this, filler alloys whose brazing temperatures were likely to cause significant grain growth were unacceptable,
(iv) other unacceptable filler alloys were those containing boron, cobalt, or gold as constituents as these affected the efficiency of the nuclear process.

From the alloys commercially available 5 were selected which appeared to be suitable namely, pure copper: 55 Cu-20 Pd-15 Mn; Ni-P eutectic: Ni-13 Cr-10 P and 52.5 Cu-38.5 Mn-9 Ni. Each alloy was assessed after brazing in 10⁻² mm Hg vacuum for joint filling, wettability, attack on the can material, and grain size. Some tensile and shear tests were carried out at 650°C. Due to the joint configuration where, at assembly 0.008 in. (0.2 mm) designed gaps varied between zero and +0.008 in. (0.2 mm), 100% uniformly sound joints were not available.

(a) Copper-Palladium-Nickel-Manganese Alloy:
Brazed at 1120°C. this alloy gave only 45% average joint filling, and was not proceeded with further due additionally to the grain growth which developed in the can material during the heating cycle allowed by the design of the furnace.

(b) Copper
This was a convenient filler to use, and resulted in 80% sound joints by applying as 0.002 in. (0.05 mm) Cu-plate to the cans and adding Cu powder to the joint assembly. However at the brazing temperature excessive grain growth had developed, and further work was abandoned.

(c) Nickel-Phosphorous :
Cans were electrolessly nickel plated to 0.002in. (0.05mm). The nickel plate obtained from this process contained 5-10%P. This, supplemented at the joint with a powdered Ni-11%P alloy brazing at 1030°C, resulted firstly in joints being made at the Ni-P eutectic temperature of 877°C. Proceeding to the higher temperature resulted in diffusion effects dispersing brittle compounds from the joint area without any significant increase in can material grain size, and gave joints which were 90% sound.

(d) Copper-Manganese-Nickel Alloy :
The filler was only available as powder. On average joints made at 1000°C. were only 40% sound. It was satisfactory in respect of grain growth and alloy penetration with reasonably short brazing cycles.

(e) Nickel-Chromium-Phosphorous :
This alloy was applied as a powder; joints tended to be brittle and easily damaged during metallographic sectioning after brazing at 980°C. Increasing the brazing temperature to 1010°C resulted in a marginal increase in grain size and joints were assessed as 70% sound. When mechanically tested against joints made with the other alloys it was concluded that on balance this was the best of the 5 alloys tested and became the subject of further work carried out within the UKAEA's own locations. (As a result of this work using an alloy
modified to Ni-25% Cr-10% P it is understood that for service in CO/CO₂ eventually over 900,000 joints were irradiated without failure (<sup>61</sup>).

2.5.4-Other High Temperature Brazing Applications: UK/Europe/USA

(a) UK/Europe

In general the UK were leaders of the European scene, and during visits to the Low countries, W.Germany, Sweden and Switzerland, all of whom had shown interest in work carried out by Mond and Delaney Gallay, it appeared that most ideas originated from the UK or USA. Because of the close location of DG (Cricklewood) to London Airport, and the fact that there were speedy air links to the major centres, DG got involved in a number of sub-contract orders from these other countries, although in most instances, similar projects had already been investigated with British companies. Apart from nuclear and aero engine applications, already discussed, other interesting projects involving this method included the following:

(i) English Electric Company
Experiments with SPM1, SPM2, NMP1 alloys to join parts of a turbine to be used in a guided weapon system.

(ii) British Rail
To prevent blade flutter in an experimental gas turbine used SPM1 alloy to braze Nimonic 80A lacing wires to stainless steel blades.

(iii) PARMATRADA
This Association was using NMP1 alloy for an experimental marine engine to be cooled by the sodium/potassium eutectic. Joints were compatible with the molten eutectic after one month's immersion at 600°C.

(iv) British Heat Resisting Glass Company
In the manufacture of molten glass, molybdenum electrodes were brazed to mild steel using SPM1 alloy.

(v) H.M.Hobson Ltd.
This company were using SPM1 alloy to braze together the 10 different stainless steel parts used in making gas pressure regulating valves, controlling fuel to a rocket motor through a micro-jet.

(vi) Rankin & Blackmore Ltd.
The components of the astern nozzle box assembly used in the free-piston gas turbine engine of the 9,200 ton ore-carrying ship MORAR were brazed with SCP3 alloy.

(vii) Sperry Gyroscope Company
Gimbal assemblies made from mild steel pressings and forgings were copper brazed in vacuum for a gyroscope housing. Another production application for the same firm involved copper-brazing mild steel attachments to a nickel-iron spinning.

(viii) Jabsco Pump Company
For a dairy pump application, the disc of a nozzle ring made from stainless steel had Nimonic 80A blades brazed in vacuum with Endewrance (Coast Metals) 53.

(ix) Centrax Ltd.
This organisation used SPM1 alloy experimentally to make segments of 18/8 stainless steel honeycomb approx 12 in. x 1 in. x 0.25 in. (30.48 cm x 2.54 cm x 6.35 mm) deep. The segments were so placed as to give continuous rings around the inside of an aero engine, such that if growth of turbine or compressor blades occurred, the blades would have a seal formed between them and the internal engine casing. (There was a considerable amount of interest in making other reticulated or honeycomb structures to sheath guided missiles, and aircraft flying at speeds where surface temperatures could be in excess of 600°C, but this UK work was suspended as a result of the Government defence cuts referred to earlier).

(x) Hoy Carbides Ltd.
For a coal cutter, a mixture of the carbides Cr₃C₂/Cr₇C₃ was bonded with nickel, pressed and sintered. The sintered part was successfully brazed with Mond CPNM2 alloy to stainless steel.

(xi) Rocket Projectile Establishment
This Ministry Department used palladium containing alloys, Endewrance alloys and copper to join nozzles to a 2 ft. (60.96 mm) diameter stainless steel disc, approx 4 in. (10.16 cm) thick.

(b) USA Assessment:
A visit in 1962 served to impress that UK and European manufacturers were merely 'scratching at the surface' of prospects for this engineering method of joining metals. The Ibsen Furnace Company were making cold wall vacuum retort furnaces, with work zones of up to 8 ft. (243.84 cm) tall by 8 ft. (243.84 cm) diameter, and capable of temperatures of circa 2,100°C. These were mainly being supplied to companies concerned with aero engine manufacture, such as Pratt & Whitney and General Electric, who were using the Endewrance and Nicrobraz alloys for engine components.

Honeycomb manufacture using the brazing process was impressive, with panels of the material as used for wings being some 10 ft. by 8 ft. (304.8 cm x 243.8 cm) with sections ranging from one quarter inch to 5 inches (6.35 mm - 12.7 cm) thick. Brazing alloys were preferably foils, and heating was by concentrated banks of radiant quartz lamps. Smaller assemblies could be made in a retort furnace after piece parts had been loaded into a box which was welded with the parts to be made inside, and heated in an inert gas. Purge tubes were connected from the loaded box to a vacuum pump, and the box was then raised to brazing temperature. After the brazing cycle was completed the box was cut open, and the brazed part was removed.

The majority of the USA honeycomb work involved precipitation hardened stainless steels, such as 17/7PH (1.15 Al-0.07 C-17 Cr-0.6 Mn-7 Ni-0.4 Si-Fe Remr.) or various titanium alloys e.g. A110 AT (5 Al-2.5 Sn-Ti Remr.) with NAmerican, Rockwell, Airsearch, Ruhr and Northrup leaders in the field.

The space programmes provided a powerful driving force with USA requirements for heat shields, involving honeycomb for strength-to-weight and acoustic considerations, and rocket engines having long pipe runs vacuum brazed to casings. The method had clearly become well established in the minds of the USA designers as opposed to the Europeans who still tended to regard brazing as a last resort method of joining.

On the strength of DG's experiences, and the observations made following the American exchanges, their Board decided to order an extra furnace from Degussa, and eventually an order was placed in 1965 for a 5 ft. x 5 ft. (152.4 cm x 152.4 cm)
cm) unit. (In any event by this time the existing unit was calling for increasing maintenance, and was over-loaded).

2.7-Aluminium Brazing

Joining aluminium long presented problems due to the tenacious oxide forming on both parent and filler metals. It was found possible to solder, torch braze, argon-arc, resistance or ultrasonically weld a number of the alloys so long as well defined conditions were observed. However in many applications, notably heat exchangers, where long paths had to be joined, none of these methods were appropriate. Attempts had been made to furnace braze in an air oven with a flux additive, but this was unsuccessful. Vacuum brazing was examined at a later date, but results were unacceptable, presumably because heat control in the unit discussed in section 2.6.3. was insufficiently fine at 600°C, for a furnace designed to work at higher temperatures (the charge could not be viewed at this temperature). Also it was probable that breakdown of the oxides could not be promoted in the vacuum achievable at this temperature by the particular furnace available.

Success was obtained in a flux bath, and this was the unit standardised for brazing aluminium and its alloys. At that time while flux baths were in regular use in the USA, apart from units being used by Morris Radiators (Cowley) and Marston Excelsior (Fordhouses) no other unit was known to be in use in Europe.

2.7.1-Description of Flux Bath

The unit used was made by Efco-Upton Ltd. The working area was 28 in. x 26 in. x 18 in. (96.52 cm x 66.04 cm x 45.72 cm) and had a refractory lining to contain the salt (flux). The lining was supported on insulating materials, and all held within a frame of refractory brick work. 2 electrodes passed, horizontally from each side, through the brickwork, insulating material and refractory liner. Initially molten flux was introduced until a bridge formed between electrodes so that current could pass. Additional flux was progressively added until the bath surface was at its working level. The flux used was the proprietary Efco-Park D, essentially a mixture of sodium chloride and fluoride plus potassium and lithium chlorides, melting at 535°C, and with a working range 565°-650°C. Density at 586°C was c.100 lbs. per cubic foot (1600 kg/m³). The current used to heat the bath of molten flux originated from a low voltage alternating supply (60kVA), a method of heating which resulted in high heat transfer from the salt to the component undergoing treatment with uniformity of temperature throughout the bath. Simultaneously the salt had excellent fluxing action on the oxides present on the aluminium and its alloys, and compared to other salts available reports suggested that sludge formation (calling for weekly removal) was at a minimum, probably due to inclusion of sodium fluoride in the flux which caused dross to rise to the top, from where it was readily skimmed off. Accurate control of bath temperature was vital, bearing in mind that certain of the alloys which were brazed had a liquidus temperature which was within 5°C of the brazing temperature. Due to the closeness of the densities of aluminium alloys and the flux, there was only a slight tendency for brazing alloy to flow downwards due to gravity effects, and capillary attraction was regarded as the principal force involved in retaining molten brazing alloy in the joint. However it was believed that a further factor which assisted in placing brazing alloy in the joint was the downward
flow of filler alloy due to 'flux drag', when components were removed from the bath.

### 2.7.2-Brazeable Aluminium Alloys

There were 14 brazeable alloys, some requiring a final precipitation-hardening treatment to develop optimum properties. They were given brazeability ratings. The first 11 alloys required an additional lower melting point filler alloy. The last were clad with 10% coating thickness of brazing alloy if total sheet thickness was 0.048 in. (1.219 mm) or less, or 5% coating thickness if the sheet was thicker.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nominal % Composition</th>
<th>Melting Range°C</th>
<th>Condition</th>
<th>UTS. (tsi)</th>
<th>Elong % on 2&quot;</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS1470/77</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- S1</td>
<td>99.99 A1</td>
<td>660</td>
<td>Annealed</td>
<td>4 max. 45 min.</td>
<td>Excellent</td>
<td></td>
</tr>
<tr>
<td>- S1A</td>
<td>99.80 A1</td>
<td>645-657</td>
<td>&quot;</td>
<td>5 &quot; 35 &quot;  &quot;</td>
<td>&quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>- S1B</td>
<td>99.50 A1</td>
<td>635-650</td>
<td>&quot;</td>
<td>6 &quot; 30 &quot;  &quot;</td>
<td>&quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>- S1C</td>
<td>99.00 A1</td>
<td>630-655</td>
<td>&quot;</td>
<td>6.5 &quot; 30 &quot;  &quot;</td>
<td>&quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>- NS3</td>
<td>Al-1.25 Mn</td>
<td>643-655</td>
<td>&quot;</td>
<td>7.5 &quot; 30 &quot;  &quot;</td>
<td>&quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>- NS4</td>
<td>Al-1.7/2.8 Mg -0.6 Si</td>
<td>595-650</td>
<td>&quot;</td>
<td>11-14 18 &quot;  &quot;</td>
<td>&quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Can braze up to 2% Mg if part is clean)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HE9 Al-0.4/0.9 Mg -0.3/0.7 Si</td>
<td>580-680</td>
<td>Annealed</td>
<td>7 min. 15 min.</td>
<td>III</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot; &quot; &quot;</td>
<td>&quot; &quot; &quot;</td>
<td>&quot;</td>
<td>12 min. 12 min.</td>
<td>&quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HE19 Al-0.4/1.5 Mg -0.6/1.3 Si</td>
<td>580-660</td>
<td>Annealed</td>
<td>7 min. 15 &quot;  &quot;</td>
<td>&quot; &quot; &quot; &quot;</td>
<td></td>
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<tr>
<td></td>
<td>&quot; &quot; &quot;</td>
<td>&quot; &quot; &quot;</td>
<td>&quot;</td>
<td>18 &quot; 10 &quot;  &quot;</td>
<td>&quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HE20 Al-0.8/1.2 Mg -0.4/0.8 Si -0.2/0.8 Mn -0.15/0.35 Cr</td>
<td>580-660</td>
<td>Annealed</td>
<td>11 max. 18 &quot;  &quot;</td>
<td>Good</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot; &quot; &quot;</td>
<td>&quot; &quot; &quot;</td>
<td>&quot;</td>
<td>18 min. 8 &quot;  &quot;</td>
<td>&quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HS30 Al-0.4/1.5 Mg -0.6/1.3 Si -0.4/1.0 Mn</td>
<td>580-650</td>
<td>Annealed</td>
<td>11 max. 18 &quot;  &quot;</td>
<td>&quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot; &quot; &quot;</td>
<td>&quot; &quot; &quot;</td>
<td>&quot;</td>
<td>19 min. 8 &quot;  &quot;</td>
<td>&quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DTD5008 Al-0.5/0.7 Mg</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>casting.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- 0.25 Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- 4.8/5.7 Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- 0.4/0.6 Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Impalco-PA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17/19 Al-7/8 Si clad on NS3 alloy</td>
<td>565-600</td>
<td>Annealed</td>
<td>7½ max. 30 &quot;</td>
<td>Excellent</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16/19 Al-4½/6 Si clad on NS3 alloy</td>
<td>565-625</td>
<td>&quot; &quot; &quot;</td>
<td>7½ max. 30 &quot;</td>
<td>Excellent</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alcoa-22 Al-7/8 Si clad on HS30.</td>
<td>565-600</td>
<td>&quot; &quot; &quot;</td>
<td>11 max. 18 &quot;</td>
<td>Good</td>
<td></td>
</tr>
</tbody>
</table>

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It will be noted that the NS4 alloy was brazeable if magnesium was up to 2%. If greater, joints were often porous, probably as a result of the tenacious MgO film on the parent metal.

### 2.7.3 Aluminium Based Filler Alloys

<table>
<thead>
<tr>
<th>Designation</th>
<th>Nominal % Composition</th>
<th>Melts-°C.</th>
<th>Brazes-°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS 1941-1</td>
<td>Al-2/5 Cu-10/13 Si</td>
<td>550-570</td>
<td>580-640</td>
</tr>
<tr>
<td>&quot; -2</td>
<td>Al-10/13 Si</td>
<td>565-575</td>
<td>585-640</td>
</tr>
<tr>
<td>BS 1475-NG2</td>
<td>-- &quot; --</td>
<td>-- &quot; --</td>
<td>-- &quot; --</td>
</tr>
<tr>
<td>BS 1941-3</td>
<td>Al-7/8 Si</td>
<td>565-600</td>
<td>600-615</td>
</tr>
<tr>
<td>&quot; -4</td>
<td>Al-4.5/6.5 Si</td>
<td>565-625</td>
<td>620-640</td>
</tr>
<tr>
<td>BS 1475-NG21</td>
<td>-- &quot; --</td>
<td>-- &quot; --</td>
<td>-- &quot; --</td>
</tr>
</tbody>
</table>

On the grounds of temperature latitude the first three (BS1941) were the preferred filler alloys. The fourth alloy's melting range prevented its use with the H20 and H30 alloys where the solidus was 580°C. Even using the aluminium-silicon eutectic as filler alloy for H20 or H30 with very short immersions, times could be critical, as otherwise 'burning' or blistering could arise. The higher melting brazing alloy had been used on occasion when graded joints were called up, when the first joint was made using the Al-5% Si alloy (NG21), and the second joint with the Al-11.7% eutectic (NG2).

### 2.7.4 Joint Design-Clearances

There were two standard ways of making joints in the flux bath. The alloy could be arranged in the joint by means of foil (shim) or clad sheet. Alternatively brazing alloy in the form of wire or powder (applied by camel hair brush or eye-dropper) was applied to the mouth of the joint. In this method molten brazing alloy at the appropriate temperature was drawn into the joint by capillary attraction, and 'flux-drag'. When alloy was placed in the joint prior to brazing, clearances ranged from zero to 0.004 in. (0-0.1 mm) but high compression on the filler should be avoided as this could prevent the molten flux from entering the joint to remove oxides on the metals. Practice had proved the desirability of using a slight excess of brazing foil which on melting fed the joint, hence ensuring that supply of filler alloy was adequate. In the case of wire or powdered filler alloys the clearance had to allow the filler to bridge and flow through the joint, and these were therefore planned to range from 0.002 in. to 0.006 in. (0.05-0.15 mm). If less than 0.002 in. (0.05 mm), due to alloying with the parent metal, alloy would not run completely through the joint unless it was very short. On the other hand if clearances exceeded 0.006 in. (0.15 mm) it was possible that there could be insufficient alloy to fill the joint, or filler alloy might not be retained where wanted, and thus the final joint became porous.

Design of joints followed the principles given in Sect.2.3. with preferences in practice found to be butt, lap or spigot designs for aluminium. In the case of the heat treatable parent metals where the filler alloy does not precipitation-harden on subsequent heat treatment, the lower properties of the filler are
offset by using lap joints, and the designer must bear this in mind. Care must be given when designing aluminium alloy parts likely to be fatigue stressed in service. In one simple waveguide, where a large end plate was rigidly retained, and the other subjected to vibration in service, the waveguide fractured through the parent metal, but there was no sign of rupture of the brazed joint. Generally a brazed joint which is uniform distributes stresses evenly, and there are no stress concentrations due to the fillet where, for example, flange and waveguide are brazed together.

2.7.5-Assembly

Whenever possible assemblies were designed so that jigs were unrequired for holding piece-parts tightly in position and parts were made to be self-locating. The reason was that external jigs frequently caused distortion since on heating Al alloys expanded at approximately twice the rate of the jig materials -18/8 stainless steel or Inconel 600 being preferred. If any form of screw or bolt jigging was used these must not be made from mild steel or free-cutting steel as these metals quickly erode due to the action of flux and subsequent cleaning treatment. Inconel or stainless steels are the only metals to use as other materials could further affect the flux by leaving deposits in the bath. Any screws had in any case to be subsequently removed to off-set possible galvanic corrosion effects in service. As the complete assembly would be immersed in the salt, and any blind holes would fill, considerable cleaning time would be necessary after brazing to get rid of flux residues if such holes were present. Potential air pockets had to be vented otherwise flux would not enter the joint, inhibiting brazing alloy from wetting surfaces in such regions. Similarly an undercut on a shaft or behind a screwhead could prevent flow because of non-venting or alternatively a locally excessive clearance. It was essential that there were no cavities inside the assembly to become hermetically sealed by the brazing alloy on solidification. If the part was subsequently re-heated as in a solution or ageing treatment after brazing, it could blister due to local high pressure in the area of the cavity, particularly if this had a thin-walled section. If argon-welded tacks were used as an aid to jigging the tacks should be as small as possible as tacks could keep brazing wire away from the mouth of the joint, as a consequence of which when the filler melted it might be too far away to flow into the joint.

2.7.6-Brazing Procedure

(a) Cleaning
All piece parts were chemically cleaned by initially subjecting for 15 minutes in a trichlorethylene vapour de-greaser, followed by 10 minutes in a 5% nitric acid solution at 60°C. It was important to braze components as soon as possible after cleaning, and if delays occurred this part of the cycle was repeated. It had been shown that if cleaning was incorrectly carried out or parts left with a thin film of oil, grease or dirt from the atmosphere, then the brazing alloy (despite the flux) was less than satisfactory in wetting the parent metal.

(b) Applying Filler Alloy
Parts and brazing alloy were assembled in a clean area. Operators had to handle parts after cleaning with cotton or terylene gloves. Stop-off materials
such as magnesia, graphite, or on occasion by anodising, were employed when it was necessary to keep regions free from exposure to brazing alloy. For example the waveguide designers often required a slot in the vicinity of joints, and where these existed there was always a tendency for the brazing alloy to enter, due to normal capillary attraction, or flux-drag on removal from the bath. The assembly was then placed on a brazing jig, which bearing in mind the advisability of keeping parts self-jigging was of the support type to hold the assembly during the brazing heating cycle.

(c) Brazing Cycle
The jigged assembly was next heat treated in an electric forced-air circulation furnace until a uniform temperature was recorded. This temperature was approx. 40°C below final brazing temperature to obviate distortion on transferring the pre-heated assembly into the flux bath. Upon transfer the assembly was carefully dipped into the molten flux with immersion times being critical, particularly for the more highly alloyed materials. Bath temperatures were controlled to be below the solidus of parent metal but in excess of the liquidus temperature of the filler alloy. As it took some considerable time for the flux bath to stabilise at temperature it was not possible for practical purposes to braze all combinations of parent and filler at the same time, calling for batching to keep the process economical. By the procedure of pre-heating the times of dipping in the flux bath were minimal e.g. 3 minutes at brazing temperature. After brazing the flux was drained back into the bath to remove the majority from the brazed part.

(d) Post Braze Treatments
After cooling in still air the residue of the flux was removed by immersion in agitated water at 80-100°C, until all visible flux residues had disappeared, after which the brazed assembly was removed from the jig. The brazed part was then placed in 5% HNO₃ to remove the last traces of flux, and also to eliminate water staining from the preceding treatment. Concentrations and temperatures of HNO₃ solutions, and immersion times were critical factors, as certain of the alloys would dissolve if any of these conditions were excessive. Finally the assembly was rinsed in running water before being oven dried. In the case of hard water the component was given a last immersion in de-mineralised or distilled water to obviate all staining on drying. Chemical checking was necessary in the case of complex structures to ensure that all flux traces were removed since residues were highly corrosive. The technique was to immerse the component in a 0.1% HNO₃ solution. An aliquot portion of the liquor was then titrated against silver nitrate, and if any halide was noted the assembly was re-cleaned followed by another chemical check, the process being repeated as necessary. Another chemical check as part of the process control involved the condition of the bath to ensure that concentrations of copper and iron were minimal, as transfer of these elements from the salt bath to the parts being treated would affect their corrosion resistance in service, due to galvanic effects.

(e) Inspection Of Brazed Components
Even using an intrascope it was difficult to visually examine interiors of all joints. A good witness of the alloy flowing through joints indicated that these were sound in the case of complex parts. Even when a continuous fillet was evident it was possible that large voids were inside due to faulty design, faulty assembly, or inadequate pre-cleaning. Conclusions were reached that the
only reliable type of visual examination was when a fillet was found at both sides of a joint when filler alloy had only been applied to one side. If fillets showed signs of porosity it was considered that this was due to time of dip in salt bath: if too short flux was trapped in the brazing alloy on its solidification; porosity of this nature could be overcome by re-dipping for a longer period. If joints brazed by placing alloys at the mouth failed to show a 'witness' of alloy through the joint, this could be due to:

(i) insufficient brazing alloy,
(ii) excessive joint clearances,
(iii) joints too long for capillary flow to be effective, usually associated with inadequate clearances,
(iv) time too short in the flux bath, or
(v) inadequately precleaned parts within the joint.

With some assemblies braze quality could be established by carrying out a pressure test, as in the case with heat exchangers, or pressurised boxes being used to contain airborne radar equipment. The pressure test could be an air-underwater test, or resort could be made to a spectrometer when high vacuum soundness was a mandatory requirement.

In the case of simple type joints frequently radiography was specified. Ultrasonic testing had been used on occasion, but if complex joint configurations were used at that time with the equipment available, it was difficult to determine whether sealing was unsound, and in the case of really complex assemblies often metallographic sectioning of complete units on a sampling basis was specified; very expensive but worthwhile if for example an aircraft's safety was dependent on the type of part concerned.

Dye penetrant methods did not find favour. Investigation of them showed that cracks in a braze retained the dye. Re-dipping of the component for repair showed that the flux failed to remove the dye and such cracks would not therefore repair on re-processing.

Flux growth was sometimes noted, and often confused with a blotchy and somewhat similar growth which can appear all over an assembly left to stand, due to relatively harmless residues in the water, which did not arise if parts were properly dried after cleaning. If flux growth was noted reprocessing through the cleaning cycle was carried out as per para.(d) above.

(f) Treatment After Machining

Despite the greatest care, a flux-bath brazed joint could contain hidden small pockets to retain flux. If these were not exposed they were not necessarily harmful depending on the service application. If components were to receive a subsequent machining operation however exposure of such flux pockets to the atmosphere, with consequent corrosion, was usually seen within 24 hours of machining. The corrosion was manifest as white cotton-wool like growth in the joint area. It therefore proved advisable to re-clean as in 2.7.6.para.(d) in a final operation after machining.

2.7.7-Other Applications For Aluminium Brazing

Early in this paper the point was made that Delaney Gallay's interest was in making heat exchangers, and this was the principal reason for acquiring vacuum furnace equipment for high temperature alloys, and a flux bath for joining aluminium alloys. The under-utilisation of both units resulted in the spare capacity being offered to industry at large. This approach not only brought in extra machining work for the factory in general, where they were often invited to make the complete component but it also gave a great deal of experience of
other materials, as evidenced by the sections on HF brazing and high temperature brazing respectively. In the case of aluminium alloys a parallel situation occurred with some interesting applications for this process given below:

(a) Waveguides
The flux bath technique was regularly used in the production of waveguides for airborne radar and guided missile applications, where distortion had to be minimised, and tolerances often held to +/- 0.001 in. (0.025 mm). Probably one of the largest aluminium alloy waveguides was the feed unit of the experimental dish aerial used in the G.P.O.'s 2-way trans-Atlantic telecommunications system sited at Goonhilly Downs, near Lands End. This used the Telstar and Relay satellites, and was over 6 feet (1.83 m) long. Brazing was in four operations, with sections bolted together. Different sections were successfully brazed to an exacting specification.

Waveguides were particularly susceptible if any flux were left in the joint, and "whiskers" quickly grew if cleaning had been inefficient, which would completely throw-out the performance of a waveguide, as well as attacking the parent metal.

(b) Heat Exchangers
Aluminium secondary surface heat exchangers especially presented difficulties in producing a metal bonded corrugation sandwich, capable of withstanding pressures in excess of 200 lb/sq.in. (14.05 kg/cm²) and having adequate thermal conductivity properties. This type of heat exchanger was built up from aluminium corrugations separated by sheets of Al-1.25% Mn alloy clad with Al-7.5% Si brazing alloy. Cladding was present on both sides of the Al-Mn alloy i.e. a 0.036 in. (0.91 mm) thick sheet clad with 10% thickness of brazing alloy had a core thickness of 0.036 in. = 0.0288 in. (0.73 mm). The coating of brazing alloy on clad sheet was hard to detect visually as supplied, and experience therefore proved the advisability of using double-sided sheet to obviate dangers of brazing alloy being wrongly positioned, to cause a scrapped assembly. A further feature was that while clad sheet cost twice as much as parent metal plus brazing alloy foil, there was considerable saving in labour as positioning of brazing alloy in a separate operation was unnecessary.

For larger heat exchangers foil was used. However for thin structural members foils could affect tolerances and result in alloy excess. For example if 0.006 in. (0.15 mm) thick aluminium was brazed with 0.002 in. (0.05 mm) foil, the excess brazing alloy would tend to block the cooling passages of the matrix on solidification, thereby impairing designed characteristics of the unit in service.

(c) Complex Pressurised Boxes For Airborne Equipment
Use of the flux bath compared to other methods gave sound joints in boxes with high strength-to-weight ratios. The corrugation for boxes made in this way were consistently strong, and also served as means by which a cooling medium was circulated around the equipment.

(d) Brown Boveri Aluminium Alloy Impeller
This company were producing impellers in Switzerland to operate at high speed in service. The impeller vanes were machined from bar stock. The shroud was also machined from wrought material. Machining was arranged to be 0.02 in. (0.5 mm) oversize before stress relief annealing. Both components were then machined to final size. Brazing alloy powder (Al-Si eutectic) was applied as a mixture with alcohol to the vanes before loading onto a brazing jig and dipping. A major consideration was given to the grain flow in the heavily cold worked aluminium alloys, and its effect on the development of maximum strength in the
components [up to 11 in. (27.94 cm) diameter x 3 in. (76.2 mm) thick] after brazing.

(e) UKAEA Radioisotope Applications
Many thousands of cobalt discs approximately 0.5 in. (12.7 mm) diameter x 0.2 in. (5.1 mm) deep were encapsulated in the salt bath. The customer provided cans open at the top. A cobalt disc was dropped into the can. A flat disc of aluminium was then laid on top of the cobalt. The aluminium brazing foil took the form of a flat ring, ca. 0.5 in. (12.7 mm) diameter x 0.2 in. (5.1 mm) wide, and was next laid onto the aluminium disc. The side walls of the can were then turned over and inwards to give a mechanical joint. Finally the assembly was dip brazed. All parts were carefully cleaned as earlier described, and assembly took place in clean room conditions.

(f) Experimental Work In Conjunction With Other Laboratories.
High Duty Alloys Ltd. had developed an experimental casting alloy containing 3.3% manganese. Attempts to braze this with the aluminium-silicon eutectic alloy showed that while the brazed alloy had adequate strength there was evidence of liquation in areas near the brazed joint (in the parent metal). Resulting from this experience it was concluded that 3% manganese was the maximum to be tolerated in the straight Al-Mn series of parent metals. Swiss Aluminium Ltd. wished to know whether there were problems in joining their proprietary alloy, SAP. This alloy was made by sintering aluminium powders, as a result of which the structure included both aluminium and its oxides. Using the aluminium-silicon eutectic brazing alloy failed to wet the SAP, and a successful outcome to this series of experiments only resulted when the SAP was pre-clad with pure aluminium when the braze became an aluminium to aluminium joint with Al-Si filler between.

(g) The American Scene
Similar observations apply to those made in the final section of high temperature brazing 2.6.4 para. (b). The U.S.A. was making very large heat exchangers and other components in flux baths (notably Hamilton Standard Co.). Apart from aerospace requirements the impetus was given by the needs of air-separation plants, and oxygen plants which required light-alloy heat exchangers.

(h) U.K. Competition:
At about this period Marston Excelsior were entering the field in Europe and operating a bath 14 ft. long x 4 ft. wide x 6 ft. deep (4.26 x 1.22 x 1.82 m); in 1964 they stated that they were processing something like 100 tons (98.42 t) of aluminium alloy a year. Further, in their bath it was possible to braze an assembly weighing one ton (0.98 t) and to produce 200,000 ft. (60.9 km) of joints, all in the space of 15 minutes immersion time in the flux bath. Morris Radiators bath was marginally larger than Delaney Gallay's, and was concentrating on brazing motor car radiators. At that time only high performance motor cars had gone to such radiators in the U.K. but there was a production line in Japan reportedly producing automobile radiators for the normal mass-production car market, the high cost of copper operating in favour of aluminium, whose thermal conductivity was acceptable to their designers. It was clear that aluminium brazing was an acceptable engineering technique, and one which worldwide was on the upsurge.
3-Changes And Developments Since 1965

The study has shown changes in a number of brazing alloys featured in revised British Standard Specifications and elsewhere, in improved methods of making the traditional 'powdered' brazing alloys, in aluminium's capability of being joined in vacuum and in controlled atmospheres, and in changing methods of making car heaters on going from cuprous materials to aluminium alloys. Disadvantages inherent in making glass-metal, ceramic-metal and ceramic-to-ceramic seals appear to have been overcome in many instances, notably by Japanese workers who included foils between parents and fillers of the materials of different expansions to be joined, to minimise expansion differences in the parent materials. The American space requirements for heat shields and honeycomb materials have brought about new combinations of filler and parent metals for service at temperatures up to c.2,000°C. The development of hot stage scanning microscopes and Auger and x-ray spectroscopy techniques, has led to a better understanding of surface contaminants and their effects on spreading, wetting and capabilities for certain fillers to join selected materials. There were found to be a number of areas where answers to fundamental questions still cannot be given in the light of present knowledge, and these will be considered later.

3.1-Improved Methods of Making Brazing Alloys

In general the depression which started in 1974 affected the U.K. alloy producers. Inco closed their Platinum Metals Division Research & Development Laboratory, and transferred their activities to Birmingham when all work on brazing alloys stopped. Engelhard appeared to have continued their interest for some years but have stopped further U.K. development work. Johnson Matthey on the other hand had retained their interests and in 1986 set up a Technical Department which is concerned with metal joining developments. In America there has been continuing activity and Europe had also seen increased interest, possibly promoted by an E.E.C. sub-committee which has examined many aspects of the technique. While a feature of the study has revealed greater international co-operation a number of comments have been received that this has been accompanied by corresponding reticence by U.K. users of the process to publish their work. Two areas which have been of particular interest to customers for the systems are in the manufacture of amorphous metal foils (Metglas Process) in the United States, and in Osprey Metals manufacture of high purity alloy powders in South Wales.

3.1.1-Metglas Process

A not insurmountable problem in using hard and brittle brazing alloys, hitherto only capable of being made as powders, were their applications to joints to avoid undesirable build-up of alloy in some places, "misses" due to variations in brazing powders (possibly due to oxidisation of the powders during manufacture), and placement to ensure that adequate alloy was available, notably in positions where long runs of alloy were desirable, as in heat exchanger manufacture. Allied Signals Inc., a firm in the U.S.A.'s Allied Corporation have produced a range of materials, albeit only up to 305mm (12 ins.) wide but in long
coils which go a long way to meeting these conditions; these coils of course do
not apply to foils or to clad materials to the same extent. 'Allied' are
marketing in the U.K. through Neomet Ltd. While details of the process have not
been fully disclosed it has been claimed that to super-cool certain molten
brazing alloys in a continuous casting process results in foils which have a
glassy or amorphous structure. Rapid cooling does not give the metal time to
take up its appropriate stable FCC, BCC or HCP structure. As a result while the
solid alloy's elasticity in tension is said to be poor it has good compressive
and bend strength properties, permitting it to be shaped, blanked, punched and
manipulated for inclusion in a joint area prior to brazing.

The Metglas Process involves loading the raw materials required for the brazing
alloy into an induction furnace. Once molten the alloy is charged into an
accumulator feeder, which appears to be a tundish with a tubular bottom,
terminating in a bottom cone with a pump in the tube to accelerate the rate of
discharging the molten metal through the cone. It is claimed that molten metal
is discharged from the cone onto a rotating wheel, which produces a cooling
rate of about 10°C/s and generates foils at speeds of approximately 80 km/hr.
(50 m.p.h.). A feedback system ensures that ribbon dimensions are closely
controlled at 0.05 mm +/- 0.0125 mm (0.002 +/- 0.0005 ins.) before winding onto
spools ready for shipment.

Alloy compositions which form metallic glasses when quenched from the liquid
state according to De Cristofaro and Henschel[15] belong to one of two groups, a
transition metal e.g. Fe or Ni or mixtures of two transition metals or
alternatively noble metal Au or Pd containing c.20 at.% of the metalloids, B, C,
Si or P.

Most of the glass-forming alloys are at or near eutectic compositions. Of
particular interest to brazing is the transition metal-metalloid group. Most
alloys of this system demonstrate an unusual stability of the liquid state,
notably a deep liquidus slope to the eutectic. The Ni-P phase diagram was
specifically mentioned as illustrative of a deep eutectic in which the melting
temperature of Ni can be depressed 32°C by the addition of 19 at.% P. Ni-B
and Ni-B-Si alloys are said to behave similarly with B depressing the melting
point of Ni by 31°C. Any significant departure from the eutectic point affects
the glass-forming regions and the structure of the solidified alloy then
contains partially or completely crystalline metal when liquid quenched.

However, the emphasis paid to nearness of composition to a "deep eutectic"
causes one to wonder whether it is not so much the variation from the eutectic
composition which is the important feature but the difference between the
eutectic temperature, and the maximum temperature capable of being obtained in
the melting pot, such that a more mobile atomic state is achieved immediately
prior to casting the higher the melt temperature achieved.

A second claim for the alloys is that careful control of the constituents
enables good reproducibility and a range of Differential Thermal Analysis (DTA)
curves are available to show that solidus and liquidus temperatures on
remelting and cooling the brazing alloys agree within reasonable limits. DTA is
the subject of current work in Aachen, Ettinger and Rise in attempts to persuade
alloy manufacturers to work to closer limits of composition. There appears to
be good correlation between the different workers who have shown that minor
variations in the Ni-Si-B ternary series (notably BS1845 : 1984, Type HTN 4) can
bring about +100°C variation in the solidus temperature in alloys of the same
specification. The TWI Committee while apparently sceptical of Allied's claims
told that if compositional limits could be closely controlled this gave them a
further advantage over competitors not using this practice of making brazing
foil.

- 45 -
Finally the literature stressed that a most significant feature of the process was the speed of heat removal by the rotating wheel onto which the liquid was ejected, and reference was made to the advantages of the high conductivity of copper used in early work in heat removal for lower melting point systems. Metglas literature shows that a wide range of different materials have been produced as evidenced by the following list:


Group (B). Alloys intended to limit the liquidus temperature to 1010°C with the intention of replacing the expensive gold bearing series, give a graded joint series and which when free from boron can be used in nuclear engineering.

Group (C). Alloys which are cadmium and silver free, are satisfactory for fluxless brazing of copper, relatively inexpensive, and finding applications in solar panels, plumbing, air conditioning, electrical industry, and car heaters and coolers.

Group (D). Alloys suitable for brazing aluminium and its alloys, but only available on an experimental basis.

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition - wt.%</th>
<th>Melting Range-°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group (A) Ni-Based Alloys</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBF10</td>
<td>14 Cr-4.5 Fe-4.5 Si-3.2 B-0.06 max.C-Remr.Ni</td>
<td>1080-1205</td>
</tr>
<tr>
<td>MBF15</td>
<td>13 Cr-4.2 Fe-4.5 Si-2.8 B-0.03 max.C-1 max.Co-Remr.Ni</td>
<td>1080-1205</td>
</tr>
<tr>
<td>MBF17</td>
<td>11.3 Cr-4 Fe-1.5 Si-2.2 B-0.06 max.C-8W-Remr.Ni</td>
<td>1150-1200</td>
</tr>
<tr>
<td>MBF20</td>
<td>7 Cr-3 Fe-4.5 Si-3.2 B-0.06 max.C-Remr.Ni</td>
<td>1010-1175</td>
</tr>
<tr>
<td>MBF30</td>
<td>4.5 Si-3.2 B 0-06 max.C-Remr.Ni</td>
<td>1010-1175</td>
</tr>
<tr>
<td>MBF35</td>
<td>7.31 Si-2.17 B-0.06 max.C-Remr.Ni</td>
<td>1000-1040</td>
</tr>
<tr>
<td>MBF50</td>
<td>19 Cr-7.3 Si-0.08 max.C-1.5 B-Remr.Ni</td>
<td>1176</td>
</tr>
<tr>
<td>MBF60</td>
<td>11 P-0.1 max.C-Remr.Ni</td>
<td>925-1095</td>
</tr>
<tr>
<td>MBF65</td>
<td>14 Cr-0.08 max.C-10.1 P-Remr.Ni</td>
<td>982</td>
</tr>
<tr>
<td>MBF75</td>
<td>10 Cr-5.5 Fe-0.06 max.C-3.5 B-23 Co-7 Mo-Remr.Ni</td>
<td>1175-1230</td>
</tr>
<tr>
<td>MBF80</td>
<td>15.2 Cr-0.06 max.C-4 B-Remr.Ni</td>
<td>1065-1265</td>
</tr>
<tr>
<td>MBF90</td>
<td>4 Si-0.06 max.C-2.7 B-20 Co-Remr.Ni</td>
<td>1065-1150</td>
</tr>
<tr>
<td><strong>Group (B) Pd-Containing Alloys</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBF1001</td>
<td>4.63 Fe-8.63 Cr-35.32 Pd-2.69 B-Remr.Ni</td>
<td>945-996</td>
</tr>
<tr>
<td>MBF1002</td>
<td>0.93 Fe-8.61 Cr-32.25 Pd-2.69 B-Remr.Ni</td>
<td>935-994</td>
</tr>
<tr>
<td>MBF1005</td>
<td>46.7 Pd-6.1 Si-47.2 Ni</td>
<td>811-856</td>
</tr>
<tr>
<td>MBF1007</td>
<td>53.8 Pd-6.1 Si-38.1 Ni</td>
<td>830-873</td>
</tr>
<tr>
<td>MBF1010</td>
<td>21.2 Fe-57.6 Pd-6.2 Si-15.0 Ni</td>
<td>954-1020</td>
</tr>
<tr>
<td>MBF1011</td>
<td>45.5 Pd-6.0 Si-5.0 Co-4.5 Mo-40.0 Ni</td>
<td>848-894</td>
</tr>
<tr>
<td>MBF1020</td>
<td>46.8 Pd-5.0 Si-5.0 Co-43.2 Ni</td>
<td>821-870</td>
</tr>
<tr>
<td>MBF1022</td>
<td>45.8 Pd-3.8 Si-0.7 B-10.0 Co-4.5 Mo-35.2 Ni</td>
<td>838-874</td>
</tr>
<tr>
<td><strong>Group (C) Cu-Based Alloys</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBF2002</td>
<td>9.9 Ni-4 Sn-7.8 P-Remr.Cu</td>
<td>610-660</td>
</tr>
<tr>
<td>MBF2005</td>
<td>5.7 Ni-9.4 Sn-7 P-Remr.Cu</td>
<td>592-655</td>
</tr>
</tbody>
</table>
This series of alloys appears to have offered one of the most spectacular improvements with a melting technique giving readily reproduceable foils. Structural differences on departing from eutectic compositions do not appear clear but examination of patents, and reference to the makers of the series may clarify the queries. If not there could be scope for further work.

3.1.2 Osprey Metals Powders

This company is in the Sandvic of Sweden Group. They produce powders by an atomisation process which are marketed for both brazing and metallisation processes. With the exception of alloys containing toxic materials, notably cadmium, beryllium and mercury, they will prepare brazing alloy powders to any specification placed on them. They particularly mentioned making a series for U.K. Atomic Energy Authority based on the Ni-Cr-P and the Ni-Si-B ternary systems. By quick heating under vacuum and passing through an inert gas (nitrogen or argon) they claim that they produce alloys of great constituent consistency and free from surface contamination. During a tour of the works one was impressed with the quality of both staff and the "high-tech" equipment; with regard to staff these have been most carefully selected and 7 of the 50 personnel are graduates. The process is fully computerised.

Carefully controlled master alloys and raw materials are charged into a high frequency heated melting furnace capable of very rapid heating. At the chosen degree of super heat in vacuum the melt is poured into a tundish under an inert gas cover. It passes downwards through an atomising zone where jets of nitrogen or argon are injected at low pressures to break up the molten stream of metal into hot powder. This powder passes down into a cyclone chamber which has a conical exit orifice. From there, still under the inert gas cover, the powders pass along a vibrating table into collector cannisters. (The effect of the earlier gas injections is that in a secondary requirement, powders are introduced onto the table in such a manner that the table is caused to vibrate). Containers are sealed off so that the final product is sold under a gas cover. Osprey claim that the quick heating method gives a closely controlled product with a minimum of constituent change from batch to batch. They also advised that their method of melting resulted in a very clean product in that oxides forming on the high surface area of each grain of powder are minimal. Many reports have confirmed that their powdered brazing alloys have superior wetting
and spreading properties over other methods of making powders, as a result of which their customers have reported that there is less call for reworking to repair braze "misses". They provided lists of all brazing alloys made, and offered non-precious metal samples, and good liaison.

3.2-Brazing Alloys Available

The opinion of the Chairman of the 1986 British Association for Brazing and Soldering was that it is reasonable to consider engineering brazing as divisible into three main groups:

(a) Aluminium salt bath brazing - He was unaware of any major production change over the past quarter century with this method which is well established. However, he was aware of Harwell's work on examining dissolution of aluminium surface oxides in vacuum, and referred in particular to an excellent video film made in support of their work.

(b) Silver soldering including the BS1845 alloys and copper-phosphorus both with and without cadmium. Health hazards due to cadmium had resulted in a number of alternative compositions being developed over the years.

(c) He considered that there had been most developments with the nickel-boron-silicon series for aerospace and nuclear applications. Use of vacuum had become widespread, and there had been interest in improved glass/ceramic-metal seals, and in different bonding techniques.

With regard to soft soldering his own company (Fry's Metal) had noted few changes, and the same alloys were supplied for similar purposes to those in 1965.

It was concluded from the foregoing that this section of the review should concentrate on brazing alloys available, using the BS1845:1984 specification groupings as a basis.

3.2.1-Aluminium Brazing: B.S.1845 Group A1

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition- wt.%</th>
<th>Melting Range-°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4004</td>
<td>Al-9/10.5 Si-0.8 Fe-0.25 Cu-0.1 Mn-0.2 Zn-1/2 Mg</td>
<td>555 - 590</td>
</tr>
<tr>
<td>4043A</td>
<td>Al-4.5/6 Si-0.6 Fe-0.3 Cu-0.15 Mn-0.1 Zn-0.2 Mg-0.15 Ti</td>
<td>575 - 630</td>
</tr>
<tr>
<td>4045</td>
<td>Al-9/11 Si-0.8 Fe-0.3 Cu-0.05 Mn-0.1 Zn-0.05 Mg-0.2 Ti</td>
<td>575 - 590</td>
</tr>
<tr>
<td>4047</td>
<td>Al-11/13 Si-0.6 Fe-0.3 Cu-0.15 Mn-0.2 Zn-0.1 Mg-0.15 Ti</td>
<td>575 - 585</td>
</tr>
<tr>
<td>4104</td>
<td>Al-9/10 Si-0.8 Fe-0.25 Cu-0.1 Mn-0.2 Zn-1/2 Mg-0.02/0.2 Bi</td>
<td>555 - 590</td>
</tr>
<tr>
<td>4145A</td>
<td>Al-9/11 Si-0.6 Fe-3/5 Cu-0.15 Mn-0.2 Zn-0.1 Mg-0.15 Ti</td>
<td>520 - 585</td>
</tr>
<tr>
<td>4343</td>
<td>Al-6.8/8.2 Si-0.8 Fe-0.25 Cu-0.1 Mn-0.2 Zn</td>
<td>575 - 615</td>
</tr>
</tbody>
</table>

Except where a range of composition is quoted impurities must not exceed the figures given. Be is limited in all alloys to 0.0008 max. Apart from the impurities cited no 'other element' may exceed 0.05%, with the total of all
'other elements' restricted to 0.15%.

These brazing alloys are available as powders, wires and foils. Additionally, U.S.A. alloys 4004, 4045, and 4343 are clad onto cores of AA3003 (Al-1.25% Mn alloy, solidus 643°C), and AA3005 (Al-1.2% Mn-0.4/0.5 Mg alloy; solidus c.635°C) where cladding may be 5%, 7% or 15% of the total thickness.

Supplies of British produced parent or brazing materials are not always readily accessible, usually due to suppliers minimum order stipulations. As a result recourse may be made to sources in Germany (VAW), France (CLAL), Sweden (KORRUGAL), and to the U.S.A. who have alternatives to British specifications. Alloy combinations called up by designers may therefore use any of the following metals as appropriate for their designs:

(a) Parent metals

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Solidus</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA3004</td>
<td>Al-1.2 Mn-1.0 Mg</td>
<td>629°C</td>
</tr>
<tr>
<td>AA3105</td>
<td>Al-0.5 Mn-0.5 Mg</td>
<td>635°C</td>
</tr>
<tr>
<td>AA4343</td>
<td>Al-7.5 Si</td>
<td>574°C</td>
</tr>
<tr>
<td>AA6061</td>
<td>Al-1.0 Si-0.7 Fe-0.15/0.4 Cu-1.0 Mg</td>
<td>635°C</td>
</tr>
<tr>
<td>AA6063</td>
<td>Al-0.4 Si-0.35 Fe-0.7 Mg-Traces Mn, Cu, Ti</td>
<td>635°C</td>
</tr>
<tr>
<td>AA6082</td>
<td>Al-1.0 Si-0.5 Fe-0.7 Mn-1.0 Mg-Tr.Zn, Cu, Cr</td>
<td>635°C</td>
</tr>
<tr>
<td>AA6951</td>
<td>Al-0.3 Si-0.25 Cu-0.6 Mg</td>
<td>Range 590-616°C</td>
</tr>
<tr>
<td>AA7072</td>
<td>Al-1.0 Zn</td>
<td>590-646°C</td>
</tr>
</tbody>
</table>

(b) Brazing alloys

| Agecla AL6 | Similar to 4004 Al-Si-Mg alloy (from CLAL) |
| Agecla AL61 | " 4047A Al-Si " |

Observations showed that the preferred alloys for vacuum brazing were 4004 clad on to 3003 alloy, with other suitable core materials being 6063 and 6082 as used with or without cladding for special applications. 6082 is the modern equivalent of the earlier HS30 heat-treatable alloy.

6061 calls for extra caution: Cu is present as a temperature depressant and calls for care in times at temperature, but is not really favoured in the U.K. The most used parent metal was 3003. It is widely employed as fins for heat exchangers where a final age hardening treatment is not required. Korrugal produce a similar alloy for fin spacers - S61221.

6951 is an American heat treatable alloy which is vacuum brazed with the lower melting brazing alloys in the range.

The 7072 alloy contains Zn, and has a cladding for a vacuum brazing application but evaporation of Zn is a problem which can be inhibited by adding Ca.

(c) Processing

While flux baths have continued in service with a report of General Motors calling for 250,000 radiators made in this approach for the Corvette automobile, the difficulties of cleaning has brought about other methods of joining. In Europe three methods have been developed.

In one established approach radiator and car heater manufacturers have turned to a mechanical technique known as the French, SOFICA process. In this approach there is a mechanical fit of fins to expanded tubes, with the end 'tanks' being glass-fibre reinforced nylon. In car heaters, while this approach has largely displaced the copper block in Europe, the designers are still clearly unhappy.
with consistency of results, and are seriously considering vacuum brazing or Alcan's developed Nocolok process, as alternatives.

(d) Vacuum Brazing Aluminium

The change towards vacuum brazing has been spectacular, and is said to be the main means now of brazing aluminium. During a visit it was noted that neither of Normalair's two salt baths were in use. They said that together with their parent company they now have seven vacuum installations at Yeovil, their latest acquisition being a Consarc unit. (Consarc advised that one unit they are marketing has a brazing zone 4ft wide by 4 ft high by 20ft long (1.22m x 1.22m x 6.1m), has a charge weight of 12½ tons (12.7t), and is designed for a maximum operating temperature of 800°C with temperature uniformity +/- 5°C. The working vacuum in this unit is in the range 10^-6 to 10^-9 mbar). Three developments appear to have made vacuum brazing a reliable brazing technique for Al:

- The first feature contributing to success is the level and speed of vacuum attainable in present day furnaces with fast heating rates to treatment temperature.
- Secondly is the improved purity of foils and clad sheets now available, with surface oxide layers controlled to 100 Angstroms maximum thickness on the underlying metal.
- Thirdly is the inclusion of 1-2% by weight of magnesium in the composition. As a result of Auger spectroscopy and hot stage electron microscopy studies at Harwell it is believed that volatilisation of magnesium in the oxide layer at the brazing temperature results in discrete holes which allow molten aluminium filler alloy to penetrate through the oxide and simultaneously to sweep away displaced oxides from the surfaces which are to be joined. In an experimental approach Ford demonstrated using 3 alloys,
  - Reynolds MD133: Al-7.5 Si-2.5 Mg.
  - Reynolds MD150: Al-9.8 Si-1.5 Mg.
  - Reynolds MD177: Al-9.8 Si-1.5 Mg-0.08 Bi.

that reducing Mg and increasing Si extended the pressure range for a good braze from 10^-3 Pa (10^-5 Torr) up to 10^-2 Pa. They reasoned that the total system pressure is used as an indication of the partial pressures (which were not directly measured) of reacting contaminants.

Normalair Garratt referred to inconsistencies, results which could not be related, in that they had found that while a constant vacuum of 10^-4 mm mercury pressure was specified and shown as present by their gauges, sometimes "misses" occurred in brazed heat exchangers which they put down to 'volatiles' in the furnace retort from earlier treatments. Ford concluded that a braze in vacuum is promoted by the Mg from the filler alloy which modified the oxide barrier during brazing. It was confirmed that small concentrations of Mg developed in the aluminium oxide barrier film at c.400°C when volatilisation of magnesium begins. This build up has been interpreted as the onset of an (Al,Mg)O spinel on free surfaces of the oxide, and in the pores that are created by the evaporating Mg. Once the filler metal reached its melting point of 551°C it was observed to penetrate and cover the modified oxide. This process which resulted in dispersion of the oxide, was interpreted as being caused by wetting of the porous oxide by molten filler metal. Characteristics of the Mg vaporization were also examined for 2 fillers, one with 1.5% Mg, and the other with c.1.0% Mg. In the case of the lower Mg concentration, only partial coverage by molten filler was noted, whereas with the higher level complete coverage took place.
While it seems probable that Mg is the initiator for break up of the oxide, there appears from this to be divergent opinions on the mechanism, which may be worthy of further study.

(e) Nocolok Process

While European sources remain to be convinced it is understood that this is an effective method for joining aluminium both in the U.S.A. and Japan. In this process a batch or continuous muffle-type furnace may be selected, therefore cheaper to install and run than either flux bath or vacuum furnaces. Brazing takes place in nitrogen or other inert gas having low oxygen and water vapour contents. Flux is applied to the work as an aqueous slurry, by total immersion of work piece into the flux, or by spraying the individual components. The flux used is the eutectic of K₃AlF₆ and KAlF₄. The flux begins to melt just below the melting temperature of the brazing alloy, being completely molten at brazing temperature. The molten flux reacts with aluminium skin oxides but does not attack either solid or molten aluminium alloys. The flux is inert before, during, and after brazing, and is not hygroscopic. It also has an unlimited shelf life. It has been concluded that all alloys as used in flux bath brazing are acceptable but the Nocolok Process cannot tolerate more than 0.5% Mg in the filler alloy. In the case of components which do not require a post brazing treatment but want enhanced corrosion resistance, the finished parts may directly receive a chromate treatment or zinc coating.

3.2.2-Silver Brazing Filler Metals-Group AG

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition - wt%</th>
<th>Melting Range°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG1</td>
<td>49/51 Ag-14/16 Cu-14/18 Zn-18/20 Cd</td>
<td>620-640</td>
</tr>
<tr>
<td>AG2</td>
<td>41/43 Ag-16/18 Cu-14/18 Zn-24/26 Cd</td>
<td>610-620</td>
</tr>
<tr>
<td>AG3</td>
<td>37/39 Ag-19/21 Cu-20/24 Zn-19/21 Cd</td>
<td>606-650</td>
</tr>
<tr>
<td>AG11</td>
<td>33/35 Ag-24/26 Cu-18/22 Zn-20/22 Cd</td>
<td>610-670</td>
</tr>
<tr>
<td>AG12</td>
<td>29/31 Ag-27/29 Cu-19/23 Zn-20/22 Cd</td>
<td>600-690</td>
</tr>
<tr>
<td>AG14</td>
<td>54/56 Ag-20/22 Cu 21/23 Zn-0.025 max Cd-1.7/2.3 Sn</td>
<td>630-660</td>
</tr>
<tr>
<td>AG20</td>
<td>39/41 Ag-29/31 Cu-27/29 Zn-0.025 max Cd-1.7/2.3 Sn</td>
<td>650-710</td>
</tr>
<tr>
<td>AG21</td>
<td>29/31 Ag-35/37 Cu-31/33 Zn-0.025 max Cd-1.7/2.3 Sn</td>
<td>665-755</td>
</tr>
<tr>
<td>AG5</td>
<td>42/44 Ag-36/38 Cu-18/22 Zn-0.025 max Cd</td>
<td>690-770</td>
</tr>
<tr>
<td>AG7</td>
<td>71/73 Ag-27/29 Cu-0.025 max Cd</td>
<td>780-780</td>
</tr>
<tr>
<td>AG9</td>
<td>49/51 Ag-14.5/16.5 Cu-13.5/17.5 Zn-15/17 Cd-2.5/3.5 Ni</td>
<td>635-655</td>
</tr>
<tr>
<td>AG13</td>
<td>59/61 Ag-25/27 Cu-12/16 Zn-0.025 max Cd</td>
<td>695-730</td>
</tr>
<tr>
<td>AG18</td>
<td>48/50 Ag-15/17 Cu-21/25 Zn-0.025 max Cd-6.5/8.5 Mn-4/5 Ni</td>
<td>680-705</td>
</tr>
<tr>
<td>AG19</td>
<td>84/86 Ag-0.025 max Cd-14/16 Mn.</td>
<td>960-970</td>
</tr>
</tbody>
</table>

Impurity limits applicable to this group are Al 0.001-Be 0.0005-Bi 0.005-Pb 0.025-P 0.008-Si 0.05-Ti 0.002-Zr 0.002 Total of all to be 0.025% max.
It will be noted that these alloys may broadly be considered as alloys based on
the copper-silver-zinc ternary system, and the copper-silver-zinc-cadmium
quaternary system, in which Cd is added as a temperature depressant and to
improve flowing characteristics. However Cd is a toxic material, and there have
been a number of alloys developed which do not contain this element, which has
been replaced by other temperature depressants, notably In and Ga. Such
development in this country has been provoked by the Health and Safety at Work
Act, 1974 and its associated legislation. Johnson Matthey have developed 10
'Silver-flo' alloys covering the temperature range 618°C to 830°C (solidus
temps. corresponding liquidus temps. 652°C to 870°C). Similarly CLAL (Comptoir
Lyon Alemand Louget) have produced many alloys which straddle the compositions
given in the British Specification and which are obtainable through D.Fennelier &
Co. Ltd. JM currently list 32 different alloys made from these systems under
trade names 'Easyflo', 'Argoflo', 'Silverflo'. CLAL also quote a further 24 alloys.
Engelhard are in the same field, and offer their own range which are made by
their French associated company C.M.P. (Companie Metaux Precieux).
Apart from the health requirements, special materials have been developed to
enable hard carbides to be joined to metals, giving a graded transition of
thermal expansion to provide thick stress-absorbing joints. The approach has
been to make a sandwich of copper between outer layers of brazing alloy in the
ratio 1 part brazing alloy: 2 parts copper: 1 part brazing alloy.
The sandwich is rolled to foil as provided to brazers.
Alloys of note are:

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition - wt %</th>
<th>Melting Range-°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>JM-Easyflo</td>
<td>Trifoil'C' (brazing alloy is AG1)</td>
<td></td>
</tr>
<tr>
<td>JM-AB49</td>
<td>Trifoil (Cd-free equivalent of Trifoil'C' where brazing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>alloy composition is 49 Ag-27.5 Cu-20.5 Zn-0.5 Ni-2.5 Mn</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(670-710°C. melting</td>
<td></td>
</tr>
<tr>
<td></td>
<td>range)</td>
<td></td>
</tr>
<tr>
<td>CLAL</td>
<td>equivalent materials are CW500 Tr and Cd-free, CW97.</td>
<td></td>
</tr>
</tbody>
</table>

It will be noted that the large range of materials in this group provide the
user with ample scope from long tight clearances to wider gaps. Chemical
fluxes may be used with air, or controlled atmospheres in muffles can be used.
This is a very versatile group of brazing alloys widely used for many
applications.

3.2.3-Copper-phosphorous Brazing Filler Metals-Group CP

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition - wt %</th>
<th>Melting Range-°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP1</td>
<td>Cu-4.3/5.0 P-14/15 Ag</td>
<td>645 - 800</td>
</tr>
<tr>
<td>CP2</td>
<td>Cu-6.1/6.9 P-1.8/2.2 Ag</td>
<td>645 - 825</td>
</tr>
<tr>
<td>CP3</td>
<td>Cu-7.0/7.8 P</td>
<td>710 - 810</td>
</tr>
<tr>
<td>CP4</td>
<td>Cu-5.7/6.3 P-4.5/5.5 Ag</td>
<td>645 - 815</td>
</tr>
<tr>
<td>CP5</td>
<td>Cu-5.6/6.4 P-1.8/2.2 Sb</td>
<td>690 - 825</td>
</tr>
<tr>
<td>CP6</td>
<td>Cu-5.9/6.5 P</td>
<td>710 - 890</td>
</tr>
</tbody>
</table>

The total of all other impurities must not exceed 0.25% with upper limits for
the following:- Al-0.1, Be-0.0005, Bi-0.001, Cd-0.025, Pb-0.02 and Zn-0.05. None
of these alloys should be used to join ferrous metals, nickel-based or copper
alloys containing Ni, due to formation of brittle phosphide phases in joints.
Johnson Matthey, Engelhard and CLAL all supply these alloys and varieties to
suit individual requirements. The main reason for this series is that they are self fluxing and no additional flux is therefore required when making copper joints in air. The P acts as a deoxidant. The addition of Ag improves ductility of the filler, and alloy CPI has the best mechanical performance, where service conditions call for shock loading and resistance to tension.

### 3.2.4-Copper Brazing Filler Metal-Group CU

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition - wt %</th>
<th>Melting Range-°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CU2</td>
<td>99.9 Cu-0.0025 max.Bi-0.04 max.imps. (excluding Ag and O₂)</td>
<td>1085</td>
</tr>
<tr>
<td>CU3</td>
<td>99.95 Cu-0.001 max.Bi-0.03 max.imps.(excluding Ag)</td>
<td>1085</td>
</tr>
<tr>
<td>CU5</td>
<td>99.00 Cu-0.001 max.Bi-0.1 max.imps.(excluding P and O₂)</td>
<td>1085</td>
</tr>
<tr>
<td>CU6</td>
<td>9.85 Cu-0.013/0.05P-0.003 max.Bi-0.06 max.imps.(excluding Ag, As, Ni, P)</td>
<td>1085</td>
</tr>
<tr>
<td>CU7</td>
<td>2.5/3.5 Ni-0.02/0.05 B-0.01 max.Bi-0.15 max.imps.(excluding Ag) Remr.Cu</td>
<td>1085-1100</td>
</tr>
<tr>
<td>CU8</td>
<td>0.2 Zn-1.5/2.5 Mn-0.01 max.Bi-0.01 max.Al-0.1 max.Fe-0.02 Pb (Total imps.0.5) Remr.Cu</td>
<td>1045-1065</td>
</tr>
</tbody>
</table>

In all cases the Be limit is 0.0005 and Cd 0.025%. CU2 is tough pitch copper; CU3 is classified oxygen-free, and CU6 is phosphorous-deoxidised copper. CU5 is available as powder or paste only, marketed by Wall Colmonoy as 'Cubraz'.

### 3.2.5-Copper-Zinc Brazing Filler Metals-Group CZ

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition - wt %</th>
<th>Melting Range-°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZ6</td>
<td>58.5/61.5 Cu-0.2 max.Sn-0.2/0.4 Si-Remr.Zn</td>
<td>875-895</td>
</tr>
<tr>
<td>CZ6A</td>
<td>58.5/61.5 Cu-0.2/0.5 Sn-0.2/0.4 Si-Remr.Zn</td>
<td>875-895</td>
</tr>
<tr>
<td>CZ7</td>
<td>58.5/61.5 Cu-0.2 max.Sn-0.15/0.4 Si-0.05/0.25 Mn-Remr.Zn</td>
<td>870-900</td>
</tr>
<tr>
<td>CZ7A</td>
<td>58.5/61.5 Cu-0.2/0.5 Sn-0.15/0.4 Si-0.05/0.25 Mn-Remr.Zn</td>
<td>870-900</td>
</tr>
<tr>
<td>CZ8</td>
<td>46.0/50.0 Cu-0.2 max.Sn-0.15/0.4 Si-0.2 max.Mn-8.0/11.0 Ni Remr.Zn</td>
<td>920-980</td>
</tr>
</tbody>
</table>

Except for Fe @ 0.25, total impurities to be a maximum of 0.2 % with individual elements set @ Al 0.01-Sb 0.01-As 0.01-Be 0.0005-Bi 0.01-Pb 0.02-Cd 0.025

**General Notes On Copper-Containing Brazing Alloys:**

(i) Slow heating rates are prone to give liquation consequently filler metals with short melting ranges are preferable.

(ii) Ag-Cu-Zn and Ag-Cu-Zn-Cd alloys should not be used in vacuum since Zn
and Cd rapidly evaporate. They may be used in a protective atmosphere but considerable fuming, to attack furnace elements, must then be expected.

(iii) Wherever possible filler metal should be free of oxide forming elements which are more stable than those present in the parent metal, notable elements being zinc and manganese. While Zn is not exceptionally stable its high volatility limits its brazing temperature, calling for atmospheres with dewpoints around -40°C.

(iv) In the case of furnace brazing with Mn in the filler alloy, a dewpoint of -60°C is required to reduce its oxide at 1000°C.

(v) Ag-Cu eutectic: This filler alloy is widely used in electron tube assemblies, surge arrestors etc. for brazing Cu, Fe-Ni, and metallised ceramic. A 50:50 Ag:Cu alloy has a wider melting range but is only suitable with a fast heating rate due to this wider melting range. Both alloys can result in stress corrosion cracking when used with Fe-Ni alloys.

(vi) Ag-Cu-Ni: It has been noted that Ni enhances wetting on ferrous materials and reduces fluidity, which can be advantageous where joint gaps are difficult to control. Also suitable for brazing tungsten contacts to Ni-plated steel.

(vii) Ag-Cu-In: The addition of In to Cu-Ag reduces liquidus and fluidity but increases melting range.

(viii) Ag-Cu-Sn: The effects of Sn additions are similar to In but more acute. A 60 Ag-30 Cu-10 Sn alloy (melting range 602-718°C) has been used for silver knife handles as well as Cu-Ni heat exchangers.

(ix) Ag-Cu-P and Cu-P: The self fluxing nature of these alloys makes brazing of Cu very simple, also greatly assists in wetting brass. A 17.75 Ag-85 Cu-7.25 P alloy brazing at 650°C is particularly well suited to brazing brasses as Zn losses are minimal at the brazing temperature.

(x) Cu-Ni: The 95.97 Cu-3 Ni-0.03 B alloy (melting range 1081-1101°C) is used when joints are too great for the use of copper as a brazing filler, where interference fits are preferred; or where the presence of Cu in the joint could interfere with a subsequent hardening treatment.

(xi) Cu-Sn: Tin reduces the liquidus, increases melting range and reduces the ductility of the filler alloy. The 93.5 Cu-6.5 Sn alloy (melting range 910-1040°C) is used with cast iron, where temperature can be critical, and on stainless steels. A 90 Cu-10 Sn alloy, (melting range 845-1015°C) is satisfactory for Cu to steels. An alloy of 80 Cu-20 Sn (798-890°C) is suitable for brazing Cu to steel, copper to copper, or steel to steel, provided joints are not subjected to high stress.

(xii) Cu-Mn-Ni: The 86.5 Cu-11 Mn-2.5 Ni alloy (965-995°C) has been used in a protective atmosphere for tipping carbide masonry drills: it has also been used for vacuum brazing stainless steels.

(xiii) Ag-Mn: This 85 Ag-15 Mn alloy (951-960°C) can be used in a controlled atmosphere or in vacuum with back-filling with argon or nitrogen. Its principal application is for brazed assemblies exposed to ammonia.

(xiv) Discussions with Engelhard gave instances of jewellery manufacture which had become metallurgical engineering applications. One of the biggest users of the Cu-Ag range of materials is in the production of 9 ct. gold chains, and attachments to ear-rings. In the case of chains, a brazing alloy wire is inserted into a 9 ct. Au tube, and the composite is drawn to the required size. Specialist machines cut and locate adjoining chain links with ends of the composite wires abutting. The chain is then passed on a continuous belt through a furnace under a cover of forming gas or cracked ammonia. For ear-rings, atomised produced brazing powder is mixed with a paste in a dispenser. The precise amount of paste/alloy is placed on the parts to be attached to the
earing, which are then passed through a similar furnace. There is interest in such pastes for other applications.

### 3.2.6-Nickel and Cobalt Brazing Filler Metals—Group HTN

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition - wt %</th>
<th>Melting Range-°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTN1</td>
<td>Ni-13/15 Cr-4/5 Si-2.75/3.5 B-4/5 Fe-0.6/0.9 C-0.02 max.P</td>
<td>980-1060</td>
</tr>
<tr>
<td>HTN1A</td>
<td>Ni-13/15 Cr-4/5 Si-2.75/3.5 B-4/5 Fe-0.06 max.C-0.02 max.P</td>
<td>980-1070</td>
</tr>
<tr>
<td>HTN2</td>
<td>Ni-6/8 Cr-4/5 Si-2.75/3.5 B-2.5/3.5 Fe-0.06 max.C-0.02 max.P</td>
<td>970-1000</td>
</tr>
<tr>
<td>HTN3</td>
<td>Ni-4/5 Si-2.75/3.5 B-0.05 max.Fe-0.06 max.C-0.02 max.P</td>
<td>980-1040</td>
</tr>
<tr>
<td>HTN4</td>
<td>Ni-3/4 Si-1.5/2.2 B-1.5 max.Fe-0.06 max.C-0.02 max.P</td>
<td>980-1040</td>
</tr>
<tr>
<td>HTN5</td>
<td>Ni-18.5/19.5 Cr-9.75/10.5 Si-0.1 max.C-0.02 P-0.03 max.B</td>
<td>1080-1135</td>
</tr>
<tr>
<td>HTN6</td>
<td>Ni-0.1 max.C-10/12 P</td>
<td>875</td>
</tr>
<tr>
<td>HTN7</td>
<td>Ni-13/15 Cr-0.1 max.Si-0.01 max.B-0.08 max.C-9.7/10.5 P-0.4 Mn-0.02 max.Fe</td>
<td>890</td>
</tr>
<tr>
<td>HTN8</td>
<td>Ni-6/8 Si-0.1 max.C-0.02 max.P-4/5 Cu-21.5/24.5 Mn</td>
<td>980-1010</td>
</tr>
<tr>
<td>HTN9</td>
<td>Ni-13.5/16.5 Cr-3.25/4 B-1.5 max.Fe-0.02 max.P-0.1 max.C</td>
<td>1055</td>
</tr>
<tr>
<td>HTN10</td>
<td>Ni-10/13 Cr-3/4 Si-2/3 B-2.5/4.5 Fe-0.02 max.P-15/17 W-0.4/0.55 C</td>
<td>970-1055</td>
</tr>
<tr>
<td>HTN11</td>
<td>Ni-8/12 Cr-3/4.5 Si-2/3.5 B-2.5/4.5 Fe-0.02 max.P-10/14 W-0.3/0.5 C</td>
<td>970-1095</td>
</tr>
<tr>
<td>HTN12</td>
<td>Co-16/18 Ni-18/20 Cr-7.5/8.5 Si-0.7/0.9 B-0.35/0.45 C-0.02 max.P-3.5/4.5 W</td>
<td>1120-1150</td>
</tr>
</tbody>
</table>

The maximum of all other elements is not permitted to exceed 0.5%. However if Al, Ti, and Zn are present neither must exceed 0.05%.

**General Notes On Ni-And Co-Containing Brazing Alloys:**

(i) There has been surprisingly little shift in the compositions of the popular alloys, and on comparing with section 2.3 para. e, most of the alloys listed are still in use. Alloys which are no longer specified are Stellite SF6 (but still available as a hard facing material), Endewrance 57, Endewrance 62 and Nicrobraz WG.

(ii) With regard to the other alloys, while some manufacturers have changed designation numbers most conform to the B.S Specification. There have been modifications to some of the earlier alloys, in some cases taking these outside the revised 1984 B.S. specification. Wall Colmonoy offer 3 alloys in this category namely:

- Nicrobraz 35 Ni-19.5 Cr-9.5 Mn-9.8 Si; melting range, 1080-1110°C
- Nicrobraz 51 Ni-25 Cr-10 P-0.05 max.B-0.15 max.C-1 max.Fe; 880-950°C

(This alloy conforms to Springfields alloy 3A, being a modification of HTN7)
Microbraz 200 Ni-7 Cr-4.5 Si-3.2 B-0.06 C-6 W-3 Fe; 975-1040°C

(iii) The most used alloys for nickel-based alloys and stainless steels for heat exchangers appear to be HTN3 (Microbraz 130), and HTN2 (Microbraz LM). The Culham Laboratory also confirmed a wide use for HTN3 (Microbraz 130), but they also use a lot of HTN6 alloy (Microbraz 10). Another alloy used by them is a mixture comprising 70 parts Microbraz 10, and 30 parts Microbraz 130.

(iv) There have been a number of attempts to use this series of alloys for wider joints gaps than the makers advised but Aachen workers' conclusions may be summarised as follows:

High temperature brazing with nickel base filler metals require clearances below 0.004 ins.(0.1 mm) due to stabilization of brittle phases in the joint. Such tight clearances involves costly machining to achieve. If gaps are large a fall off in mechanical properties must be expected.

They have found that the addition of a second additive to the gap, either in a separate pre-sintering operation, using for example nickel powder in the gap, followed by a second run with HTN5 alloy, or by pre-mixing the nickel powder with HTN5 powder and applying to the gap, can lead to the use of gaps up to 0.04 ins.(1 mm) wide. The additive should not melt during the brazing process. Depending on the additive used the phase equilibrium shifts to the solid solution region. This approach has resulted in joints that are free from continuous layers of brittle intermetallic compounds.

(v) Another approach which appears to depend on light pressure being exerted on the joint during brazing depends on high temperature diffusion. By careful choice of brazing alloy, furnace temperature, and heating cycle, high strength joints are regularly obtained. The alloys used are parent metal match with addition of alloying elements B and Si deposited on surfaces by spraying to lower the melting point. By utilising high furnace temperatures and long cycle times the low melting point depressants are diffused away from the joint. Rolls Royce Derby commented that stress-to-rupture and fatigue properties of joints made in this way were similar to returns given by unbrazed parent metals. They said that high pressure was not exerted during the brazing run and the pressure was a gravitational one as a result of one component of the assembly bedding down on the other part to which it was to braze. The lengthy brazing/heat treatment run made Derby question the need for such prolonged treatment, pointing out that they would normally expect stress-to-rupture and fatigue properties to equate to 90% of the parent metal and this short fall could be taken care of in design stages.

3.2.7-Palladium Bearing Brazing Filler Metals-Group PD

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition - wt.%</th>
<th>Melting Range-°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PD1</td>
<td>68/69 Ag-26/27 Cu-4.5/5.5 Pd</td>
<td>805-810</td>
</tr>
<tr>
<td>PD2</td>
<td>58/59 Ag-31/32 Cu-9.5/10.5 Pd</td>
<td>825-850</td>
</tr>
<tr>
<td>PD3</td>
<td>67/68 Ag-22/23 Cu-9.5/10.5 Pd</td>
<td>830-860</td>
</tr>
<tr>
<td>PD4</td>
<td>64.5/65.5 Ag-19.5/20.5 Cu-14.5/15.5 Pd</td>
<td>850-900</td>
</tr>
<tr>
<td>PD5</td>
<td>51.5/52.5 Ag-27.5/28.5 Cu-19.5/20.5 Pd</td>
<td>875-900</td>
</tr>
<tr>
<td>PD6</td>
<td>53.5/54.5 Ag-20.5/21.5 Cu-24.5/25.5 Pd</td>
<td>900-950</td>
</tr>
<tr>
<td>PD7</td>
<td>94.5/95.5 Ag-4.5/5.5 Pd</td>
<td>970-1010</td>
</tr>
<tr>
<td>PD8</td>
<td>81.5/82.5 Cu 17.5/18.5 Pd</td>
<td>1080-1090</td>
</tr>
</tbody>
</table>

Impurity limits applicable to all alloys as maxima: 0.001 Al, 0.0005 Be, 0.008 P, 0.002 Ti, 0.002 Zr; total all = 0.15%.
<table>
<thead>
<tr>
<th>Type</th>
<th>Composition - wt.%</th>
<th>Melting Range-°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AU1</td>
<td>79.5/80.5 Au-18.5/19.5 Cu-0.5/1.5 Fe</td>
<td>905-910</td>
</tr>
<tr>
<td>AU2</td>
<td>62/63 Au-37/38 Cu</td>
<td>930-940</td>
</tr>
<tr>
<td>AU3</td>
<td>37/38 Au-62/63 Cu</td>
<td>980-1000</td>
</tr>
<tr>
<td>AU4</td>
<td>29.5/30.5 Au-69.5/70.5 Cu</td>
<td>995-1020</td>
</tr>
<tr>
<td>AU5</td>
<td>81.5/82.5 Au-17.5/18.5 Ni</td>
<td>950-950</td>
</tr>
<tr>
<td>AU6</td>
<td>74.5/75.5 Au-24.5/25.5 Ni</td>
<td>950-990</td>
</tr>
</tbody>
</table>

Total 'other elements' must not exceed 0.15% with individual element limits of 0.001 Al, 0.0005 Be, 0.008 P, 0.002 Ti, 0.002 Zn.

General Observations On Au-And Pd-Containing Alloys:

(i) Both gold and palladium series were developed for use in vacuum service applications, notably for electronic valves which found zinc and cadmium due to their vapour pressures to be unacceptable. Customers did not at first like the high cost of the gold alloys, and Mond/Engelhard using the patented Pd alloys established a leading position. In self defence the other manufacturers again looked at the gold series, as a result of which both are now available, notably for step-by-step brazed joints. Because the gold alloys were more expensive than the palladium containing ones as soon as patents expired Johnson Matthey added these to their product list as the "Orobraz" series.

(ii) The gold bearing alloys appear to have corrosion resistant advantages in fatigue and creep over the palladium containing alloys, and are important in rotating jet engine parts in high service temperatures.

(iii) There appears to have been very little research into further developments with the Pd series over the past 25 years in the U.K. However a number of new alloys have been reported in America, all of which are palladium-containing, and listed as follows as indicative of the continued interest in Pd as an additive:

(a) 57.1 Ni-30 Pd-10.5 Cr-2.4 B: 982-1093°C; For gas turbine application
(b) 97 Pd-3 Ti: Ductile alloy for brazing molybdenum
(c) 25-95 Pd, up to 3.5 B and 5 Si, balance Co for turbine engines
(d) Cu-Ni with 0.05/5 Ti (and/or Zr) and 5/30 Pd. Ductile brazing foils
(e) 25/35 Pd-15/25 Si-Remr. Ni. This alloy was designed for service temperatures around 1000°C, and excludes B and P from its composition.
(f) 36 Pd-48.7 Ni-11 Cr-2.2 Si-2.1 B. This alloy and associated alloys braze stainless steels and Inconel 718 at around 1000°C.

(g) Pd-Ni-Fe. Characteristics of this series are claims to be good for vacuum brazing.

(h) Pd-Au-Reactive metal brazing alloys.

(i) Pd-Ag-Reactive metal brazing alloy.

(j) Pd-Ni-Cr-B brazing alloy.

(k) Additionally are the compositions given in section 3.1.1.Group B.

(l) Normalair reported the development of a Pd-Ag-Ga alloy for an experimental titanium alloy heat exchanger.

(m) 35 Au-14 Ni-10 Pd-9.5 Mn-31.5 Cu: melting range 982-1004°C

(n) 31 Au-10 Ni-10 Pd-16 Mn-33 Cu: melting range 926-949°C.

The last two alloys are claimed to be excellent for high temperature resistance for iron, nickel, or cobalt-base parent metals, and are particularly good for joining thin sections as little undercutting is experienced with them. The objectives behind the development of these two alloys were to improve the ductility of joints brazed with Ni-Cr-Si-B alloys by combining their best alloy and technological characteristics with the high gold or palladium containing nickel filler alloys. Side objectives were to cost-optimize use of the precious metals, find lower brazing temperatures, and reduce hard phases in the brazed joints. The project was of particular interest to the Space Shuttle main engine assembly where 1080 tubes of nickel-plated precipitation hardened A-286 stainless steel were joined together to an outer jacket of Inconel 718 to give 6.4 Km of brazed joints in a single assembly using these materials.

(iv) Discussions with Engelhard showed that while the Pd-containing alloys are still being used requirements have not significantly altered from amounts sold in 1958; this was surprising, even allowing for the fact that Matthey also make the series. It seems that lower priced alternatives have been made to replace the series. There were said to be practical difficulties in making foils, notably of the PD9, PD10 and PD11 alloys, and Engelhard have preferred for this reason to supply in atomised powder form. With regard to the Ag-Cu-Pd series however these are still provided in reasonable quantities for the electronics industry.

(v) Matthey had investigated the proneness to crevice corrosion of a ferritic stainless steel (EN60) brazed with 50Ag-15Cu-16Zn-19Cd alloy which had been subjected subsequently to 8 days in running tap water. There was severe interface corrosion resulting in destruction of the bond between brazing alloy and steel at the end of the test. Repeating with the 54 Ag-25 Pd-21 Cu alloy, using both ferritic and austenitic stainless steels resulted in interface corrosion resistant joints.

### 3.2.9-Filler Metals For Vacuum Or High Vacuum Applications

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition</th>
<th>Other Impurities (Max. PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG7V</td>
<td>As AG7</td>
<td>C-20</td>
</tr>
<tr>
<td>PD1V</td>
<td>As PD1</td>
<td></td>
</tr>
<tr>
<td>PD2V</td>
<td>As PD2</td>
<td>C-50</td>
</tr>
<tr>
<td>PD3V</td>
<td>As PD3</td>
<td>-58</td>
</tr>
</tbody>
</table>
PD4V  As PD4  Mn-10
PD5V  As PD5  P -30
PD6V  As PD6  Ti-10
PD7V  As PD7  Zr-5
PD8V  As PD8

PD14V  As PD14  Al-100  Sb-20
AU1V  As AU1  Bi-10
AU2V  As AU2  Cd-10
AU3V  As AU3  Ca-20
AU4V  As AU4  In-20
AU5V  As AU5  Pb-30
AU6V  As AU6

Total all impurities  1,500

(a) Comments On Recommended Vacuum Brazing Alloys:

Two puzzling features of this list relate to:

(i) why such a limited range was given in the B.S.Specification 1845 of alloys suitable for brazing in vacuum, and

(ii) why the list should combine alloys suitable for brazing in vacuum with those which are subject to vacuum in service.

With regard to (i) all of the quoted suitable alloys were in use in the 1960's, although with the vacuum furnaces then available it was not considered good practice to involve Ag-containing alloys for vacuum brazing due to evaporation of Ag to both contaminate the furnace and to increase the liquidus temperature; indeed even the lower vapour pressure of Cu was sufficient to give evaporation on to furnace parts, calling for careful time and temperature restrictions at brazing temperature with this lower vapour pressure metal. In view of this observation it was particularly surprising to find alloys AG7V, PDIV through PD8V all recommended for brazing in vacuum. The fact that they are now recommended emphasises the various improvements in heating rates and vacuum control over the past quarter century.

One would certainly have expected the list to contain other alloys which are regularly used for vacuum brazing, notably alloys AL4004; Cu5; HTN1 through HTN12, the Cu and HTN alloys and their modifications having been brazed in vacuum on a production scale since this mode of heating was first adopted. Turning to (ii) while 25 years ago there would have been reservations about vacuum brazing alloys AG7, and PDIV-PD8V, even with fast H.F. heating, once the joints were made these alloys were perfectly sound for vacuum applications particularly graded joints as referred to in section 2.4.5.para.i.

(b) UKAEA Work:

The Culham Laboratory have assessed various protective atmospheres, and have given the following conclusions:

High quality furnace brazing is nearly always carried out in a protective atmosphere to eliminate job oxidation and the use of flux, the consequent need for post-braze cleaning and the possibility of flux inclusions in the joint. For viable flux-free brazing, the protective atmosphere must keep oxidation low enough to enable the following practical criteria to be met:

(i) The braze alloy must exhibit good penetration to produce consistently sound joints and wet uniformly enough to give good external joint
(ii) The workpiece should be cosmetically acceptable with bright surfaces free from visible discoloration.

(iii) There are three main classes of protective atmosphere: reducing gas atmospheres containing H₂ or CO, inert gas atmospheres such as argon or nitrogen and high vacuum. Possible mechanisms for oxide removal include:

- **Reduction:** \[ \text{MeO} + \text{H}_2 = \text{Me} + \text{H}_2\text{O} \]
- **Dissociation:** \[ 2\text{MeO} = 2\text{Me} + \text{O}_2 \]
- **Evaporation:** \[ \text{MeO} = \text{MeO} \]
- **Dissolution:** \[ \text{MeO on Me} \rightarrow (\text{MeO into Me}) \]

Higher temperatures and lower H₂O/H₂ concentrations or O₂ partial pressure favour oxide removal.

The chemical activity of reducing brazing atmospheres can be very effective in preventing formation of oxide on metals near the top of an Ellingham diagram, notably Cu, Ni and Fe, and with care down to Cr-containing alloys such as stainless steels. However for heat resisting "super alloys" which may additionally contain Si, Ti and Al it is extremely difficult to maintain the required gas purity to prevent surface oxidation.

In inert atmospheres some oxide formation will always occur, since with the possible exception of Cu, the dissociation pressures of all the oxides of interest are far less than the partial pressures of O₂ or H₂O impurities which could possibly be maintained in the inert gas. Evaporation of most oxides from the surface as they are formed is negligible. However, at sufficiently high brazing temperatures, dissolution of the oxide into many base metals can be sufficiently rapid to keep the surface essentially oxide-free, providing the partial pressures of oxidising gases in the brazing atmosphere are sufficiently low.

Low partial pressures are most easily achieved by using high vacuum as the brazing atmosphere when advantages include:

- **(A)** Better atmosphere capability, e.g. a vacuum furnace pressure of \(10^{-5}\) mbar corresponds to a gas purity of 0.01 ppm. continuously maintained in the furnace.
- **(B)** Oxidising gases evolved during the braze cycle can easily be pumped away several hundred times faster than they could be swept away in an inert gas stream.
- **(C)** No need for supplies of pure gas.

The majority of furnaces have water cooled vacuum chambers with internal heaters surrounded by concentric radiation shields or layers of fibrous insulation. They are usually pre-evacuated by oil-sealed rotary pumps augmented on large furnaces by booster pumps; final evacuation during the braze cycle is by high speed oil diffusion pumps.

In a leak tight furnace, the most important residual gas is H₂O, initially absorbed from the atmosphere on internal surfaces, usually dominated by those of the insulation. Typically, in a cold furnace, H₂O will constitute more than 90% of the residual gas with the partial pressure decreasing by a factor of 2-5 times during the heating cycle as degassing proceeds. As the temperature increases during a typical 2 hour heating cycle, CO₂, CO and H₂ appear at about the same level as the H₂O. Some of the H₂ and CO are desorbed bulk gases dissolved in the metal, whilst the remainder and the CO₂ are probably formed by the water-gas reaction with carbon impurities on internal surfaces or graphite furnace furniture. Hence CO₂ is not to be considered as an additional possibly oxidising gas.

Therefore it is necessary only to consider continual evolution of water vapour as the most important oxidant during the braze cycle, and the common practice
of prolonging the ramp-up time during heating to keep the pressure below some nominal value is usually counter productive in terms of the possibility of oxidising the job. Measurements show that Types 304 and 321 stainless steels and Inconel 625 are most sensitive to oxidation at about 750°C. Threshold discoloration of any of these alloys is produced when the product of the partial pressure and the time of exposure exceeds about $10^{-3}$ millibar minutes for water vapour and a little less than $10^{-3}$ millibar seconds for air. The criterion for good appearance and wetting on these alloys is that for heating rates of around 5°C/min between 730 and 770°C, the partial pressure of H₂O must be adequately less than c.3x10⁻³ mbar. In a leaky furnace however, the partial pressure of air must be less than 4x10⁻⁵ mbar. Partial pressures 2-3 orders of magnitude lower than this can be easily attained. At temperatures of 900-1000°C surfaces of stainless steel, previously oxidised in a poor vacuum with an exposure integral in water vapour of 200 times the threshold, clean up in a few seconds and braze easily. The oxide on Inconel 625 however does not clean up but wetting can still occur by undermining. Undermining can also occur at 860°C when using a 10% Pd-Ag-Cu alloy on heavily preoxidised 304 stainless steel and on lightly but not heavily preoxidised 321, or on Inconel 625. Ag 72-Cu 28 at 840°C would not successfully wet even the unoxidised metals.

Culham advised that they offer a commercial brazing service to Industry. 67% of their work involves joining copper to stainless steels using the silver-copper eutectic or a Microbraz alloy—a useful alloy proved to be a mixture of 70% Microbraz 10 and 30% Microbraz 130. They also use Cu-Ni, Cu-Au, and Ag-Cu-Pd alloys as occasion demands. Of particular interest was work in preparing clear quartz windows for the Jet European Torus Project where one problem is due to a phase transformation at c.500°C; they overcame this by placing the quartz into a nickel plated stainless steel holder with a disc of aluminium between quartz and holder and applying pressure at the melting point of the Al. An excellent diffusion bond resulted.

Culham have 3 vacuum furnaces the largest having a working volume of 1.2m dia.x 1.5m high. The vacuum achievable is 10⁻⁵ mbar. The time to reach brazing temperature is 2 hours.

(c) Surrey Work:
For vacuum brazing to succeed molten filler alloy must wet and spread across the surface of the parent metal where surfaces of both parent and filler are inevitably covered with oxides. A high temperature scanning stage has been developed by Surrey on an Auger electron microscope, enabling surface diffusion and oxide penetration which accompanies spreading to be analysed. Observations have shown that with some systems the oxide becomes locally blistered around each braze droplet, whereas in others much more generalised spalling of oxide takes place. Surrey have studied wetting and spreading phenomena over the past decade using this technique when they have systematically considered factors influencing oxide disruption, comparing different sub-strates (alloy or plain steel), oxide composition, thickness and geometry, parent metal temperature and type of braze alloy used. It has been established that oxide penetration is accompanied by the immediate appearance of sub-strate alloy components in the surface of the braze droplet, providing a zero time marker for the spreading mechanism. During spreading it has been found that the developing alloy film can be located by X-ray mapping with Auger electron spectroscopic analysis simultaneously revealing any surface diffusion.
Studies have been assisted by use of video film and cameras which tilt, enabling visual examination from different angles of braze droplets during the wetting process; this has been well demonstrated in a film made by UKAEA Harwell in their own collaborative studies with Surrey of the wetting of aluminium alloys - materials having tenacious oxides. This film revealed an explosive reaction disrupting an MgO layer where Mg was 2% of the brazing alloy. A rippling effect only was noted at lower Mg percentages, where vacuum brazing on a commercial scale was shown to be satisfactory.

Other alloys which have been explored by Surrey workers include Metglas MBF1001 (35.32 Pd-48.73 Ni-8.63 Cr-4.63 Fe-2.69 B), Ag-Cu alloys, 82 Au-18 Ni alloy, and 60 Pd-40 Ni brazing alloy on mild steel and Jetheat M152 (Composition: 0.08 C-12.5 Cr-1.5/2 Mo-2/3 Ni-0.35 max.Si-0.25/0.4 V-0.5/0.9 Mn-0.03 max.P-0.025 max.S-0.02/0.04 Ni).

In the case of gold-nickel brazing alloy a Hot Scanning Stage Electron microscope (HSSEM) was used in conjunction with Electron Probe Micro Analysis (EPMA) and Auger Electron Spectroscopy (AES). With HSSEM the melting process could be recorded under a vacuum of 13mPa. and with EPMA and AES the surface could be explored analytically to increase information available as interaction between substrate and braze alloy as it melted. It was noted that as the Au-Ni alloy flowed it was preceded by a halo ahead of the edge of the molten mass. The haloes were clearly identified by photography at high tilt angle to be a lifting of a surface layer on the steel by the molten alloy flowing beneath. Analysis of the cold specimen with AES and X-ray photoelectron spectroscopy revealed the layer as Cr2O3. It was shown that an important step in initiating the flow was the breakdown of the surface oxide layer at points where the molten Au-Ni had reduced the oxygen potential, also that Si in the steel played a role in the process. Sub-oxide spreading was the only mechanism of flow discovered.

(d) Aero-Engine Work:
Rolls Royce co-ordinate all Group brazing work from Derby and they described the alloys used, taking the RB211 engine as an example. While they have not markedly changed compositions over the years they have found new methods of applying alloys most helpful and specifically mentioned the Metglas series (foils), and plastic bonded alloys which can be positioned in joints rather than depending on capillary flow. The alloys now used in production are HTN1, HTN2, HTN3, HTN4, HTN5, HTN6, MBF-15A, MBF-80A and Wall Colmonoy 300 (11 Ni-25 Cr-2 Fe-2.75 Si-3 B-0.75 max.C-W 10-Remr.Co), AU5, and a special JM alloy 60 Au-20 Cu-20 Ni called Orobraz 980. The Au-Cu-Ni alloy is superior in fatigue to AU5 but both are used with Orobraz preferred where possible on the grounds of cost; even so they hazarded a guess that gold alloys only accounted for around 5% of all brazing alloys used. Rolls said that all their brazing work is carried out in vacuum and with the exception of a hydrogen furnace still used for heat treatment at Leavesden Green all other types of furnace have been discarded. On the subject of surfaces they have found it expedient to grind all surfaces prior to brazing.

3.3-U.S.A.Developments - Brazed Honeycomb Structures
Initially workers were devoting their efforts to brazing PH stainless steels and titanium alloys for military aircraft and for their Boeing Supersonic Transport (all titanium) aircraft, intended to be a competitor to Concorde. However, the U.S.A. Government's cancellation of the SST project did not offer a major setback, and subsequent efforts were concentrated on space shuttle, and more
recently 'star wars' requirements, Grumman Corp., Hexel Corp., Aeronca Corp., and
the Martin Company in particular advancing the technique of making reticulated
structures. Honeycomb panels are now included in designs for jet engine
shrouds, firewalls, jet blast deflectors, combustion chambers, turbine casings,
heat exchangers, lightweight high-temperature pressure vessels, lorry trailers,
and inner cabinets to refrigerators (where refrigerant circulates inside a
honeycomb sandwich). Nuclear space generators, powered by an isotopic fuel
system which converts heat produced by the decay of radio isotopic fuel
directly into electricity also require honeycomb. Future manned space craft call
for refractory and "super alloy" honeycomb wing panels. High performance aero
ingines are calling for titanium honeycomb for duct assemblies. Honeycomb
sandwich structures are thus being installed in many situations, viz. aero space
for heat shields, aircraft, engine and nuclear applications, where the nature of
the honeycomb structure gives local stiffness, low weight for good compressive
and tensile strength up to 425°C, and thermal and acoustic insulation.
Depending on the heating method used a wide variety of final shapes may be
produced from thin foil metals (down to 0.001 in. (0.02 mm) thick).

With regard to heating methods an essential requirement is to keep the spot-
welded honeycomb nodes with pre-placed filler alloy in contact with the facing
sheets on either side throughout the heating cycle. Rolls Royce use honeycomb
for acoustic reasons and as seals at the ends of blades as well as for
titanium blades in their later generation fan engines. They commented
favourably on the Metglas alloys. By adding these with separating foils spot
welding locates the correct amount of brazing alloy where most wanted). In
addition to the heating types of 2.6.4. para.(b) two other methods are widespread,
respectively electric blanket heating, and the Glasrock die method.
However, in a recent survey by BAJ-Vickers the conclusion was reached that
large retort vacuum furnaces are now preferred, and they anticipate that all
other methods will gradually disappear.
The electric blanket method is at present used for large panels 6 ft. x 2 ft.
(1.829 x 0.609 m), where the core is sealed between two facing sheets which are
contained between copper plattens having included cooling passages. These
plattens are in contact with Inconel heating elements. A variable pressure
diaphragm, fitted to a purge tube is used to introduce clean inert gas to the
faying surfaces. Pressure is maintained on the sandwich in one approach by a
cushion made from a heat resisting foil (stainless steel or Inconel) which
expands during the heating cycle. Controlled cooling as required for certain
heat resisting honeycombs is achieved by introducing water into the copper
plattens during cooling.

In the Glasrock method contoured panels are made in shaped refractory dies in
which Chromel-Alumel or Kanthal resistance elements are prepositioned in tubes
set in the refractory, approx. 0.25 in. (6.35 m) below the surface. The honeycomb
is set up on the lower plat ten and when satisfactorily positioned a matching
die, also with elements inserted, is lowered onto the work piece. The work
stays in the die during the heating and cooling cycle, this is a method also
used for Ti sheet material which is hot-creep formed (experience has shown that
unless Ti is formed to shape hot it will recover its original flat form on
standing).

(a) The following combinations of parent metal/filler metal
reportedly have been used for production scale honeycomb structures:-

(i) Parent Metals:
### Principal Brazing Metals For Sandwich Structure:

<table>
<thead>
<tr>
<th>Designation</th>
<th>Composition - wt.%</th>
<th>Braze Temps-°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>99Ag-Li</td>
<td>99.8 Ag-0.2 Li</td>
<td>982-996</td>
</tr>
<tr>
<td>97Ag-Li</td>
<td>97 Ag-3 Li</td>
<td>732-760</td>
</tr>
<tr>
<td>85-15 Li</td>
<td>84.5 Ag-15 Mn-0.5 Li</td>
<td>982-996</td>
</tr>
<tr>
<td>Lithobraise 925</td>
<td>92.5 Ag-7.3 Cu-0.2 Li</td>
<td>899-927</td>
</tr>
<tr>
<td>Airco T50</td>
<td>62.5 Ag-32.5 Cu-5 Ni</td>
<td>899-927</td>
</tr>
<tr>
<td>BT4P</td>
<td>71.5 Ag-28 Cu-0.5 P</td>
<td>760-788</td>
</tr>
<tr>
<td>SPM1-Ni,Clad 422</td>
<td>75 Ag-20 Pd-5 Mn</td>
<td>1121-1135</td>
</tr>
<tr>
<td>Perrabraz 101</td>
<td>54 Pd-36 Ni-10 Cr</td>
<td>1232-1260</td>
</tr>
<tr>
<td>Au-Ni</td>
<td>82 Au-18 Ni</td>
<td>996-1010</td>
</tr>
<tr>
<td>Pernobraz 128</td>
<td>72 Au-22 Ni-6 Cr</td>
<td>1010-1052</td>
</tr>
<tr>
<td>Endewrance 53</td>
<td>82.1 Ni-7 Cr-3 Fe-2.9 B</td>
<td></td>
</tr>
<tr>
<td>(Coast Metal)</td>
<td>-4.5 Si-0.5 Others</td>
<td>1043-1052</td>
</tr>
<tr>
<td>Microbraz 130</td>
<td>92 Ni-4 Si-2.7 B-0.5 C-0.8 Others</td>
<td>1010-1024</td>
</tr>
<tr>
<td>GE-J8100</td>
<td>80 Ni-10 Cr-10 Si</td>
<td>1149-1177</td>
</tr>
<tr>
<td>GE-J8102</td>
<td>Ni-19 Cr-10 Si-1 Fe-0.07 C</td>
<td>1177-1204</td>
</tr>
</tbody>
</table>

---

(ii) Principal Brazing Metals For Sandwich Structure:

<table>
<thead>
<tr>
<th>Designation</th>
<th>Composition - wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A110AT</td>
<td>Ti-5 Al-2.5 Sn</td>
</tr>
<tr>
<td>B120VCA</td>
<td>Ti-13 V-11 Cr-3 Al</td>
</tr>
<tr>
<td>17-7PH</td>
<td>Fe-17 Cr-7 Ni-1.15 Al-0.6 Mn-0.4 Si-0.07 C</td>
</tr>
<tr>
<td>PH15-7Mo</td>
<td>Fe-15 Cr-7 Ni-2.25 Mo-1.15 Al-0.6 Mn-0.4 Si-0.07 C</td>
</tr>
<tr>
<td>AM350</td>
<td>Fe-16.5 Cr-4.3 Ni-2.75 Mo-0.8 Mn-0.1 C-0.1 N-0.25 Si</td>
</tr>
<tr>
<td>AM355</td>
<td>Fe-15.5 Cr-4.3 Ni-2.75 Mo-0.95 Mn-0.25 Si-0.13 C-0.1 N</td>
</tr>
<tr>
<td>A286</td>
<td>Fe-25.5 Ni-14.25 Cr-2 Ti-1.6 Mn-1.2 Mo-0.6 Si-0.25 Al-0.25 V-0.05 C</td>
</tr>
<tr>
<td>R235</td>
<td>Ni-15.5 Cr-10 Fe-5.5 Mo-2.5 Ti-2.5 Co-2 Al-1 Mn-1 Si-0.16 C</td>
</tr>
<tr>
<td>Haynes 25</td>
<td>Co-20 Cr-15 W-10 Ni-2 Fe-1.5 Mn-1 Si-0.15 C</td>
</tr>
<tr>
<td>Rene 41</td>
<td>53 Ni-19 Cr-11 Co-10 Mo-3 Ti-2.5 Fe-1.5 Al-0.09 C</td>
</tr>
<tr>
<td>422</td>
<td>Fe-13 Cr-1 W-1 Mo-0.75 Mn-0.75 Ni-0.35 Si-0.3 V-0.2 C</td>
</tr>
<tr>
<td>Ni Clad 422</td>
<td>422 Clad with SPM1 alloy</td>
</tr>
<tr>
<td>TZM</td>
<td>Mo-0.5 Ti-0.07/0.08 Zr</td>
</tr>
<tr>
<td>D36</td>
<td>Cb-10 Ti-5 Zr</td>
</tr>
<tr>
<td>Hastalloy C</td>
<td>Ni-16.5 Cr-5 Fe-17 Mo-4.5 W-0.75 Si-0.75 Mn-0.35 V-0.08 C</td>
</tr>
<tr>
<td>Ferrabium</td>
<td>Fe-25 Cr-5 Ni-3 Cu-2 Mo-1 Si-1 Mn-0.06 C</td>
</tr>
<tr>
<td>Hastalloy X</td>
<td>Ni-22Cr-1.5 Co-0.5 W-9 Mo-18.5 Fe</td>
</tr>
<tr>
<td>Incoloy 625</td>
<td>Ni-22.16 Cr-0.02 C-0.04 Cu-0.07 Mn-2.25 Fe-0.26 Si-0.14 Al-0.2 Ti-8.65 Mo-3.39 Cb+Ta</td>
</tr>
</tbody>
</table>

---

(iii) Common Base - Braze Alloy Combinations:
Skin/Core Matl. | Braze Alloy | Service Temp-°C
---|---|---
A286 | Endewrance 53 | 427-650
422 | Ni-clad SMP1 | RT-427
422 | 99 Ag-Li | RT-427
Rene 41 | Endewrance 53 | 1046-1051
R 235 | Endewrance 53 | 1046-1051
Haynes 25 | Endewrance 53 | 1046-1051
Haynes 25 | J 8102 | 1046-1051
B 120 VCA | 97 Ag+Li | RT-315
17-7PH | Lithobraz 925 | RT-426
PH15-7Mo | or | RT-426
AM 350 | Airco T50 | RT-426

(b) Beryllium
The inherent brittleness of this metal as well as its reactivity with many filler alloys calls for brazing at low temperatures, rapid heating and cooling cycles, minimum time at brazing temperature, and minimum amounts of filler alloy to minimize formation of undesirable intermetallics. All Be sandwich structures, Be panels with Ti core, Be panels with cores of Type 321 stainless steel, 17-7PH and 15-7PH precipitation hardening steels and A286 heat resistant alloy have been brazed on a production scale. Flat panels with chemically pure Ti core, and 0.06 in. (1.52 mm) thick Be have been brazed in argon with Ag-5 Al-0.2 Mn as a filler alloy at 840°C. The other alloys joined to Be used a Ag-7 Cu-0.2 Li brazing alloy at 940°C. Six more experimental brazing alloys are under evaluation, all brazing at 760°C namely:

- Ag-59.4 Cu-9.5 Ge-1.9 Ti-5 Mn
- Ag-25.2 Cu-9.5 In-5 Mn
- Ag-23.6 Cu-8.9 In-8.8 Pd-2 Ti
- Ag-24.6 Cu-9.5 Sn-5 Mn
- Ag-33 Cu-7 Sn-3 Mn
- Ag-53 Cu-5 Zn-0.2 P

(c) Aluminium
The preferred technique was to braze in argon using clad aluminium X7005 alloy. To reduce diffusion of Si from brazing alloy into parent metal a thin pure Al barrier was inserted between parent and filler alloy. Two brazing alloys were clad to the X7005 alloy. 716 braze alloy, Al-10 Si-4 Cu and 719 alloy Al-10 Si-10 Zn-4 Cu are both brazed at 575°C.

Two recent filler alloys showing promise are Al-7 Si-15 Ge-10 Zn, and Al-7 Si-15 Ge-10 Ag; both braze at 550°C and look interesting for fluxless brazing of X7106 alloy.

(d) Steels
The preference was to use silver base alloys, with brazing temperatures c.940°C as less erosion and grain growth takes place compared with the Ni-base alloys. However the alloys used depended on the type of steel to be brazed and the 4 classes of steels used in making honeycomb structures are considered as:

(i) Cr-Ni Stainless Steels
AISI 300 series of austenitics are among the most readily brazed alloys, and
used for honeycomb because of their excellent high temperature corrosion resistance. While Ni-based filler alloys result in maximum strength and oxidation resistance other fillers based on silver, palladium and gold systems are also widely employed.

(ii) Martensitic Stainless Steels
(1) Low Cr, low C (types 403, 410 and 416), (2) High Cr, high C (types 440A, B and C): These steels are only rarely used in honeycomb since they air harden on cooling from the 760-870°C range, calling for heat treatment as an extra treatment after brazing unless a filler alloy is used which will allow brazing and heat treatment to take place at the same time. This treatment must be followed by fairly rapid cooling to ensure proper transformation of austenite to martensite.

(iii) Ferritic Non-Hardenable Stainless Steels
Most commonly used alloys of this type (405, 406, 430 and 446) are not often used for honeycomb as they cannot be hardened nor can grain size be refined by heat treatment. They can be brazed with high temperature filler metals but strengths are impaired if brazed above 985°C as a result of grain growth.

(iv) Precipitation Hardening Stainless Steels
While this class of alloy is more difficult to braze than austenitic stainless steels they are widely used. As in the cases of the martensitic steels the brazing cycles used must be compatible with recommended heat treatments. Brazing alloys successfully used are Endewrance 53 (BS.1845 type HTN2), GE-J8100 (HTN5), Microbraz 130 (HTN3).

(6) Nickel-Base Alloys
These can be considered as solid solution-strengthened alloys such as the Monels, Hastelloy's and Inconel 625, and the precipitation hardened alloys like Rene 41, Waspalloy and Inconel 718, known as "super-alloys". A newly developed third group has been introduced in which thorium is added (TD-Ni). Thorium has also been added to give TD-Nickel-Chromium and TD-Nickel-Cobalt. The effect of the dispersed thorium is to give superior strength, and oxidation resistance for service in the range 980-1350°C.

(i) Solid Solution-Strengthened Alloys
The alloys are not heat treatable and give no concern regarding compatibility of brazing thermal cycle and base-metal properties. They have been brazed with filler metals based on nickel and the noble metals. A recent filler metal showing promise is a Ni-23 Mn-7 Si-5 Cu alloy for thin nickel foils. Fillers containing P, Al and Mg must be avoided otherwise brittle intermetallics form during brazing.

(ii) Dispersion-Hardenable Alloys
A recently introduced alloy, TD-Ni for honeycomb for service at 1200°C is showing good stability and compatibility with the base metal; it brazes at 1300°C and is 58 Ni-16 Cr-17 Mo-5 W-4 Si. Another brazing alloy, TD-50, composition Ni-20 Cr-10 Si-9 Mo-21 Fe-2 Co is used for TD Ni-Cr and exhibits excellent wetting characteristics and strength at 1100°C. GE-J8100 is good for temperatures to 1040°C. Microbraz 130 is excellent for TD Ni to 925°C.

(iii) Precipitation-Hardened Alloys
These alloys present problems due to oxide barriers formed from Ti and Al in the composition. The alloys are intended to withstand moderate to high stresses in the range 540-1200°C and are referred to as "super-alloys". There are also iron-based and cobalt-based super alloys. In the case of Fe-and Ni-based alloys if Al+Ti exceed 1% brazing should take place in vacuum. Brazing alloys used to make Rene 41 panels include 67 Mn-16 Ni-16 Cr-1 B and Ni-20 Cr-10 Si-10 Mn but the most suitable proved to be Ni-33
Cr-24 Pd-4 Si. It has the ability to braze Rene 41 in thicknesses less than 0.015 in. (0.38 mm) without erosion or embrittling.

Inconel 718 honeycomb components have been successfully joined with Ni-4.5 Si-2.9 B brazing alloy (HTN3). It has also been successfully joined with Au-22 Ni-6 Cr and Au-18 Ni (AU5 alloy).

Cobalt-Based Alloys

These are said to be the easiest to braze of the "super-alloys". L605 suffers moderate strength losses due to grain growth during brazing, and preferred alloys are Au-Pd-Ni, J8100 (Ni-19 Cr-10 Si), J8400 (Co-21 Ni-21 Cr-8 Si-4 W-0.8 B), J8600 (54 Pd-36 Ni-10 Cr) Endewrance 53 (HTN2) and 82 Au-18 Ni (AU5 alloy).

Titanium And Its Alloys

Filler alloys must be carefully chosen to avoid preferential corrosion of the joint. Ti is an active metal but its activity tends to decrease in an oxidising environment, because its surface undergoes anodic polarization, in a manner similar to Al. Vacuum brazing has been accomplished with Ag-base filler alloys, and among various alloys which have been successfully used for honeycomb structures are 95 Ag-5 Al, 56 Ag-24 Cu-19 Ge-1 Ti, 82 Ag-9 Pd-9 Ga. However, users do have reservations due to severe crevice corrosion of joint interfaces in less than 100 hours in typical marine and industrial environments, and a new alloy has been developed notably Pd-15.4 Ag-3.5 Si, liquidus 695°C; Ti-15 Cu-15 Ni, and Ti-48 Zr-4 Be were also suitable for brazing with good resistant joints.

To avoid the problem, which revolves around the solubility of Ag in Ti, current U.S.A. thought is that Ti-Ag in contact with Ag is the combination producing the susceptibility to crevice corrosion and oxidation. The Pd-Ga alloy particularly offers a barrier which inhibits Ag diffusion, thereby preventing excessive amounts of Ti-Ag at the base metal-braze interface. The brazing temperature never exceeds 900°C.

The major alloy being used for honeycomb is the Ti-6 Al-4 V material as facing sheets with core material Ti-3 Al-2.5 V or CP Ti.

The Westland Group are interested in vacuum brazing thin foils for heat exchangers and commented that while they have experimented with the Ag-Pd-Ga alloy there is a real need for an alloy suitable for joining Ti and its alloys, from which it may be inferred that they were not satisfied with the alloy in their trials (which appear to have been limited). Rolls Royce have mentioned success with treble metal foils, where Cu-Ag eutectic is sandwiched between chemically pure Ti. However they are also brazing large fans where honeycomb core is placed between two Ti alloy sheets, where surfaces of the sheets have been plated with Ni and Cu. The composite is vacuum brazed and satisfactory results are always reproducible. Both core material and facing sheets were made from Ti-6Al-4V alloy on a production scale.

Refractory Metals And Their Alloys

Space programmes calling for re-entry resistant structures have given impetus to joining alloys based on columbium, molybdenum, tantalum and ceramics. Temperatures on re-entry call for resistance to breaking up at 1650°C and above.

Columbium (Niobium)

Development work is continuing, with various Cb alloys successfully meeting the service stipulations. The proprietary compositions have not been fully disclosed, but D36 alloy (Cb-10 Ti-5 Zr) has been brazed with Ti-8.5 Si filler.
alloy at 1454°C. The Ti alloy B120 VCA (Ti-13 V-11 Cr-3 Al) has also been successfully used at 1649°C to join the Cb alloys Cb752, C129Y and core materials, D43, FS82 and F48. Other alloys used as brazing fillers for Cb alloys include Pt-10 Ir at 1815°C, Pt-10 Rh at 1899°C, pure Ti at 1732°C, Ti-33 Cr and Ti-30 V-4 Be alloys.

Production of the Ti-Cr involved vacuum depositing Cr on both sides of a 0.0015 in. (0.038 mm) thick Ti foil, followed by a brazing cum diffusion cycle at 1343-1371°C (lap joints made in Cb alloy with this brazing filler exceeded 1900 p.s.i. (134 kg/cm² at 1370°C).

In the case of the Ti-V-Be alloy, joints were brazed with the diffusion sink approach at 1285-1315°C, followed by a two stage diffusion heat treatment (a) for four hours at 1121°C temperature then raised to (b) for sixteen hours at 1315°C. A temperature of 1854°C was required to remelt joints after this sequence.

(ii) Molybdenum

Apparently the TZM alloy is most used (Mo-0.5 Ti-0.7/0.8 Zr) but it does present problems due to re-crystallization at 1150°C such that ductile Mo joints are hard to achieve above 1093°C. Use of the diffusion-sink approach is said to have overcome this problem, and employing it to braze TZM with the Ti-8.5 Si eutectic at 1330°C has resulted in ductile brazements, free from cracks and exhibiting excellent filleting and wetting. The process was helped by mixing the Ti-Si eutectic brazing powder with Mo powder.

Other materials used as brazing alloys for Mo include Haynes 25 alloy at 1315°C, pure Ti at 1815°C and B120VCA alloy at 1655°C in vacuum. Recently developed alloys are Ti-25 Cr-13 Ni and Ti-25 Cr-3 Be. The latter alloy was brazed at 1260°C for 1 minute and diffusion heat cycled for 8 hours at 982°C + 16 hours at 1038°C + 8 hours at 1093°C + 40 hours at 1121°C. Both alloys were successfully employed to make TZM brazed structural honeycomb panels.

(iii) Tantalum

Honeycomb applications for this metal are for elevated temperature applications in excess of 1650°C. Investigations have involved conventional brazing, diffusion-sink brazing and reactive brazing concepts. The reactive concept involves a braze alloy containing a strong melting temperature depressant. The depressant is selected to react with the base material or powder additions to form a high melting intermetallic compound during a post braze diffusion treatment. By removing the depressant in this way the joint remelt temperature is increased. Successful application of this concept is dependent on controlling the intermetallic compound to form discrete particles. In some instances continuous intermetallic compound films are in grain boundaries or along the base metal-fillet interfaces giving seriously impaired joint ductility.

Comparative results have shown that using a Cb-1.3 B alloy was excellent for conventional brazing in vacuum for Ta honeycomb panels.

Diffusion-sink brazing: Using Ti and Ti-30 V alloy at 1676-1760°C has produced remelt temperatures exceeding 2093°C. Diffusion-sink brazing Ta with 33Zr-34Ti-33 V braze alloy at 1426°C has given remelt temperatures of plus 1760°C. The remelt temperatures indicate that the maximum service temperatures are as high as 1925°C for Ti 30V alloy, and 1650°C for Ta honeycomb made with the Zr-Ti-V filler. A major problem using the diffusion-sink approach was that braze alloy was found to volatilize in sealed honeycomb core cells and deposited on the foil to diffuse inwards leading to embrittlement. This did not arise in the case of
conventional brazing and good panels have been acceptable brazing Ta-8 W-2 Hf parent alloy with the Cb-1.3 B composition brazing alloy. Other combinations undergoing evaluation include Ta-10 W and Ta-30 Cb-7.5 V for service in the 2200°C range. Studies indicated that the Hf-7 Mo filler metal was preferable for Ta-10 W honeycomb for reusable service at 1925°C, but for reusable service in the range 1370-1925°C a Ti-30 V-3 Be filler metal was acceptable. Adequate joint properties were also obtained when brazing Ta-30 Cb-7.5 V and Ta-8 W-2 Hf base metals with Ti-34 Cr and Hf-7 Mo filler alloys. It is said that while producers are developing newer alloys to meet varying environments (creep strength at 1650°C, oxidation resistance) new braze alloy development is continuing. Currently 90/95% filler alloy is only available as powder, sometimes difficult to work at elevated temperatures. New braze alloys under development are Hf-40 Ta, Hf-19 Ta-2.5 Mo being produced by direct rolling of alloys or pack-diffusion heat treatment of Hafnium foil.

(1) Ceramics

Honeycomb structures have been developed as flat panels, curved panels, u-shaped components, and nose cones where the lightweight compared to steel or refractory metal honeycomb is compensated for by the inherent high-temperature capability for service temperatures in excess of 1100°C. The materials used are characterised by good resistance to thermal shock, low coefficient of thermal expansion and a bulk specific gravity of 0.5 g./cm². One system was made from 54% SiO₂-44% Al₂O₃ and bonded with a SiO₂ and Al₂O₃ cement between core and skin.

Ceramic honeycomb has also been made from Pyroceram, a glass-ceramic used for nose cones. The structure consists of multiple layers of thin 0.005 in. (0.127 mm) ceramic sheets separated by similar thin corrugations. The thin sheets are fused together without adhesive. Low expansion to 300°C, coupled with high surface area leads the developers of the system to believe that this would be an excellent structural material where aerodynamic heating is a problem and the cellular passages could be used to circulate liquid or gaseous cooling media in a method of cooling missiles and spacecraft during re-entry. Honeycomb panels may be made of metal skins brazed to a ceramic cone which has been flame-sprayed with metal. In this case the coefficient of thermal expansion of metal and ceramic core must be matched so that the bond will not be parted with changing temperature; in one approach thermal conductivity can be reduced by arranging evacuation of the air from within the panel.

Finally honeycomb panels are being made from aluminium and zirconium oxides which withstand temperatures of 1370-1925°C. Work is also in progress with oxides and carbides of elements such as hafnium and thorium in attempts to withstand service temperatures of 2200-2760°C.

3.6-Japanese Ceramic Joining Work

Two approaches have traditionally been employed for joining cermets or ceramics to themselves or to metals.

In one approach the ceramic is first precoated with a liquid suspension of copper, silver, copper-silver, or a molybdenum-manganese mixture before nickel plating. The metallised surface is then treated as a metal with joints suitably arranged to minimise the effects of different thermal expansions before brazing with Au-Cu, Cu-Ag-Sn, Ag-Pd-Mn, Cu-Pd-Ni-Mn, Pd-Ni, Cu-Ni, Cu-Pd, Ag-Pd, Ag-Cu-Pd, or Au-Ni alloys as given in B.S.S.1845:1984. Metallised alumina as used in sparking plugs is a typical application used for many years.

The second approach as given in B.S.S.1723:1986 (Pts I & II) & 1988
(Pts III & IV) involves the active metal technique. In this method the brazing filler alloy has titanium or zirconium included in the composition. The Ti or Zr acts as a flux to the ceramic surface so that there is direct wetting of the ceramic by the filler metal, usually Ag-Cu based. Brazing can take place in hydrogen, dewpoint -50° C, argon or vacuum at \(10^{-3}\) mm Hg pressure.

For either approach Sheward makes the point that built in stresses due to the different expansion characteristics must not be such that the liquid brazing metal at the brazing temperature gives grain boundary penetration. This is a phenomenon which was little appreciated in practice. During 1986 there was a D.T.I. sponsored study mission to Japan to assess the status of ceramic joining technology in that country. It is interesting to compare their conclusions with the present situation in the U.K.

(a) Ceramics Joined

The report of the mission revealed many efforts at joining \(\text{Al}_2\text{O}_3\), \(\text{Si}_3\text{N}_4\), \(\text{ZrO}_2\), \(\text{AlN}\), \(\text{SiC}\), \(\text{TaC}\), \(\text{TiC}\), \(\text{TIN}\) to themselves, to steels, to \(\text{Si/Mo}\) and \(\text{Cu}\), where the economics of using unsupported ceramics called for a composite of ceramics and metals.

The references suggest that much of the Japanese effort towards new techniques has arisen under a Ministry of International Trade and Industry (M.I.T.I.) 10 year plan from 1981. While a number of techniques are being actively explored (by 12 Research Institutes and Industrial organisations) few new bonding techniques have reached the stage of commercial production. The most notable advances however are in the automotive area for rocker arm tips, glow plugs, and turbo-chargers for use in a revolutionary diesel engine design. In this engine the development of a ceramic turbo-charger is claimed to be an important landmark, both for benefits conferred on engine performance, and because it is the first example of a high stress, moderate temperature, dynamic component which is being produced commercially, with good reliability. NTK/Nissan Ltd. installed 3,000 of these units from late 1985 to Spring 1986 in its Fairlady 2. The rotor appears to be \(\text{Si}_3\text{N}_4\) and results in a 36% reduction in time to reach a rotational speed of \(10^4\) RPM over a conventional metallic turbocharger, which suffers from inertial lag. Joints are statistically checked on rotors spun-tested in a practical environment.

(b) Joining Methods

Ceramic/ceramic diffusion-bonding requires high temperatures and pressures. Few laboratory problems arise but in practice this is only a suitable method for simple joint configurations.

Ceramic/metal pressure diffusion bonding suffers from similar strictures but additionally results in inferior joint strengths. The most common joint configurations are those of \(\text{Si}_3\text{N}_4\), \(\text{Al}_2\text{O}_3\), \(\text{SiC}\), and \(\text{ZrO}_2\) with steel, for which satisfactory interlayers have been developed for high strength. However service temperatures are limited by the usual Ag-Cu eutectic, which softens around 500°C in such joints.

A novelty within the Japanese programme is in the development of multiple layers for thermal stress relief, an extension of the Trifoil approach of Johnson Matthey and European alloy producers.

It appears that most research is concerned with the \(\text{Si}_3\text{N}_4\) material which, apart from the piston cap and steel piston mechanically locked together, is being considered for valve rocker arm tips and glow plugs in diesel engines. The relatively high thermal conductivity grade of \(\text{SiC}\) (developed by Hitachi) is of interest for components calling for high electrical insulation and high temperature corrosion resistance, while providing a level of thermal...
It is of interest to note that the U.K. has also embarked on a programme with the support of the D.T.I., into Ceramic Applications in Reciprocating Engines (CARE). A consortium has been formed of approximately 30 U.K. companies: ranging from suppliers of ceramic materials to engine manufacturers. Also in the U.K. is the Advanced Ceramic Turbine Programme, started in 1984 by DTI and RR, and involving seven others who are looking at ceramic turbines. There is also apparently a large Government supported programme in the U.S.A., which leads to the conclusion that leaders in this field are convinced that there is great potential for these classes of materials, and that effecting sound joints between such materials and cheaper materials to support them, calls for extra work in this field.

(c) Titanium-containing Activated Brazes

Ti has been used by Toshiba with Cu, Ni and Cu-Ag alloys, with optimum Ti concentration around 5% Ti in the filler alloy. The braze metal acts as a carrier for the Ti, which reacts with ceramic surfaces to enhance wetting. Surface compounds have been identified as TiN, Ti₃Si₃ and Ti₅Si. Maximum joint strength is achieved by adjusting Ti to avoid forming brittle intermetallic silicides. Brazing is in vacuum to minimise TiO₂ formation. Joint strength varies with time and temperature, and for Cu-Ag alloys is at an optimum after holding at brazing temperature for 30 mins. at 880°C. The Japanese regard this as a useful method for joining ceramics to metals, provided precautions are taken to accommodate thermal mis-matching.

(d) Aluminium-Silicon Inserts

Si₃N₄ is joined to metal which incorporates a stress-relieving buffer layer of pure Al at 0.002-0.004in.(0.05-0.1 mm). This Al layer is sandwiched between two Al-10% Si foils at ca. 0.0015 in.(0.38 mm) thick. Brazing is effected by hot pressing in vacuum under a pressure 10mPa at temperatures above the Al-Si eutectic but below the melting point of pure Al with maximum strength achieved at 610°C according to Hitachi. The maximum usable service temperature is 300°C.

(e) Copper-Manganese Brazing

This is used for brazing SiC to Cu or stainless steel via a Cu-carbon fibre compliant composite interlayer. The brazing alloy is Cu-35% Mn brazing at c. 900°C. Wetting is improved by the presence of the carbon "flux", the mechanism of which is unclear but the Mn has been observed to promote formation of silicides and carbides. Bonds are made with similar strength equivalents to using Mo-Mn + Al₂O₃ joints, and are usable for service at 300°C.

(f) Liquid Phase Joining

Methods undergoing exploration are intended to raise maximum usable temperatures from above 300°C. In the Nissan/NTK turbo charger rotor it is appreciated that the key to successfully implementing the joining method between ceramics and metals is not the braze alone but the system devised to combat thermal mismatch. The geometry of the rotor is a relatively simple butt-joint with a number of interlayers between the ceramic rotor shaft faying surface and the steel shaft faying surface. A liquid phase is first applied to the ceramic. This may be Giri’s recipe of mixed Si₃N₄ powder, magnesia ytttria, and lanthana designed to give a low viscosity oxy-nitride liquid at the joining temperature. It is expected that this liquid will wet and diffuse into the Si₃N₄ surface. The treated surface is brazed using Ag-Cu as braze material to
successive layers, consisting of metals with different properties, one of which has a low thermal expansion coefficient and another provides a low Young's modulus, and is therefore easily deformable. Such composite joints made between Si₃N₄ and steel bring residual stresses to acceptable limits. However location of the joint must be at a point where maximum temperature of use is below the capability of the brazed joint (300°C); also that it maximises the use of metal in the critical shaft area which is exposed to bending stresses, which a ceramic shaft may not survive.

Hitachi have approached the interlayer concept by developing a composite 2 mm. thick Cu-C material in which the thermal expansion coefficient and Young's modulus can be tailored by varying the amount of carbon fibre in the composite. Their system has been used to join 10 mm. thick SiC plates to stainless steel or water cooled Cu using the carbon-activated 65 Cu-35 Mn braze, the sequence across the joint being SiC / Cu-C / 65 Cu-35 Mn / stainless steel.

(g) Summary Of Ceramic Joining Problems

(A) Mechanical joining requires difficult precision diamond machining to avoid stress concentrations and is not gas tight.

(B) Due to thermal shock or ceramic decomposition welding is inapplicable.

(C) Adhesion bonding is limited to low temperature stress applications.

(D) Requirements are for high cohesion levels, preferably maintained to high application temperatures, consistent with properties of the ceramics to be joined.

(E) Frequently noted is incompatibility in thermal expansions between materials to be joined, particularly for ceramic-to-metal combinations.

(h) Solutions Possible

(1) High cohesion dictates that chemical interdiffusion or reaction should take place at the ceramic interface during joining - normally inhibited by slow diffusion rates, and the chemically inert nature of the ceramic components. Chemical interaction calls for high temperatures or additions of active elements to the joining liquids e.g. 'active' metal brazing in which for example Cu-Ag eutectic liquid contains a strong nitride, oxide or carbide-forming element.

(2) Thermal expansion stresses generated, either during joining or in-service and thermal cycling failures may be overcome via the interlayers technique, with graded thermal expansion coefficients for layers between ceramic and steel.

(3) A question raised by the knowledge that the U.K. has programmes is whether Surrey could be included in one of the DTI sponsored programmes to get support for materials, and learn where others are working. Surrey's experiences using Hot Stage EM and Auger spectroscopic analysis is in the forefront of learning why things happen, whereas the implied criticism about the Japanese workers is that their approach has been almost wholly empirical in concept.
4-Brazing: Areas To Benefit From Further Research

To recapitulate, the objectives of the surveys which have been reported in the foregoing sections were threefold:

(1) To review the status of brazing as known in 1965, detailing the principal techniques and parent metal/filler alloy combinations applicable for the different engineering applications which call for this method of metal joining.

(2) To consider the present position of the process, commenting on alloys and methods replaced or further developed over the intervening years, and attempting to identify the driving forces bringing about changes.

(3) To suggest areas where future research would be beneficial, as listed later in the paragraphs of this section of the thesis.

The surveys have brought out that due to the depression which started in 1974 the inevitable cut back in funds available has inhibited U.K. research effort, major laboratories having their resources curtailed. Compared to America, Europe and Japan the conclusion reached must be that the U.K. has made less satisfactory advances with the possible exception of nuclear power developments. Never-the-less as a technique, brazing is now widely used in its own right rather than as a method to be turned to when all else has proved unsatisfactory.

Taking a worldwide look the research and development picture is less dismal with the U.S.A., European countries and Japan all benefitting from Government support with new alloys produced in the U.S.A. permitting the widespread use of honeycomb sandwich structures of good rigidity, strength-to-weight ratio and elevated temperature performance. In particular the space and aero-engine projects have brought about methods and alloys allowing the brazing of the refractory metals niobium, tantalum, molybdenum, titanium, zirconium and improved precipitation-hardening stainless steels, as well as the nickel-and cobalt-based "super alloys".

Developments have been assisted by the widespread use of large vacuum furnaces which can be quickly evacuated and speedily raised to operating temperatures. Another major contribution to the technology has been the development and application of the scanning electron microscope, tilting hot stage electron beam microscope, video photography and Auger/x-ray spectroscopic techniques allowing researchers to follow surface reactions at the instance of brazing, and largely pioneered by this University.

Resulting from the surveys a number of areas have been identified as worthy of consideration for further research programmes as follows:

(a) Aluminium Brazing

In view of the success with vacuum and controlled atmosphere furnace brazing compared to flux bath brazing as the only satisfactory method in 1965, there is scope to find improved filler alloys to widen the usage of this process, as the number of alloys which can be brazed in vacuum are few. It is believed that UKAEA Harwell are looking into the effects of Bi in Al alloy 4104 as while the mechanism of Mg has been studied there is little knowledge of the effects of other constituents on the brazing process.

It was interesting to note that while copper had given way to mechanically fitted aluminium for car heaters there is clearly dissatisfaction with mechanical joints as evidenced by the Alcan-developed Nocolok furnace brazing approach. U.K. manufacturers continue to have reservations about this process.
and it is believed there is scope for collaboration with Alcan or Delanair in studying the reactions taking place.

(b) Palladium-containing Brazing Alloys
There has been little research in the UK into reasons for the success of these alloys over the past 25 years, unlike the USA where a number of alloys have been developed for aerospace applications. It has not been established why American workers have added this element to different systems, and a useful study would be to trace metallographic changes across a number of joints made with UK established alloys and the later USA series.

(c) Copper-Silver-Palladium Alloy Series
Stress corrosion cracking of low expansion iron-nickel and iron-nickel-cobalt joints made with silver-copper eutectic, and intergranular penetration of stainless steels can be prevented if palladium is added as a constituent to the alloy. Reasons for these effects of Pd need establishing.

(d) Metglas Alloys
The wide range of rapidly solidified alloys made by Allied Signal Corporation suggests that the process is flexible. These alloys offer the practical advantage that alloys normally capable of only being produced as powders are made as foils, aiding placement prior to brazing. However the claim was made that the production of glassy brazing alloys was conditioned by the steepness of the liquidus curve as it approached a eutectic composition. The reason for this claim should be explored with metallographic examinations taking place as constituents move away from eutectic compositions, calling for collaboration with the makers of this series.

(e) Nickel-Chromium-Silicon-Boron Series
(i) Metallography Versus Brazing Temperatures
Differences in liquidus and solidus temperatures of apparently identical alloys made at different times have resulted in compositions specified being challenged. UKAEA Springfields have had series made by Osprey Metals, varying the minor constituents and noting the effects of these on reproducibility of melting points. They are particularly sceptical that while in one series, where HTN alloy (Ni-3/4 Si-1.5/3.5 B = Nicrobraz 135) was assessed by three European laboratories, who noted an apparent closeness of liquidus temperatures using DTA (differential thermal analysis), the results did not agree with earlier Japanese and subsequent Springfields work on the Ni-Si-B ternary diagram. Recent results made UKAEA query the relevance of DTA results to brazing practice, and they expressed the view that the metallography of brazed joints with this series needs further exploration, offering to collaborate with Surrey in an agreed project.

(ii) Wide Gaps
Filling of wider gaps has been achieved using alternative approaches;
(A) the relatively close tolerances required for "super alloys" has led to use of diffusion-sink methods adding e.g. Ni powder to HTN4 alloy prior to brazing.
(B) in another approach, gaps have been packed with nickel powder and pre-sintered. HTN3 alloy was subsequently applied to the joint area before a brazing cycle.
Compounds formed in both approaches during brazing need evaluation as mechanisms are unclear. The establishment of a sound system to deal with large
clearances would offer advantages, most notable being a reduction in costly machining prior to brazing.

(f) Titanium Alloys
While American workers are successfully brazing thin metal foils for honeycomb production and heat exchangers, the UK workers do not consider that an alloy has been produced which would be satisfactory for heat exchanger production due to the formation of brittle compounds. Titanium is susceptible to oxide, nitride and carbide, brittle phases formation, and an interesting study could be to take a number of known brazing alloys and to endeavour to trace the effects of these on the metallurgy of the titanium joints. It is believed that Titanium & Metal Alloys Ltd. would be willing to co-operate. There is undoubtedly a need for a suitable alloy for thin sheets/foils for heat exchangers in the opinion of the Westland workers.

(g) Ceramic Joints
With the success of the Japanese using multilayers, including a carbon-fibre insert, notably in the production of the stressed butt joints for steel to ceramic rotors in their Nissan turbo-charged automobile design, there is bound to be interest in this technique. The point made by the delegation who looked into Japanese methods highlighted that the joining mechanism was uncertain and studying effects across joints would be a laudable outcome, particularly if it was possible to participate in the two UK sponsored projects.
5-Research Project: The Role Of Palladium In Silver-Copper Braze Alloys

After considering the areas likely to benefit from further research (section 4) it was concluded that a worthwhile project would be to examine reasons for the reported failures of the nickel-iron low expansion alloys when brazed with the silver-copper eutectic alloy and to find why such failures can be overcome on replacing that alloy with modifications using different percentages of palladium.

5.1-Objective

Practical experience has shown that the addition of palladium to the silver-copper range of filler alloys reduces tendencies at the time of brazing to intercrystalline embrittlement and cracking of the nickel-iron and nickel-iron-cobalt series of low expansion alloys. It was not known why palladium has these beneficial effects and the aims of this project are firstly to seek reasons for the alleged cracking in the absence of palladium and secondly to find why cracking is overcome on adding this element to the Ag-Cu alloys.

5.2-Background

Some years ago trouble was experienced in joining the low expansion Ni-Fe or Ni-Co-Fe alloys using the Ag-Cu brazing alloys. It was found that the parent metal cracked due to penetration by the filler alloy during brazing. The trouble could be overcome by the costly double treatment of nickel-plating followed by a stress relieving anneal which also drove off residual hydrogen from plating; brazing then took place with the silver-copper eutectic.

The problem of parent-metal cracking due to contamination by liquid brazing alloy was aggravated when tensile stresses were developed in the brazing zone caused, for examples, by uneven heating, stresses applied due to jigging method, or to wide differences in the coefficients of thermal expansion of the components of the joint. In addition some filler alloys when used with the given parent metals appeared to promote cracking more rapidly than others. The nickel-base alloys used in glass-to-metal seals were often brazed to mild steel and it was found that whereas vacuum-resistant joints were obtainable using the 65 Ag-20 Cu-15 Pd alloy, liquidus 900°C, solidus 850°C, leakage of vacuum arose at joints made under identical controlled conditions with the Ag-Cu eutectic, m.p. 778°C. Precautions taken had in all cases been similar; all parts to be joined had been annealed before brazing, attention had been taken to ensure that jigging did not introduce stresses during the brazing cycle and that the same jigs and furnace were used throughout the range of the experiments.

These effects were demonstrated in laboratory tests, Fig.13, some results of which are reproduced. Ni-Fe-Co alloys in the form of strips had been hot tensile-tested after precoating at melting temperatures with various silver and copper containing brazing materials and then rapidly re-heated to the fusion temperature of the respective brazing alloys. The full line curve shows T.S. v. temp. for unbrazed strip and points A, B, C, etc, at the head of the vertical black lines indicate the strength developed in the presence of molten brazing alloys. E and F are most significant showing how 10% Pd in F improved the T.S. compared to E.
Fig. Tensile properties of Ni-Fe-Co alloy tested at melting point of brazing alloy applied to surface strip.

A 60 Ag/15 Cu/25 Zn/0.05 Sn
B 60 Ag/15 Cu/25 Zn
C 65 Ag/15 Cu/20 Zn
D 61 Ag/28.5 Cu/10.5 Zn (B.S.I. Grade A)
E 70 Ag/30 Cu
F 67.5 Ag/22.5 Cu/10 Pd
G 85 Ag/15 Mn
In another series of investigations it had been found that where silver solders (to B.S.1845) had been used in the fabrication of sheet-metal equipment made in plain chromium stainless steel there had been some peculiar failures in apparently innocuous environments. The breakdowns had been traced to crevice corrosion said to be associated with oxygen deficiency giving rise to failure at the interface between brazing alloy and parent metal and leaving a red rust line along the filler alloy fillet. Crevice corrosion occurred under stagnant conditions and it was regarded as most important to pay attention at the design stage to ensure that where there was drainage towards the brazed joint, for example at a sink outlet, that a filler alloy was used which did not lead to this type of problem.

Slobodacvso similarly reported crevice corrosion failures using both ferritic and austenitic stainless steels when brazed with 50 Ag-15 Cu-16 Zn-19 Cd alloy. His conclusions were that joints later subjected to humid atmospheres or tap water resulted in the dissolution of a very thin steel layer along the joint interface, as a result of which the bond between steel and brazing alloy was destroyed. When his experiments were repeated with the 54 Ag-25 Pd-21 Cu alloy such failures did not arise.

While the additions of palladium in the foregoing instances have been claimed to overcome the problems experienced without the need to first plate the parent metal, the mechanisms involved in suppressing tendencies to intercrystalline penetration and crevice corrosion were not known.

Brooker and Beatson made the point that joints made with palladium-containing alloys gave high oxidation resistance up to 500°C (700°C in the case of the 60 Pd-40 Ni alloy) and in the brazing of stainless steels produced joints which were resistant to crevice corrosion. However they were unable to offer any explanation as to why an addition of 5% Pd to the Ag–Cu eutectic was sufficient to overcome this defect.

In view of this background it was decided that the project would consider the effects of palladium-containing filler alloys on a Ni–Fe alloy, provided by Culham Laboratory.

5.3-Method

It was intended that the first approach to the problem would be to note whether the link between the different types of beneficial effect due to the addition of palladium to the silver–copper alloy, was that of surface or interface diffusion.

Surface diffusion from a braze deposit can be followed by Hot Stage Auger microscopy and it was regarded as a straightforward matter to contrast the behaviour of similar brazing alloys with and without the addition of palladium.

The study of interface diffusion is, however, a different proposition since the interfaces concerned are normally hidden from view. It was therefore intended to make use of the embrittling effects of the constituents in the silver–copper alloy observed with the nickel–iron alloy.

The embrittled interface should be exposed by in situ fracture of prepared test pieces and then examined for traces of copper and silver. It may be more difficult to subsequently show that palladium either suppresses the diffusion or replaces it and techniques to produce brittle fractures in palladium-brazed material might have to have to be developed.
It was probable that surface diffusion and interface diffusion could be studied on the same test pieces after they had been exposed to typical furnace processing if this proved desirable, Culham having kindly offered to make furnace capacity available.

In the event circumstances altered as will be related later under Experimental Work and for example there was no need to take up Culham's offer of facilities.
6-Experimental Work

This section of the thesis initially reports on the analyses of the materials employed; it then describes the techniques used for specimens which were prepared without extraneous loads during vacuum-furnace treatments and then compared with others which were subjected to static beam loading at brazing temperature in the furnace. Results obtained using Auger/XPS, scanning electron and optical microscopy are given and discussed as the work proceeded. Final sections evaluate the experimental work and give conclusions.

6.1-Materials Used

U.K.A.E.A., Culham Laboratories provided various alloys at different thicknesses. Major elements were determined by electron probe micro analysis with Auger spectroscopy confirming that the only additional elements were traces of carbon and oxygen on the brazing alloys; these complied with the British standard specification, both Fe and Ni being absent. The ratio of Fe to Ni in the parent metal of 1.38:1 proved to be relevant to the investigation. The materials finally selected for this project were as follows:

(a) Half-hard (HV 194) nickel-iron low expansion alloy rod at 12.7 mm diam.
   57.42 Fe-41.5 Ni-0.63 Mn-0.45 Co

(b) B.S.1845: 1984: Type AG7 "as drawn" wire at 0.25 mm diam. (silver-copper eutectic alloy: see sect. 3.2.2 for specified composition limits) -
   72.47 Ag-27.08 Cu-Trace Pd

(c) B.S.1845: 1984: Type PD1 "as drawn" wire at 0.25 mm diam. (Pallabraz 810 alloy: sect. 3.2.7 gives spec. limits) -
   68.86 Ag-26.6 Cu-4.53 Pd

(d) B.S.1845: 1984: Type PD2 "as drawn" wire at 1.00 mm. diam. (Englehard 723 alloy: see sect. 3.2.7) -
   58.8 Ag-31.32 Cu-9.92 Pd

(e) B.S.1845: 1984: Type PD3 "as drawn" wire at 0.50 mm diam. (Englehard 725 alloy: see sect. 3.2.7) -
   52.44 Ag-25.81 Pd-21.75 Cu

6.2-Configuration Of Specimens

3 x 1 mm. discs were cut transversely from the Ni-Fe rod for spreading and flowing tests. Initially 5 x Charpy Impact test specimens were then turned from the rod to give 30 mm long by 5 mm diam. specimens, with a 45° vee-notch at mid-positions where the diameter was reduced to 3 mm. Ideally the ends should have been chamfered to assist entry into the Auger microscope specimen holders (buckets) with lengths and diameters 'Go/No-Go' gauged but this was over-looked causing later trouble when attempting to mount specimens directly in the Auger facility.
As the work proceeded a further 13 specimens were prepared from the rod.

Brazing alloy was applied in the case of the proposed AG7 and PDI impact test experiments in the form of 4 turns of 0.25 mm wire, pulled into the vee notches as tightly as possible with pliers, with ends twisted together and the 'twists' arranged upper-most as specimens lay in the treatment jigs.

The PDI2 wire used for experiments with this alloy gave a placement problem due to its stiffness. It was cut to 6.35 mm in one case and 12.7 mm long for a repeat. Both were formed into 'horse-shoes' and fitted over grooves in Charpy Test specimens.

In the case of the PDI6 alloy experiment only 1 turn of 0.5 mm wire was applied to keep the amounts of brazing alloy comparable for all other heat treatments.

Normally it is considered that prime reasons for molten brazing alloy being retained in position result from inter-alloying of clean parent and filler alloys and capillary forces, arising through the close proximity of the parts of parent metal which are to be joined. It was thought that in the case of an open-vee, where such forces are virtually non-existent, brazing alloy could be expected to run out of the notches as a result of gravity. It was hoped that the position of the wire twists at the top of the jig might act to some degree in the same way as the header riser to a casting in attempting to counter the absence of capillary effects, in the cases of alloys AG7, PDI & PDI2 alloys.

The last stage before furnace treatment was to ultrasonically clean all specimens in distilled water for 3-5 minutes, followed by immersion in acetone immediately before loading onto the jigs and placing in the vacuum furnace. Pliers and tweezers used for handling specimens had been similarly cleaned before use.

6.2 Furnace Treatments

(1) Not loaded specimens:

All simulated brazed specimens were treated in an externally water cooled stainless steel (cold retort) Edwards vacuum furnace, approx. 38 cm o/d. x 90 cm tall work volume. Vertical resistance heating molybdenum electrodes, arranged circumferentially around the treatment area, were backed with a molybdenum heat-concentrating screen between the electrodes and the water-cooled furnace outside wall and also top and bottom of the furnace. Vacuum was achieved by means of roughing rotary and oil diffusion pumps. The treatment cycles required were pre-set and computer controlled. Unfortunately there was no provision to view the work during treatment, which was a disadvantage.

It was considered that the closeness of brazing temperatures recommended for AG7 (800°C.) and PDI (815°C.) would permit treatment of the Ni-Fe alloy with those 2 materials applied to it at the same time. The PDI2 alloy, recommended brazing temperature 860°C. (45°C. higher than the PDI alloy) and the PDI6 alloy, which with a recommended treatment temperature of 955°C., brazed some 140°C. higher than PDI were treated in separate furnace runs, all other preparations being as nearly as possible the same.
(a) AG7 / PDI Brazing Cycles:
While it was clearly economical of furnace time and effort to simultaneously treat specimens with the AG7 and PDI alloys, there was the reservation that there could be carry over of a constituent(s) from one set of specimens to the other as a consequence of possible volatilisation and redeposition; earlier experiences*135 having proved that cooler parts of vacuum furnaces, not capable of achieving such good orders of vacuum as now available could be coated with constituents arising from the metals being treated and calling for after-cleaning treatments before another run could take place.

It was decided to check this point by making 2 grooved alumina jigs, each accommodating 2 specimens. Jigs and specimens would be contained in 18/8 stainless steel lidded boxes, with a thermo-couple located between the boxes. The jigged AG7 wired specimens were placed in one box and identified as EP1 and EP2 respectively. A flat Ni-Fe disc was laid on top of this box with 2 crossed pieces of AG7 wire on top of the disc, which was marked EP6. The PDI wired specimens were placed in the second box, labeled EP3 and EP4. On top was placed another Ni-Fe disc with a 'U' of PDI wire, identified EP8. The logic was that if there was any volatilisation at the temperatures involved in these treatments this would be manifest after vacuum heat treatment as a deposit on the inside of the 18/8 boxes. If such volatilisation was observed the discs could be expected to provide clues as to amount of carry-over experienced as well as indicating the wetting and spreading performance experienced with the different alloys.

Before the jigged specimens were loaded into the furnace the latter was thoroughly purged to reduce dangers due to contaminants from earlier usage of the furnace. Purging took place with the boxed jigs in the brazing position (without the loaded specimens). The furnace was first evacuated at room temperature. It was then slowly raised to 1000°C, i.e. 185°C. above brazing temperature and held for 20 mins. before switching off, when recorded vacuum was \(8 \times 10^{-6}\) mbar. The furnace was left under vacuum to cool over-night, being opened when at room temperature the following morning. Examination of boxes and jigs confirmed that the stainless steel boxes had not resulted in the distortion which could have rendered removal of lids from boxes difficult; they were also clean and bright.

The specimens for treatment were immediately loaded into the purged furnace. After sealing the furnace, pumping out at room temperature took 1½ hours to achieve a vacuum of \(10^{-4}\) mbar. The power was then introduced and the temperature slowly raised to 750°C. for a 12 mins. soak, to ensure uniformity of temperature throughout specimens, jigs and boxes before proceeding to brazing temperature. The vacuum at this time was \(2 \times 10^{-4}\) mbar. The charge was then raised to 813°C brazing temperature for 12 mins, vacuum recorded \(9 \times 10^{-5}\) mbar. The furnace over ran to give a temperature peaking at 819°C before the power turned off at \(7 \times 10^{-5}\) mbar. Argon was introduced at 600°C to assist cooling and the unit was opened at 88°C.

Visual inspection of specimens removed from the furnace showed:-
(i) The alloys had spread and flowed satisfactorily and in the case of grooved specimens had concentrated where required at the root of the vee-notches. While confirmation by metallographic examination was needed this could contradict the long-held views*23-253 that capillary forces are essential...
if filler alloy is to be retained in brazed joints.

(ii) Stress cracks were not visible in any of the Ni-Fe specimens.

(iii) Probably due to the greater temperature gap between the liquidus of the AG7 alloy (780°C) and brazing temperature used, this alloy had flowed over the Ni-Fe to a greater extent than had been the case with the PDI alloy (liquidus 810°C.) The same observation applied equally to impact and disc specimens.

(iv) There was no witness of volatilisation on either of the stainless steel boxes nor obvious distortion of the boxes. However there was some discolouration of box exteriors indicating that the cooling argon was not as dry as desirable.

After the inspections the impact test specimens were immediately stored in an evacuated dessicator, care being taken to handle them only with clean tweezers.

(b) PD2 Brazing Cycle
Furnace purging before braze alloy treatment of the Ni-Fe specimens took place as previously, with the alumina jig in an enclosed stainless steel box. The evacuated furnace was taken up to 1045°C and held there for 18 mins. with vacuum at temperature of 8 x 10^{-6} mbar. After cooling the furnace was left evacuated for 3 days when a vacuum of 3 x 10^{-7} mbar. was noted before opening the furnace. Two grooved specimens were immediately loaded onto the jigs, EP11 with 6.35 mm and EP12 with 12.7 mm lengths of the same PD2 alloy wire. After closure of the furnace it took 1.5 hours to achieve a room temperature vacuum of 8 x 10^{-5} mbar. The computer-controlled furnace took 2.5 hours to reach 860°C, overrunning to 868°C during the 18 mins. dwell time at brazing temperature. The vacuum recorded was then 6 x 10^{-5} mbar. To accelerate cooling argon was introduced at 530°C the furnace being opened at room temperature.

Visual inspection of these specimens after treatment showed:

(i) The PD2 alloy had spread and flowed satisfactorily in each case.

(ii) The 6.35 mm of brazing alloy applied to EP11 had given slightly more braze alloy in the groove than experienced with the AG7, PDI and PD6 alloys but was still acceptable for comparison purposes.

(iii) Despite being "gettered" from argon contamination by containment in the stainless steel box, both specimens were discoloured.

(iv) Probably due to the larger cross sectional area of the wire used compared to the other brazements in the series, there were signs of shrinkage porosity in the braze alloy in both specimens; this was more severe in the case of EP12, made with the 12.7mm wire and it was therefore decided to defer further consideration of this specimen, (it was later used in static load tests)

(v) There was no evidence of stress cracking of the Ni-Fe parent metal.

Following visual examination it was decided not to subject these specimens to bend test and both were retained in a desicator with EP11 destined for later sectioning and metallographic examination.

(c) PD6 Brazing Cycle:
Pre-treatment purging of the same furnace took place as before with an alumina grooved jig retained in one of the stainless boxes. As a higher brazing temperature was involved, purging was at 1102°C for 30 mins. when the vacuum was 5 x 10^{-7} mbar; the furnace took 3.4 hrs. to reach this temperature. It was then switched off and left to cool over a week-end under vacuum.
When the lid of the retort was removed the PD6 wired specimen, identified as EP5, was placed on the jig inside the steel box. A straight piece of PD6 wire, resting on top of a disc identified as EP9, was put on the box lid (unfortunately movement in the furnace during treatment caused the wire to roll off the disc where it melted and spread over the lid of the box). After loading, the furnace was evacuated to 2 x 10^{-5} mbar, and slowly raised to 955-957°C, taking 2.5 hrs. The intention had been to hold for a 15 min. soak at 900°C to ensure temperature equalisation as in the case of the earlier treatment. However the computer did not bring about the anticipated arrest in power supplied to the furnace. After 18 mins. at brazing temperature, 955°C, the power switched off with vacuum at 6 x 10^{-5}mbar. The furnace was allowed to cool over night when the specimen was removed; argon was not introduced into this brazing cycle.

Visual inspection of the specimen showed:

(i) There was no discolouration of the stainless box confirming that in the earlier treatment this was caused by impure argon.
(ii) The molten brazing alloy had spread and flowed satisfactorily with again a concentration at the root of the vee-notch.
(iii) As with the other specimens no evidence of stress cracking at the time and temperature of brazing was noted.
(iv) For future reference it was evident that with the rate of heating used, associated with the relatively small charge mass there was no need to arrest the temperature 55°C. below brazing temperature as had been intended for a temperature equalisation purpose.

Following inspection the EP5 specimen was immersed in liquid nitrogen for 5 mins. It was then held in a vice and using a pair of pliers in a single one-way movement, breakage was arranged at the middle of the vee-notch in a bend test comparable to that used as will be given later, for EP1, EP2 and EP4 specimens, instead of the impact tests originally intended. Both halves of EP5 were stored in an evacuated dessicator prior to further investigation.

(ii) Static loaded beam test specimens at braze temperature:

To try and answer the question of how liquid metal penetration could occur at surfaces of Ni-Fe alloy leading to sub-cutaneous cracking was investigated, using loaded beams. This involved comparing metal as-received in the half hard machined condition with similar specimens brazed with the same furnace cycle but with different loads added. The intention was to apply varied rates of strain using identical Charpy specimens wound with brazing wires as before. The test rig developed for this work is illustrated by Fig.14 which shows specimens prewound with AG7 and PD1 wires, loaded with 454 g weights, heated as before in the vacuum furnace with both breaking at the time brazing temperature was reached, (during treatment an 18/8 stainless steel welding wire surrounded the assembly to protect the furnace elements from shorting when the specimens broke).

The method used was to take the two wired specimens. One was located in a hole drilled through a vertical stainless steel rod fixed to a base plate. The second specimen was similarly located but at a lower position in the same vertical rod and on the opposite side. Recessed sleeves having weights suspended 70 mm. from the vertical rod were fitted over the other end of each specimen. The test rig was then loaded into the furnace for treatment. Selecting loads of the desired magnitude called for care, the total furnace
Fig. 14. Static Beam Loading Fixture & Broken Specimens. Overall Dimensions 28cm Tall x 26cm Base
design charge weight being restricted to 4.54 kg. Taking Inco Data Sheets'935 and extrapolating for 0.2% offset proof stress at 800°C suggested 351.5 kg/cm² as a reasonable target figure. Substituting in the Beam Formula where \( \sigma = 34.47 \text{ MN/m}^2 \), load applied = 70 mm.(x = 0.07), diameter at root of notch = 3 mm.(d = 0.003 m.) and gravity, g at 9.81 ms⁻² resulted in force, F.

\[
F = \frac{a \pi d^2}{32g} \times \frac{3.142 \times 0.003^2 \times 100}{32 \times 9.81 \times 0.07} = 133 \text{ g}
\]

It will be noted that no account was taken of stresses due to notch effects in this calculation.

In a parallel practical workshop test using similar Charpy specimens made from 18/8 austenitic stainless steel it was found that using a hand-held flame torch (700-800°C), and weights applied by a spring balance, the specimens might withstand loads of 1.36 kg. In view of these determinations loads were varied in separate tests at 1.36 kg, 454 g, 115 g and 50 g applied to both AG7 and PDI brazing alloy treated Ni-Fe specimens. Similar tests were also carried out using the PD2 and PD5 alloys except that PD2 was a reheat having an excess of brazing alloy applied earlier (EP12) and PD5 was subject to a failure of the furnace controller (EP21) as a result of which the temperature rose such that the protective loose welding wire melted, although fortunately this did not affect results.

The following Table lists visual results obtained after all furnace treatments.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Braze alloy</th>
<th>Load applied</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP13</td>
<td>AG7</td>
<td>1.36 kg</td>
<td>Hot-short (brittle) fracture</td>
</tr>
<tr>
<td>EP14</td>
<td>PD1</td>
<td>1.36 kg</td>
<td>- - &quot; - -</td>
</tr>
<tr>
<td>EP15</td>
<td>AG7</td>
<td>454 g</td>
<td>- - &quot; - -</td>
</tr>
<tr>
<td>EP16</td>
<td>PD1</td>
<td>454 g</td>
<td>- - &quot; - -</td>
</tr>
<tr>
<td>EP17</td>
<td>AG7</td>
<td>115 g</td>
<td>- - &quot; - -</td>
</tr>
<tr>
<td>EP18</td>
<td>PD1</td>
<td>115 g</td>
<td>- - &quot; - -</td>
</tr>
<tr>
<td>EP19</td>
<td>AG7</td>
<td>50 g</td>
<td>(No break @ braze temp. Withstood ca.45° bend</td>
</tr>
<tr>
<td>EP20</td>
<td>PD1</td>
<td>50 g</td>
<td>( @ R.T. without fracture on removal from furnace.</td>
</tr>
<tr>
<td>EP1 &amp; 2</td>
<td>AG7</td>
<td>None</td>
<td>(Specimens were ductile after liquid N₂ and only</td>
</tr>
<tr>
<td>EP3 &amp; 4</td>
<td>PD1</td>
<td>None</td>
<td>(broke after + 100° bend. EP3 not bend-tested.</td>
</tr>
<tr>
<td>EP12</td>
<td>PD2</td>
<td>115 g</td>
<td>On opening furnace noted spec. had survived 45° bend and was ductile.</td>
</tr>
<tr>
<td>EP11</td>
<td>PD2</td>
<td>None</td>
<td>Not subjected to strain at braze temperature nor R.T. bend-tested.</td>
</tr>
<tr>
<td>EP21</td>
<td>PD6</td>
<td>115 g</td>
<td>On opening furnace found spec. had bent without rupture through 45°.</td>
</tr>
<tr>
<td>EP5</td>
<td>PD6</td>
<td>None</td>
<td>Not bend-tested.</td>
</tr>
</tbody>
</table>

It was noted that a "witness" of braze alloy was present on both sides of each notch. In the cases of the static loaded specimens some braze alloy concentrated on the downhill side indicating that the specimens started to bend before finally rupturing. These observations proved that failure did not occur below the braze alloy liquidus and also that the hot-shortness was not the result of excessive brazing temperature since the solidus of PD1 alloy at 810°C
coincided with the brazing temperature employed. From the downwards drift of brazing alloy it was deduced that final rupture was by a tearing motion after crack initiation, followed by molten alloy flowing into the forming cracks. This was later confirmed by microscope where a tensile crack was observed in the top surface groove of EP18, viz. a slowly strained specimen compared to the greater weighted EP13 through EP16 specimens where no such tensile cracks were noted.

6.4-Specimen Investigations

In addition to the static loaded beam tests, assessment of the various specimens involved investigation by four approaches, namely:

(i) Auger\textsuperscript{33,39,105} and x-ray spectroscopy of fractured surfaces.

(ii) Scanning electron microscopy of fracture surfaces.

(iii) Optical microscopical examinations of sections of the nickel-iron and the commercial brazing alloys 'as received' and after the Ni-Fe had been subjected to treatment with the brazing alloys.

(iv) Scanning electron microscopy\textsuperscript{90} of polished and etched surfaces through sections taken at approximately right angles to the fracture plane to analyse and map for penetration of brazing alloy constituents into the parent metal core.

The assessments to be carried out dictated the methods of treating the specimens.

6.4.1-Auger/XPS

(i) Not loaded specimens:

Specimens were arranged for evaluation with a Vacuum Generators-MA500 Scanning Auger Microscope with associated Link Systems AN10000 X-Ray Analyser.

It was the intention to load the impact specimens into the microscope preparation vacuum chamber as quickly as possible, to minimise their contamination by air. The next objective was to transport the Charpy-type specimens so that while one end was clamped the other formed a horizontal cantilevered beam within the evacuated chamber. Release of a drop hammer to strike the free end of the beam was intended to bring about rupture at the vee-notch in the preparation unit. The broken-off part of the specimen should then have passed via a tubular shute into a holder, which takes it by remote control to the microscope viewing stage, whence it is rotated to enable the electron beam to strike it at 45°. The image can be inspected on a visual display unit at various magnifications. The spectrum is then displayed by another computer-controlled V.D.U. having Auger and X-ray spectroscopic analytical capacity.

The Ni-Fe was supplied in the part-annealed condition, but there were reservations that specimens machined from it would be sufficiently brittle to rupture in the impact test. However it is well-established that the nickel-iron series, in common with most metals, become less ductile with decreasing temperature. It was therefore decided to impact test the first 2 specimens under vacuum at cryogenic temperatures; if successful attempts would then be made to break the remaining specimens at room temperature. With this in mind it was decided to load the 4 specimens into the microscope preparation unit in the ascending order, EP1 (AG7 alloy), EP3 (PDI alloy), EP2 (AG7) & EP4 (PDI). All 4 specimens were then to be subjected in an overnight treatment to liquid
nitrogen which would be applied to the outside of that part of the microscope assembly which contained their holder. At the end of this time it was anticipated that specimens EP1 and EP3 would be impact broken. Specimens EP2 and EP4 would remain unbroken in the microscope preparation chamber until this, without addition of further nitrogen, had regained and stabilized at room temperature. The 'atmosphere' within the chamber would be maintained at circa $10^{-6}$ mbar.

However when the time came to load the specimens it was found that they were over-length and 1 mm had to be machined from the ends of each before they could be processed. After machining the specimens were ultrasonically cleaned and rinsed in acetone before loading, when the procedure outlined in the last paragraph was initiated. In the event only EP1 could be broken in the unit; due to the non-brittle nature of the Ni-Fe alloy that took 5 repeated blows with the impact hammer and was accompanied by eventual failure of vacuum due to cracking of a viewing window. It was also found that the broken off half specimen would not slide down the shute, this was mainly due to a bend introduced into the specimen by the impact hammer, causing fouling and aggravated by the end not having been chamfered. As a result of the handling caused in retrieving EP1 from the system there was concern about results which might be gained from its Auger analysis and this potential problem was kept in mind, even although EP1 (AG7 alloy) was again ultrasonically cleaned and degreased before further work was carried out.

With regard to the remaining specimens it was decided to retain EP3 (PD1) unbroken, for metallographic examination and in the cases of EP2 (AG7) & EP4 (PD1) to switch from impact testing to bend testing using the approach already quoted for EP5. The latter two specimens were immersed in liquid nitrogen for 3 mins. and broken by pliers and vice, a single one-way movement being sufficient to cause rupture. The broken parts were ultrasonically cleaned, immersed in acetone and together with EP1, half of each was placed in the microscope holding buckets, it being noted that the part which had been retained in the vice was straighter and therefore easier to load; the slight bend induced in the other halves mitigated against location in the buckets. The buckets containing the already broken specimens EP1, EP2, & EP4 after a final degrease were loaded into the microscope.

(ii) Stressed specimens after furnace treatments:

Half of each hot-short specimen EP15 (AG7) and EP16 (PD1) were Auger and XPS analysed after breaking at 810°C with a 454 g applied weight. It was hoped to trace crack formation from the top of the beam downwards as propagation continued and to compare results with similar examinations of the unloaded specimens of the last section.

6.4.2 S.E.M: Fracture Surfaces

(i) Unloaded specimens:

The remaining halves of EP1 and EP4 were assessed and photographed using a Cambridge Stereoscan 250 Scanning Electron Microscope. Particular attention was paid to the cleavage mechanism as evidenced from a study of the fractures.

(ii) Stressed specimens:
EP15 (AG7-454 g loaded at 810°C), EP16 (PD1-454 g loaded), EP17 (AG7-115 g loaded) and EP18 (PD1 loaded-115 g): Half of each broken specimen was submitted for examination by Cambridge Stereoscan 100 Scanning Electron Microscope.

6.4.3-Optical Microscopy

Examinations were concentrated on the specimens which had not been subjected to extra load.

13 specimens were mounted in conducting Bakelite and using the Struers Pendamax 2 Grinding and Polishing Machine were given the following sequence, with the appropriate Struers lubricants as follows:

<table>
<thead>
<tr>
<th>Base</th>
<th>SiC</th>
<th>SiC</th>
<th>SiC</th>
<th>DP Durcloth</th>
<th>DP Durcloth</th>
<th>OPS (KOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain</td>
<td>320</td>
<td>500</td>
<td>1000</td>
<td>6μ</td>
<td>1μ</td>
<td>1:1:OPS:H₂O</td>
</tr>
<tr>
<td>Lubricant</td>
<td>H₂O</td>
<td>H₂O</td>
<td>H₂O</td>
<td>Blue</td>
<td>Red</td>
<td>--&quot;--</td>
</tr>
<tr>
<td>Speed (RPM)</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Pressure</td>
<td>3 (90N)</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Time</td>
<td>1 min.</td>
<td>1 min.</td>
<td>1 min.</td>
<td>1 min.</td>
<td>1 min.</td>
<td>2 min.</td>
</tr>
</tbody>
</table>

All were rinsed with 'Inhibisol' then acetone and hot air dried after each operation.

In the light of experience the 1 micron DUR silk cloth was occasionally replaced with 1 micron MOL cloth for 1 min. followed by finishing with a 50/50 OPS (KOH in water)-distilled water polish for 2 mins. at 150 r.p.m., pressure 2.

It was expected that due to the different metals involved, a two-part etching technique might be necessary, initially testing etchant effects on the alloys as supplied.

Effects of subjecting the materials to different temperatures ranging from cryogenic to 955°C. could result in varied structures and implications should be considered.

Phases resulting from inter-alloying and diffusion at brazing temperatures would be explored both in the 'as polished' states and after etching.

The mounted specimens have been retained and identified as:

- EP-AG7: Ag-Cu eutectic as supplied brazing alloy
- EP3: Longitudinally sectioned through unbroken PD1-treated impact specimen. Also had prolonged exposure to liquid nitrogen.
- EP6: Section through disc having AG7 applied. No Liquid N₂.
- EP7: Ni-Fe disc cut from as supplied rod.
- EP8: Section through disc having PD1 applied. No N₂.
EP9: Section through disc heated to 955°C. No N2 or braze.
EP10: Other half-sections of EP2, EP3 & EP5 in one conducting Bakelite mount, as sent to Link Analytical Ltd.
EP11B: Other half section of PD2 braze, as for EP11A-Surrey examined.

6.4.4-S.E.M: Polished Surfaces

With the exception of work at Link discussed later, a Jeol 35M 35CF scanning electron microscope with x-ray energy dispersive system was used for this section of the investigation which was devoted to specimens which had not been loaded during furnacing. It was intended to use x-rays to:

(i) ascertain compositional variations due to colour changes noted in the microstructures of specimens EP2, EP3, EP11B and EP5
(ii) note whether flow of brazing alloy into the parent metal was inter- or transcrystalline, using the spot analytical technique of (iii) below
(iii) by using a spot analytical technique, noting distances from the interface of braze and parent metal, to determine the amount of penetration of the different brazing alloy constituents into the core.
(iv) obtain an indication of intensity of Cu and Ag + Pd in relation to the ratio of Fe to Ni from the spectra and hence double check the depth of penetration of the main alloying constituents into the parent alloy
(v) compare back-scattered photographs of EP2 and EP3 for cracking
(vii) dot (spot or x-ray) map the 4 specimens for Cu, Ag, Pd, Fe & Ni.

Link Analytical Ltd. (High Wycombe) learned of this investigation at this time. They had developed a modified AN10000 computer which was claimed to separate Ag from Pd spectra and they requested Surrey's collaboration. Consequently they were provided with the other halves of the specimens with which we were working (EP10 & EP11A) for mapping and quantitative analysis of the different phases.

6.5-Results & Observations

6.5.1-Auger/XPS

(i) Non-loaded specimens:

EP1 (AG7-Ag/Cu Eutectic Alloy)

The EP1 specimen was spot analysed by Auger and x-ray, with the electron beam traversing outwards from the core of the Ni-Fe towards the shoulder of the groove where rupture was initiated. Brazing alloy could be identified as a 'sea' at the shoulder, with 'rivers' and 'tributaries' flowing inwards. It was originally thought from the topography of these rivers that the brazing alloy was following grain boundaries, but this could not be confirmed in Auger/XPS work with this specimen.
Throughout all Auger examinations, not only EP1, the microscope tilt was maintained at 45° (equivalent vernier setting 280°)

A/X.EP1.SP1—Analysis of core. Both methods confirmed main constituents as Ni & Fe. (25nA. x100 magn.)

A/X.EP1.SP2—This analysis was at the meeting of core and brazing materials. Auger and x-ray proved that Ag and Cu were present, together with Ni and Fe.

A/X.EP1.SP3—Auger gave well defined Ag and Cu returns with small amounts of Mn and oxygen; no Ni or Fe. X-ray confirmed that Ag and Cu were the principal constituents at this spot.

An area in the vicinity of SP2 (spot 2) was then explored by means of other spot checks in endeavours to find a suitable place for a mapping base. After etching with argon a suitable position was located where the elements of prime interest Ag, Cu, Ni, Fe were all present in significant amounts. Regrettably, in adjusting the angle of beam to specimen, the latter fell out of its bucket and became lodged in the base of the microscope from which it could not be conveniently recovered, leaving EP2 and EP4 as representatives of the AG7 and PD1 treatments.

In view of the fact that the original analysis of 'as supplied' AG7 alloy returned a trace of Pd, this element was particularly considered. However neither Auger nor x-ray detected its presence.

EP2 (AG7—Ag/Cu Eutectic Alloy)

It was thought most likely at this time that the mechanism of past failures reported when nickel-iron alloys were brazed with the silver-copper eutectic, could be related to the dissociation of Ag or Cu from the eutectic, with one of these metals then preferentially penetrating the parent Ni-Fe grains to result in planes of weakness.

This ruptured specimen was probed as before in searching for a zone showing all primary constituents. Due to a computer fault, when additional spot analyses became added to previous spectra, the first three results (A/X.EP2, spots 1, 2 & 3.) were disregarded as all metals of interest were reported at the exact centre of the Ni-Fe specimen core — clearly unrealistic based on the results obtained from A/X.EP1. Other spot checks returned the following qualitative analyses (50 nA. x100 magn.):

A/X.EP2.SP4—Core returns gave only Ni and Fe as primary elements.

A/X.EP2.SP5—Ni and Fe mainly. The spot chosen was on the side of the notch of the specimen and outside the spread of the braze metal. Neither Ag nor Cu were detected.

A/X.EP2.SP6—Analysis occurred at the outer rim of brazing alloy where this met the notch of the specimen. Cu and Ag were the only Auger peaks noted.

A/X.EP2.SP7—The spot selected (x200 magn.) was slightly towards the core from SP6. Cu and Ag alone found. Fig.15 records the Auger spectrum.

A/X.EP2.SP8—Spot analysis took place just into the core at frontier
where braze metal joined core alloy. Auger revealed Ni, Fe and Ag as main constituents.

A/X.EP2.SP9-This check was on a 'river' where brazing alloy was thought to have flowed through a grain boundary from the frontier 'sea'. However absence of Ag and Cu disproved the presence of braze metal, with Fe and Ni alone detected.

A/X.EP2.SP10-Spot analysis was on a similar 'river' to SP9 with the same outcome. Ni and Fe were principal elements with C and oxygen also noted—Fig. 15. Results were concluded to parallel those gained with specimen EP1 and it was therefore now decided to map for Ag, Fe, Ni and Cu at a position where all four elements could be detected, that chosen being between spots 7 & 8. (During the Auger/XPS mapping exercises the number EP2 was transposed to EP1. This was not regarded as significant as with the exception that EP1 was broken by a part-impact mechanism compared to the straight-forward bend test of EP2, both had identical treatments.)

Mapping conditions:

<table>
<thead>
<tr>
<th>Window for x-ray maps</th>
<th>XR AFNCI. WI Ag, Fe, Ni, Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Window for Auger maps</td>
<td>AE EPI A. WI Ag, Fe, Ni, Cu</td>
</tr>
<tr>
<td>Study</td>
<td>EPI 500 R SY</td>
</tr>
<tr>
<td>Set-up parameters</td>
<td>15KV 40nA x500 magn.</td>
</tr>
<tr>
<td>Dwell</td>
<td>Auger 50ms (N.B. P50 B50)</td>
</tr>
<tr>
<td></td>
<td>X Ray 100ms</td>
</tr>
<tr>
<td>SEM image of above</td>
<td>EPI 500 SY</td>
</tr>
<tr>
<td></td>
<td>EPI 500 SEI SY</td>
</tr>
<tr>
<td></td>
<td>EPI IM 128 x128 x16.</td>
</tr>
<tr>
<td>Resolution</td>
<td>This was incorrect and on repeating it was recorded as EPI 500R SY, later being relabelled as EPIR.IM</td>
</tr>
</tbody>
</table>

Mapping resulted in 4 Auger maps based on peaks minus background for the 4 elements, 4 normalised Auger maps (peaks minus backgrounds divided by backgrounds) and 4 x-ray maps. A photograph of the V.D.U. screen, identified as EPIR.IM provided a colour record of these maps. In addition there are records of all results, retained on 12 floppy discs. Since the photograph was taken a development has allowed colour print-outs to be taken directly from the V.D.U. and the 4 elements are included as Fig.16(a) for smoothed Auger and x-ray maps.

Assessments of the maps showed:—

(i) Ag penetration beyond the frontier of brazing alloy into the core of parent metal was minimal. The change from brazing alloy to Ni-Fe was reasonably clear cut.
(ii) Fe similarly presented a well defined frontier with the Ni-Fe core material.
(iii) Ni: the frontier was well defined in the x-ray photograph but Auger pictures showed Ni on both sides of the frontier, raising the question as to whether there had been preferential alloying with Cu, resulting for example in different density phases of varied intensities.
(iv) Cu resulted in interesting Auger and x-ray pictures where it was found to have penetrated well beyond the frontier set by the brazing alloy and in
Fig. 15
Representative Auger Spectra Specimens EP2 and EP4
Fig. 16(a).
AG7: Ag-Cu Eutectic Braze

Fig. 16(b).
PD1: Ag-Cu + 4.53% Pd Braze
advance of the Ag with which it was alloyed. There was an appearance of plate-like phases penetrating into the Ni-Fe core, reminiscent of results found earlier by Castle and Cohen but as yet unpublished, where similar phases of Cu rich material had been found to extend into 'Jethete' stainless steel from the Ag-Cu brazing alloy used in their work.

EP4 (PD1-4.53% Pd-Ag-Cu Alloy)

The prime point of interest was to find whether mapping showed the Cu phases persisting into the Ni-Fe alloy as in the last paragraph, or whether the addition of Pd had brought about a modified structure. It was also of interest to note whether the Ni intensity had altered in mapping when compared to EP1.

A/X.EP4.SP1-The appearance of the fractured surface was similar to the earlier specimens and the first spot analysis was on the frontier of braze to parent metals. While Auger identified Ag and a trace of Cu, x-ray showed only Ag (10kV. x2000 magn.)

A/X.EP4.SP2-With beam intensity raised (15kV. 15nA.) and the core probed, both Auger and x-ray showed only Ni and Fe.

A/X.EP4.SP3-Ni and Fe were only observed by x-ray on a frontier probe.

A/X.EP4.SP4-This again was to the core side of the frontier. Auger and x-ray confirmed the presence of Ni, Fe and O.

A/X.EP4.SP5-Again this was on the core side of the frontier. Auger (Fig.15) and x-ray showed Ni, Fe, O to be present.

A/X.EP4.SP6-Both Auger (Fig.15) and x-ray reported Cu, Ni, Fe, Ag, O, C where the brazing alloy frontier coincided with the Ni-Fe core. A Polaroid Instamatic photograph was taken at x2000 magn. showing relative positions of SPs 3, 4 and 5 to this spot. To try and get an idea of the distance between white 'sea' of brazing alloy and black Ni-Fe 'core' the distance was measured between SP5 and SP6 at 36 mm. The latter figure divided by 2000 and multiplied by the sine of the probe angle of 45° (0.70711) equalled 12.7 μm. This indicated the maximum distance straddled from braze metal to Ni-Fe core in a first attempt to assess thickness of alloy interaction.

A/X.EP4.SP7-Probed on a apparent grain boundary where alloy appeared to have flowed into the core. However only Ni and Fe were found at this position.

A/X.EP4.SP8-This was another examination of an apparent grain boundary on the brazing alloy frontier. Again Ni and Fe predominated and the probe was evidently on the core side of the frontier.

A/X.EP4.SP9-The spot probed was on the brazing side of the frontier and showed the presence of Cu, Ag, Si, some Mn and a little Fe in XPS studies; Auger returned Cu, Ag, Mn and some Fe.

A/X.EP4.SP10-Auger revealed the presence of Ag and Cu and absence of Ni and Fe. XPS found Ag, a faint trace of Pd, Cu and Mn. An attempt was made to highlight the Pd, using integrated and non-integrated Auger peaks, however...
significant Auger peaks were not forthcoming. The conclusion was reached that Pd was being swamped by the Ag (atomic number Ag-47; atomic number Pd-46: Ag Auger peaks form at 304, 351 and 356 counts whereas the Pd peak is at 330). The spot analysed was on the brazing alloy side of the frontier.

A/X.EP4.SP11- The area probed was away from the core of the Ni-Fe but close to the frontier. While Ni, Fe, Mn, Cu, Ag, Si, Mo and S were found by x-ray, Auger failed to find Ag and Cu but reported Fe, Ni plus Co and Mn.

A/X.EP4.SP12- Fe, Ni and a little Mn were found by x-ray on the shoulder of the specimen where brazing alloy appeared not to have flowed to any extent. Auger noted Ni, Fe, Mn, Na, Cl and a little Cu but no Ag.

A/X.EP4.SP13- The probe was concentrated on an apparently brazed area close to the frontier. Mn, Fe and Ni were present by XPS, with Ag and Cu both absent. Auger confirmed Fe, Ni plus Co, Mn and O.

The spots taken on 'rivulets' and 'tributaries', earlier thought to be a manifestation of flow through grain boundaries, were not conclusive in supporting the view that brazing alloy was running into the metal core by an intergranular mechanism. It could not therefore be concluded from this analysis that the mode of attack of parent metal by brazing alloy was intergranular. (An early question raised by U.K.A.E.A. was whether the attack of Ni-Fe parent by Ag-Cu eutectic was intercrystalline or transcrysalline.)

It was now decided that as Pd was not apparently present to a significant degree in the spot tests carried out by Auger or XPS, although known to exist in the brazing alloy, the next stage would be to map for elements Ag, Fe, Ni and Cu and compare with the maps for the same elements and recorded as EP1R.IM. A number of spot analyses were therefore carried out on a frontier position until both Auger and XPS gave returns on one spot for all 4 elements. Mapping was then accomplished and the VDU photographed as EP4 500.SY, which is retained in a laboratory portfolio. The maps were later obtained direct as a computer print-out and are included as Fig.16(b). The conditions were the same as for EP1R.IM except that peak minus background pictures were not recorded and this resulted in 4 peaks minus background divided by background, smoothed Auger photographs and 4 x-ray photographs of Ag, Fe, Ni and Cu. (In view of the experience with A/X.EP4.SP10 no attempt was made to map for Pd.)

Assessments of the maps showed:
(a) The EP4 500.SY series displayed frontiers for Ag and Fe similarly to those noted with EP1R.IM
(b) The amount of Cu interaction, compared to EP1R.IM, appeared to be curtailed, with the frontier of Cu to Ni-Fe core giving a not dissimilar demarcation to frontiers experienced with the Ag, Fe and Ni maps.
(c) Again Ni was noted on both sides of the brazing alloy shadow but apparently to a lower extent indicating that there had been less alloying with Cu. This suggested that Pd may have preferentially alloyed with either the Ni or Cu consequently slowing the rate and magnitude of Cu diffusion into the parent metal.
(d) The inference was that Pd had inhibited the diffusion of Cu into the core material, but the mechanism required consideration of various factors, to be discussed later as these became clearer.
Again the approach was to initially straddle from the edge of the braze alloy into the Ni-Fe core.

A/X.EP5.SP1—This was analysed at the outer periphery of the specimen. Elements noted were S, Si, Pd, Co, Ni, Cu and Ru. There was also Cr but this was thought to be due to some electron scatter and arose from the specimen holder.

A/X.EP5.SP2—Cu, Ag, Ni and Fe were all present at the frontier where braze alloy met Ni-Fe core.

A/X.EP5.SP3—The position analysed was at the frontier on a 'rivulet' running into the core. Auger spectroscopy reported Ni and Fe whereas the deeper x-ray showed the presence of Ni, Fe, Cu and Ag.

A/X.EP5.SP4—The change from braze alloy frontier into Ni-Fe appeared to be more abrupt than with the EP1/2 or EP4 specimens. This impression would be checked in later phases of the investigation. The spectrum obtained from this spot is illustrated as Fig.17(a) for AEP5.SP4, where the Auger returned Ag as a small peak with Pd at 329 counts. X-rays also confirmed the Pd presence where XEP5.SP4 is shown, Fig.17(b). NB: Pd had not been isolated from or with Ag in A/X.EP5.SP2 or SP3 or in any other Auger analyses in this series.

The conclusion reached on comparing EP1 & EP4 maps and the EP5 spot analyses was that further work on mapping the latter specimen would be unproductive. However confirmatory experiments were needed, using optical and electron microscopical techniques, with respect to specimens which had not been subjected to extraneous stress during furnace treatment.

(ii) Loaded specimens:

Auger and x-ray spectroscopic analyses in traverses across the ruptured EP15 and EP16 specimens confirmed that both Cu and Ag completely covered the fractures. Sulphur was also found in the EP16 spectrum to a greater extent than with any other Auger analysis in this series. As the Pd probably originated as a by-product of Ni from the Canadian sulphide-bearing ores this could account for presence of S. Apart from this one instance no significant traces of S were noted either in the 'as supplied' materials or in other Fe-Ni specimens treated with the various brazing alloys; it was therefore discounted as contributing to the failure mechanism.

Results obtained from specimens which exhibited hot-shortness after treatment at 810°C under a 454 g load are listed as follows:

EP15 (Ag7: Ag-Cu eutectic alloy)

A/X.EP15.SP1—(Beam intensity 10 kV. 12 na.) Found C, Cu, Ag with traces of O and S only observed in the specimen between core and periphery on 1 side of a grain boundary.

A/X.EP15.SP2—The probe was moved to the other side of the previous grain boundary but a similar result was found as in SP1 at the core of the specimen.

A/X.EP15.SP3—Results were as before with SP1 & 2.
Fig. 17(a). Auger Spectrum Specimen EP5 - Beam Set as Fig. 17(b)
Fig. 17(b).
X-Ray Spectrum: Specimen EP5 -
Beam Set as Fig. 17(a)
A/X.EP15.SP4—Similar results were obtained on moving to a new area and it was now evident that Cu and Ag were uniformly spread across the fracture, irrespective of whether Auger or XPS determinations were involved.

EP16 (PD1: 4.53% Pd–Ag–Cu alloy)

A/X.EP16.SP1—Noted C, Ag, Cu and Mn at centre of grain as with EP15; while Auger and XPS gave similar returns, only Auger spectrum was collected.

A/X.EP16.SP2—Grain boundary returned C, Cu, Ag, and S.

A/X.EP16.SP3—Analysed a valley centre spot. Current adjusted (5 na.) Found C, Cu, Ag and S.

A/X.EP16.SP4—Auger and X-Rays gave a similar return, showing presence of O, Ag, Cu and S at grain centre. The sulphur presence is illustrated by the Auger map of Fig.18.

A/X.EP16.SP5—Concentrated on a 'valley', using the same beam strength as SP3 & 4. While a lot of Ag was noted Cu was not determined.

A/X.EP16.SP6—Another valley in the eutectic alloy returned Ag without Cu.

A/X.EP16.SP7—A 'hill' in the eutectic was analysed as it was thought that if Ag could exist in valleys without Cu, it was not unreasonable to anticipate that hills would be Cu-rich, with Ag absent. However the hills did not lead to the conclusion that more Cu was present. In a final check, spectra from hills and valleys were superimposed. While a computer print-out is available it was considered that this aspect of the examinations was indeterminate and of less importance than the complete absence of Ni or Fe proving that the brazing alloy had swept through the fractures to completely cover the parent metal as failures developed in the case of both specimens EP15 and EP16.

6.5.2-General Comments On Auger/XPS Examinations

(i) Not loaded specimens:

(a) Comparing the EP1 and EP4 map photographs show similar and pronounced frontiers where Ag from the brazing alloy penetrates the Ni–Fe parent metal. Ag is virtually immiscible with Fe and if the two metals are to be mixed powder metallurgy techniques are required. Because alloying does not readily occur with these two elements it was thought possible that other constituents in the brazing alloy might preferentially alloy with the parent metal leaving elemental Ag to advance via grain boundaries to weaken the iron alloy. However nickel and silver are also reluctant to alloy as proved on reference to the Ni–Ag equilibrium diagram. It will be recalled that AEP2.SP8 analysis revealed Ni, Fe and Ag present but not Cu; similarly XEP4.SP1 found Ag without Cu but conversely XEP4.SP12 showed a little Cu and no Ag which brought forward the conclusion that Ag penetration alone was unlikely to be the cause of the change bearing in mind that the Ag maps were virtually the same for both specimens.

(b) The Fe photographs in the case of EP1 (Ag–Cu eutectic) and EP4 (4.53% Pd–Ag–Cu) were equally distinct when considering the frontier of
Fig. 18. EP16 Auger Maps Show Sulphur Found With Silver & Copper On PD1 Alloy (Ag-Cu + 4.53% Pd). Brazed Fe-Ni, Following 45kg Load-To-Rupture At High Temperature.
braze alloy to core material: in neither case did there seem to be unusual alloying between Fe and other metals in the area shadowed by braze alloy.

(c) Comparisons of the Ni maps revealed Ni in both shadowed zones and in the Ni-Fe core, with the frontiers less distinct than in the case of the Ag and Fe photographs. At this time it was thought that the lighter spots in the shadowed areas could be islands of Ni-Cu alloy, remembering that this binary series gives a range of readily formed solid solutions.

(d) Another interesting study resulted from the comparisons of the Cu maps for the different brazing alloys, AG7 and PD1. The Ni-Fe treated with the Ag-Cu eutectic, AG7 alloy, revealed a far less well defined frontier between brazing alloy and parent metal, with striations or phases of Cu penetrating beyond the frontier into the parent metal core (with some evidence of counter diffusion or alloying of Ni in the Cu containing brazing alloy). The addition of 4.53% Pd in PD1 alloy showed that this striation effect had virtually disappeared. Further the Ni intensity was less pronounced in the case of the PD1-treated alloy's Ni map than noted in the case of the AG7 mapped specimen.

(e) Further consideration of the mechanisms by which this variation between the 2 brazing alloys used might arise included the following:

(i) Cu may have diffused from the Ag-Cu brazing alloy into the Ni-Fe alloy. It is known that copper-brazing of the Nimonic super alloys is inappropriate especially for aero engines, as copper can result in inter-crystalline attack and cracking of Nimonic at brazing temperature. However in that case the brazing temperature at 1100°C, is far in excess of temperatures used with AG7 and PD1 (810°C.)

(ii) Next considered was the impact of adding Pd to the alloy and the effect of this on the Ni-Fe core. Vines and Wise stress that Pd is a noble metal with excellent corrosion resistance. Thought was given to the possibility that the addition of Pd was imparting enhanced corrosion resistance to a brazing alloy which included this noble metal but it did not immediately seem likely that the differences noted between the Cu maps of EP1 and EP4 would have been influenced alone by the improved corrosion resistance of the brazing alloy. However the effect of the high position of Pd in the electrochemical and electromotive series compared to the other major elements present in the joint areas could not be rejected, (even though the electrochemical series were determined under conditions approximating to normal temperatures and pressures). One analogy which was considered in this context was the protection of bronze propellers and sea cocks on marine craft with Mg anodes, which quickly erode in sea water where the sea water becomes an electrolyte. This raised the question of whether the molten brazing alloy was behaving as an electrolyte whereby iron and/or nickel in the parent metal become anodic to copper from the braze alloy, to assist its penetration into the grain boundaries. Adding Pd could be expected to worsen the situation but equally by intensifying the attack could confine it to crystal boundaries at the parent metal surface. The Auger photographs lent credence to the thought that Fe in contact with the braze alloy had been replaced by Cu which then alloyed with Ni in the stressed surface crystals in the case of AG7 alloy. The impact of Pd in PD1 alloy was noted to have reduced penetration.

(iii) Vines and Wise also discussed the Fe-Pd binary diagram. They commented that there is a continuous series of solid solutions between the metals but noted that PdFe transforms at 34% Fe from a γ-solid solution to γ' at around 750°C. Another compound Pd₃Fe transforms at about the same temperature to γ" at 14% Fe. Consideration was given to the possibility that above brazing temperature these compounds could be forming
ionic bonds at the interface of brazing alloy and parent metal and that the amount of free copper available to penetrate into the metal would consequently be restricted. Alternatively such compounds might be forming a sub-surface barrier to inhibit penetration by elemental Cu.

(iv) Another possible reason for Pd inhibiting diffusion of Cu from the Ag–Cu alloy came from a study of the Pd–Cu binary diagram. PdCu is formed at ca. 550°C at 64% Cu to give an α" phase structure. Another intermetallic compound PdCu₃ resulting in α + β phases, forms at circa 650°C and 37.4% Cu. While the brazing temperatures used are well in excess of these temperatures, Vines and Wise cautioned that formation of these phases is accompanied by age-hardening tendencies which are enhanced by the addition of Ag to the Pd–Cu series. This raised the question of the possibility that strong bonding forces accompanying the formation of these compounds in the liquid state could act as a deterrent to Cu segregating from the alloy to preferentially diffuse through the Ni–Fe lattice to form weak planes which could result in stress failures.

(ii) Loaded specimens:

(a) Once tensile cracks had formed under stress conditions, as reported in sect.6.3(ii) the addition of the extra loads assisted flow of molten brazing alloy through them, as noted from Auger/XPS results with EP15 and EP16 where complete coverage of fractures by brazing alloy constituents was confirmed. Comparison of this effect with results from the unloaded specimens proved that in the latter cases penetration was restricted to the narrow zone where parent metal and braze alloy were in contact, no element from the braze alloy being found at cores of specimens. In each instance residual stress was expected from using half hard machined metal but stresses were insufficient with EP1 or EP4 to bring about the failures noted in the case of the specimens loaded at high temperature namely, EP13 to EP18.

(b) Having reviewed a number of variables which could lead to the attack of the Ni–Fe by constituents of the brazing alloy it was evident that further work was needed if a firm conclusion was to be reached on why the EP1 and EP4 specimens were ductile when bend-tested at R.T. but hot-short when tested under loads of 115 g or more, at brazing temperature. Also unanswered was why specimens containing 4.53% Pd were subject to stress corrosion attack but ductile at all temperatures if this element was 9.92% in the braze metal composition. It would have been helpful to carry out a bracketing exercise but no intermediate commercial alloy is available in the U.K. to allow the opportunity of establishing the percentage Pd below which the Ag-Cu-Pd series results in stress corrosion.

6.6-Scanning Electron Microscopy Examinations

(i) Un-loaded specimens:

While half of the broken specimens had been subjected to Auger/XPS investigation the other halves of specimens EP1 (Ag–Cu eutectic treated Ni–Fe) and EP4 (4.53% Pd–Ag–Cu) were examined by this technique. While 3 photographs were taken of EP1 (01/000: 01/004: 03/009) and 5 were taken from the microscope of EP4 (02/002: 02/003: 02/004: 02/005 and 02/006) only 2 are included as representative of the two specimens:-
(a) Ag–Cu Eutectic (AG7) Treated Ni–Fe
002- View of fracture-see Fig.19(a)
003- View of fracture showing braze alloy flowing over edge towards root of vee-notch
004- Striations or stress markings between brazed edge and core of specimen
005- Disturbed layer between vee-notch and core: 2 core zones were noted, separated by fine flowing grains probably due to the bending-to-rupture test mechanism
006- Disturbed layer at the core after increasing the magnification to four times that used for 005

The structure of the break was very fine grained, possibly influenced by sub-zero treatment in the Auger microscope preparation chamber before breaking the specimen.

(b) Ni–Fe Treated With 4.53% Pd–Ag–Cu (PD1)
000- Core of Ni–Fe.
001- Stress markings were far less pronounced than in case of Ag–Cu eutectic treated alloy.
009- Stress markings can be seen, where the specimen as held in the vice broke up at the rim. This suggests that this was the position where the skin was put into tension before rupture took place. Few marks were noted from the edge of the brazing alloy towards the core of specimens and were slight compared to the cleavage stress markings observed in the Ni–Fe specimens treated with Ag–Cu eutectic-see Fig.19(b)

6.6.1 Comments On Unloaded Ruptured Specimens

Cleavage planes were pronounced in the case of the AG7 alloy commencing at the rim of 'brazed' alloy towards the core of the Ni–Fe.

In the case of the PD1 alloy, cleavage planes were far fewer and the rupture had more of the appearance of a straight-forward tensile test break. These observations are in line with the earlier findings where Auger/XPS analyses suggested that the inclusion of Pd inhibits the tendency of Cu to penetrate the Ni–Fe. The striations started from zones or edges which had been subject to the Ag–Cu eutectic, and were negligible when Pd was present at 4.53%. (The original Brit. Patent quoted 1% Pd as sufficient to beneficially modify the Ag–Cu eutectic)

6.6.2 Loaded Specimens; Comments

Fractures of the 4 specimens, EP15 (AG7- 454 g load) EP16 (PD1- 454 g load) EP17 (AG7- 115 g load) & EP18 (PD1- 115 g load) were all traversed by the scanning electron microscope. Observations resulting from these examinations were:

(i) AG7-treated fractures were not substantially different irrespective of whether the load was 454 g or 115 g.
(ii) PD1-treated fractures again were similar to each other although both exhibited a white rim at peripheries; as such rims were not seen in AG7 specimens these were thought to be residues of braze alloy and could be accounted for by the S found in Auger analysis.
Fig. 19(a). SEM, EP1 Fracture - AG7, Ag-Cu Eutectic Braze

x 25 Print Magn.

Fig. 19(b). SEM, EP4 Fracture - PD1, Ag-Cu + 4.53% Pd Braze

x 36 Print Magn.
(iii) Intercrystalline cracks were noted with associated slip lines and dislocations-Fig.20 (a & b) [AG7] and Fig.21 [PD1]. A number of the holes noted in the case of the AG7-treated samples were not dissimilar to etch pits and were localised in grain boundaries. A search of the PD1 specimen failed to locate a similar severity of attack.

(iv) Tensile cracks noted at the top of the beam in the grooved specimen are illustrated in Fig.22. (PD1-115 g loaded) [ Due to inversion in the microscope these cracks are shown at the bottom of the photomicrograph].

(v) All 4 specimens confirmed that brazing alloy had flowed right across the fractures indicating that breakage was very fast.

(vi) As the Ni-Fe specimens had been taken from the same rod of metal and turned by the same machinist it was deduced that surface crystals and boundaries would effectively all be in the same state. However while the effect of loading was to cause virtually spontaneous fractures at or above 115 g applied load, there was insufficient strain to bring about non-ductility below 50 g, indicating that the core of specimens remained ductile until there was sufficient combination of strain and brazing alloy available to give failure. It was evident that the magnitude of stress played a prime role in the failure.

6.7—Optical Microscopy

6.7.1—Examinations "As Polished"

Initial examinations were conducted on the as polished specimens of metals as received.

Hardness tests on the as received Ni-Fe (EP7) were recorded at DPN [HV] 194/30Kg. Micro-hardness determinations on the same specimens recorded 160 HV (100g.load), 135 (200g.load) and 167 (500g.load). The micro-hardness differences were probably due to local variations. The hardness determinations confirmed that the metal had been supplied in the partly annealed condition as fully annealed stock is specified at HV 140 with fully hard at HV240.

Comparing specimens EP2 and EP6; EP3 and EP8; EP11 and EPS; EP11 and EP5 revealed pronounced fine pink dendrites in a floral pattern where the brazing alloy had flowed in the case of the first two specimens. The addition of Pd in the cases of EP3 and EP8 made no detectable change to the colour of the as polished specimens examined by a Zeiss metallurgical microscope, but the dendritic structure appeared coarser than EP2—perhaps influenced by the gap between liquidus and solidus temperatures:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Liquidus-°C</th>
<th>Solidus-°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG7</td>
<td>780</td>
<td>780</td>
</tr>
<tr>
<td>PD1</td>
<td>810</td>
<td>805</td>
</tr>
<tr>
<td>PD2</td>
<td>852</td>
<td>824</td>
</tr>
<tr>
<td>PD5</td>
<td>950</td>
<td>900</td>
</tr>
</tbody>
</table>

It is noteworthy that the basic Ag-28% Cu (AG7) was modified when the series was devised, primarily by replacing the Ag with Pd. Hence Cu varied from 28.08% in the Ag-Cu eutectic to 26.6% in the case of PD1 and from 31.32% in PD2 to 21.75% in PD6 alloy.

The dendritic floral pattern was much less pronounced in EP11B (PD2 alloy) and EP5 (PD6 alloy) where cooling from liquidus to solidus presented higher ranges, further the lighter shade of pink had merged into the parent metal to a
Fig. 20(a).
SEM, EP15 AG7, Ag-Cu Eutectic Braze
454g Load

Fig. 20(b).
Higher Magn. of Fig. 20(a)
Discontinuities In Grain Boundaries. Voids And Slip Lines
Fig. 21. Print Magn. x 130
SEM. EP16. PD1, Ag-Cu + 4.53% Pd.
454g Load-At-Temperature

Fig. 22. Print Magn. x 135
SEM. EP18. PD1, Ag-Cu + 4.53% Pd.
115g Load At Temperature. Stress Crack Found In Shoulder, Lower RHS
greater extent, confirming that the dilution of colour with the reduced Cu content was detectable in the "as polished" condition. PD6 alloy had spread less than AG7 or PD1 during furnacing but due to the greater amount of PD2 alloy applied a direct comparison of this with other alloys could be questionable.

When examined EP3 was still in the unbroken machined state with brazing alloy applied, and it was particularly interesting to note that wetting and spreading was uniform on both sides of the section although there were no capillary attraction forces to retain alloy in the vee-notch; in fact the alloy was very well distributed around the notch.

The EP8 disc showed the PD1 brazing alloy had not spread as well as AG7 had spread over EP6. In the latter case a miniscus had formed at the edges of the disc to inhibit the run of alloy down the sides.

6.7.2- Etching

In the Metals Reference Book, Smithells\(^{3}\) made the point that care must be taken to produce polishes of high quality, with a minimum of distortion since it is difficult to remove much surface material from high Ni content alloys during etching. He commented that there is also a tendency to dissolve inclusions and form pits during etching. This proved to be an accurate assessment in the case of the Ni-Fe (EP7 "as received" and EP9 after 955\(^{\circ}\)C treatment). These 2 specimens were taken as controls to be used in establishing etching conditions when it proved more difficult to etch the heat treated than the 'as received' specimen. The reason for this disparity could be attributed to the method of cutting. Both were cut off the rod by lathe. After EP9 had been heat treated at 955\(^{\circ}\)C it was halved by a Struers Accutan slitting wheel at 3000 rpm. which is considered to have brought about deformation and making etching difficult until repolishing and regrinding was through a Beilby layer.

The following etchants were investigated:

(i) 2% aqueous nitric acid solution.

(ii) 5\% nitric acid in alcohol (Nital)

Both resulted in severe pitting and initially neither etched the Ni-Fe alloy after first swabbing with Inhibisol (a degreaser), air drying, and swab and immersing in the etches for up to two minutes.

(iii) 50 cc. 1.42 sp.gr. nitric acid,
25 cc. glacial acetic acid,
25 cc. distilled water.

After up to 60 seconds immersion this brought out large twinned crystals on the EP7 specimen but did not etch the EP9 specimen due to non-penetration of its Beilby layer.

(iv) A 50/50 mix of concentrated nitric with glacial acetic acid, as proposed by Harris\(^{33}\). As with (iii) crystals were etched in case of EP7 and EP9 was unattacked but pitting was present on both specimens.

(v) 50 g. ferric chloride,
150 cc. concentrated nitric acid,
600 cc. distilled water.

This etch resulted in badly pitted specimens with burned surfaces, both EP7 and EP9.

(vi) Another etch recommended by Harris consisted of up to 5\% ferric chloride in distilled water. A 5\% solution was acceptable but was so quick in
action that concentration was reduced to a 2% solution. After a 10 secs. swab etch with this both EP7 and EP9 displayed large equiaxed but stained crystals. "As received" alloys PD1 and AG7 were then etched in the same solution (PD5 was lost in grinding). While it was evident that both exhibited the typical broken down structures of "as drawn" wires no phases could be identified, further the etchant burned the surface.

To bring out the structure in the brazing alloys it was then decided to vacuum anneal them at 500°C for 30 mins. Following this treatment it was noted that while a 3 secs. etch with the 2% ferric chloride stained the Ag-Cu alloys, with or without Pd, etching with solution (iv) showed all 3 brazing alloys to exhibit fine crystals.

(vii) Attempts were then made to etch the Ni-Fe specimens which had been treated with brazing alloys viz. EP2, EP3 and EP5. After repeatedly polishing and etching, etched structures largely free from pitting were developed using a two-stage approach:

The twinned structure of the Ni-Fe alloy was revealed with a 20-30 secs. swab with 5% nitric acid leaving the brazing alloy untouched. Without repolishing but after rinsing with 'Inhibisol', methanol and acetone a 3 secs. swab with freshly made 50% nitric acid-50% glacial acetic acid revealed the dendritic structures in the brazing alloys.

6.7.3-Examinations As Etched

(a) None of the etchants examined were alone successful in etching both parent metal and brazing alloy; either the Ni-Fe alloy was revealed or the structure of the braze. The problem was resolved on going to the two-stage approach of 6.7:2 para.(vii) above.

(b) Earlier it was queried whether different heat treatments applied to the "as received" Ni-Fe alloy would affect grain boundary conditions and hence influence attack by the different brazing alloys. However comparison of specimens as received (EP7), as heat treated at 955°C (EP9) and after cryogenic treatment following brazing (EP3) failed to reveal any significant difference in grain size. It will be recalled that the SEM examination suggested that broken Ni-Fe, treated with AG7 alloy had a fine grain which could have been influenced by sub-zero treatment in the Auger microscope. This examination supports the view that differences noted between the AG7 and PD1 treated alloys had nothing to do with grain size.

(c) It had been found that despite cryogenic treatment before attempting to break the Auger-Charpy impact test specimen, these specimens were still not brittle and visual examinations of specimens EP1, 2, 3, 4 and 5 had confirmed that brazing alloys had concentrated at the notch of the specimen. Metallographic examinations, both "as polished" and "as etched" confirmed a significant build-up at notches, with good spreading and flowing along notch shoulders. The effect was therefore to substantially increase the cross-sectional area of the specimen at the notch. It seems probable that this increase in cross-section would effectively have rendered the hammer inadequate (in weight) for the intended Auger-impact test, although both this and non-brittleness could have played a part in the impact test failure.

A further observation of some importance is that if less brazing alloy had been applied it is doubtful whether sufficient would have been available for detailed metallography examinations of the parting between brazed alloy and parent metal.)
(d) Having established polishing and etching conditions with specimens EP7 (as received Ni-Fe), EP9 (heat treated Ni-Fe), AG7A (annealed Ag-Cu eutectic), PD1A (annealed 4.53 Pd-Cu-Ag alloy), and PD6A (annealed 25.81 Pd-Ag-Cu alloy), further examinations were restricted to EP2, EP3, EP11B and EP5 specimens.

(e) EP2 (AG7 treated). Twinned equiaxed crystals were present in the core material. Smaller crystals were noted around the notch and it was considered that these came about in machining the specimen, followed by the subsequent heat treatment cycle, the machinist having observed that the Ni-Fe was hard to cut and dulled his lathe cutting tool. Before the preferred etching method was derived this specimen gave promise by reversing the procedure using 2% ferric chloride for 10 seconds followed by 10 seconds in HNO₃. The structure developed was over-etched but gave a reasonable appearance on back-polishing (to remove staining) with 1 micron DUR. The appearance of the brazing alloy high-lighted the floral pattern reported in the as polished condition.

(f) EP3 (PD1 treated). A similar floral pattern to EP2 was noted with the exception that there were light islands near the Ni-Fe which could be Pd-rich. Core material was equiaxed. When etched initially, as described for EP2 above there was a heavy black line just beneath the surface of the Ni-Fe, this appeared to be a shadow of very fine crystals. The black line however was less pronounced using the technique of 6.7.2(vii) and was judged to be an etching effect.

(g) EP5 (PD6 treated). Little sign of a dendritic structure was observed in the brazing zone using the procedure given above for EP2. However the method chosen finally, 6.7.2(vii), showed a finely dispersed eutectic. Sloboda showed a stainless steel brazed with this alloy with the same floral appearance as EP2. However there was little similar appearance with EP5, possibly because the parent Ni-Fe alloy suffered more inter-diffusion than when stainless steel was used. Johnson Matthey were asked if they had any record of the etchant used by Sloboda but could only comment that he may have employed ammonium persulphate dissolved in ammonium hydroxide or hydrogen sulphide which would have brought out a similar dark line to that in (f) above. They said that the former etch had been found suitable to high-light Cu, leaving other constituents untouched.

(h) The effect of phases were next considered with the help of black and white and coloured photo-micrographs, taken of EP2, EP3, EP11, & EP5 all "as polished", and "as etched". Photomicrographs (b/w only) were also taken of the un-melted brazing alloys, AG7A, PD1A and PD6A. These photographs, were taken b/w at x 520 and colour x 820 print magn. using Kodacolor Gold 200 ASA for the colour prints. All photographs have been retained. The following 2-part etch was used for the colour series:

1. All chemicals freshly prepared.
2. 5% aqueous nitric acid. 20-30 secs. swab treatment.

After initially discouraging results using colour, 2 modifications of the latter 2-part etch were explored:

(a) 1:1:2: Nitric:Acetic:Water-10 secs. failed to etch the braze filler but was good for the parent metal.
(b) 1:1:1:1 Nitric:Acetic:Water-4/5 secs. effectively etched the brazed metal without the parent metal being attacked, but the 5% nitric of the 2-part etch was satisfactory after 20/30 secs. for the Ni-Fe alloy. Re-photographing after this etching treatment, with a new battery in the light meter and the microscope stage thoroughly checked to avoid movement, still resulted in a general 'muzziness' at x820 magnification.

(i) The un-melted "as received" brazing alloys, irrespective of whether annealed or not failed to reveal any significant feature. No further work took place with them.

(j) EP2-AG7: A copper-coloured phase in the brazing alloy was randomly disposed along the frontier with the parent metal as discrete blobs in the 'as polished' state. After etching fine crystals were noted at the parent metal sub-surface whereas large twinned crystals were at the centre. (Surface crystals as mentioned earlier were believed due to deformation during machining followed by anneal in the brazing cycle.) There appeared to be traces of a silver-coloured constituent in outer grain boundaries of the Ni-Fe parent metal with some indication of this running parallel to the frontier.

(k) EP3-PD1: As polished there appeared to be more of the Cu-coloured phase at the frontier than noted with the straight Ag-Cu eutectic of EP2 and this was spread out along the "frontier" to a greater and more uniform effect than in EP2. There appeared to be a fine layer of a silver constituent at the frontier and running parallel to it, between the Cu-coloured phase of the brazing alloy and the parent metal. As with EP2 there were fine surface crystals but these did not appear to penetrate as deeply into the parent metal as with AG7 alloy.

(l) EP11B-PD2: As polished the Cu coloured phase was found to have spread at the frontier to a greater degree than noted with either EP2 or EP3. Etching confirmed the increased concentration of this phase at the interface of the brazing alloy with parent metal and further, showed that there appeared to be slight penetration of silver-coloured phase between the pink constituent and the onset of twinned crystals at the core. Penetration into the parent metal was less than observed with either of the earlier reported specimens.

(m) EP5-PD6: Again there had been segregation from braze alloy of the copper-coloured phase to concentrate at the frontier with the parent metal. As etched there appeared to be a copper-coloured phase between the brazing alloy zone and the parent metal, with a silvery constituent possibly forming a barrier to inwards diffusion between this and the Ni-Fe. The amount of penetration into the parent metal was less than found with lower Pd percentages. It also seemed significant that the silvery constituent became more evident as the palladium content was progressively increased from AG7 to PD2 alloy.

(n) No cracks were found in any of the specimens examined optically and in view of the outstanding unresolved questions it was decided to turn to a scanning electron microscope for the next part of the investigation. As is to be expected it was found that the higher magnification electron microscope photographs not only duplicated the findings of this section but resulted in clearer photographs than obtained from the older Zeiss optical microscope.
6.8-S.E.M.-As Polished/Etched Examinations

6.8.1-Analysis Of Phases

Optical microscopical examinations had revealed dark copper-coloured and silvery coloured phases in the braze; in the case of lower Pd-content brazing alloy some white constituent was also noted in the boundaries of parent metal, close to the frontier.

There was a build-up in amounts of the dark coloured phase as the Pd content in the brazing alloys increased with good correlation between the build up of this phase and the hot-short failures found from the static-beam load high temperature tests, with only a marginal increase in the distribution of the dark phase at the frontier in the case of PD1 alloy compared to AG7 alloy i.e. hot-short tendencies were present when this phase did not completely separate braze from parent metal; the constituent was pronounced in the cases of PD2 and PD6 alloy specimens neither of which exhibited any tendency to hot-shortness. It was concluded that the next requirement was to subject the different phases noted in both optical and electron microscopy to electron microprobe analysis from positions illustrated in Fig.23-AG7, Fig.24-PD1, Fig.25-PD2 and Fig.25-PD6. The following Table records the results of these analyses:

<table>
<thead>
<tr>
<th>Braze alloy:</th>
<th>Dark constituent:</th>
<th>White braze const:</th>
<th>Grain boundary:</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG7</td>
<td>88.17 Cu 7.70 Ag 2.75 Ni 1.38 Fe (Fe:Ni::0.5:1)</td>
<td>6.14 Cu 93.36 Ag 0.21 Ni 0.27 Fe (Fe:Ni::1.29:1)</td>
<td>3.56 Cu 65.52 Ag 12.44 Ni 21.48 Fe</td>
</tr>
<tr>
<td>PD1</td>
<td>73.57 Cu 8.05 Ag 14.98 Pd 1.46 Ni 1.94 Fe (Fe:Ni::1.33:1) (Cu+Pd=88.55)</td>
<td>7.90 Cu 89.22 Ag 1.57 Pd 0.50 Ni 0.82 Fe (Fe:Ni::1.64:1) (Cu+Pd=9.47)</td>
<td>3.45 Cu 80.72 Ag 1.35 Pd 5.17 Ni 9.30 Fe</td>
</tr>
<tr>
<td>PD2</td>
<td>60.43 Cu 6.40 Ag 23.61 Pd 3.75 Ni 5.83 Fe (Fe:Ni::1.55:1) (Cu+Pd=84.04)</td>
<td>9.09 Cu 85.03 Ag 4.36 Pd 0.56 Ni 0.98 Fe (Fe:Ni::1.75:1) (Cu+Pd=13.45)</td>
<td>9.62 Cu 0.03 Ag 7.45 Pd 34.01 Ni 48.43 Fe</td>
</tr>
<tr>
<td>PD6</td>
<td>35.30 Cu 18.62 Ag 40.71 Pd 1.54 Ni 3.84 Fe (Fe:Ni::2.49:1) (Cu+Pd=76.01)</td>
<td>14.63 Cu 63.48 Ag 20.83 Pd 0.37 Ni 0.69 Fe (Fe:Ni::1.86:1) (Cu+Pd=35.46)</td>
<td>No const: found</td>
</tr>
</tbody>
</table>

Points of interest arising from the analyses included:
Fig. 23. Print Magn. x 1700
SEM. AG7, Ag-Cu Eutectic Frontier With Fe-Ni. Etched

Fig. 24. Print Magn. x 1700
SEM. PD1, Ag-Cu + 4.53% Pd Braze, Compared To Fig. 23. Note Increase & Spreading Of Dark Constituent And Smaller Surface Crystals Of Ni-Fe. Etched
Fig. 25. Print Magn.x 2250
SEM. 'As Polished' PD2, Ag-Cu + 9.92% Pd Braze.
Dark Constituent Increased At Braze/Parent Interface.
Reduced Penetration Of Fe-Ni Compared To Figs. 23 & 24

Fig. 26. Print Magn.x 1700
SEM. 'Etched' PD6, Ag-Cu + 25.81% Pd.
Little Penetration Of Fe-Ni Parent Metal
(a) The dark phases noted in both the SEM and the optical microscopy sections were copper rich. The decrease in colour intensity could be related to the reduction in Cu allied to increases in Ag and Ag + Pd contents in the sequence of increasing Pd in specimens, EP2, EP3, EP11B and EP5.

(b) Conversely because the silvery phases were initially thought to be Ag and Ag + Pd, the combination of these 2 elements was totalled for comparisons e.g.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Ag+Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP2</td>
<td>93.6</td>
</tr>
<tr>
<td>EP3</td>
<td>90.79</td>
</tr>
<tr>
<td>EP11B</td>
<td>89.39</td>
</tr>
<tr>
<td>EP5</td>
<td>84.31</td>
</tr>
</tbody>
</table>

(c) Whereas the grain boundary constituent was significant in EP2 and EP3 and appeared to be substantially Ag-rich, only a small percentage of Ag was found in the surface layers of the Ni-Fe parent metal of EP11B (0.03%). None of the white constituent could be detected for analysis in EP5 showing that the increase in Pd content on going through the series EP2, EP3, EP11B and EP5 had a suppressive effect on inwards diffusion of the other alloying additions. It was concluded that the white constituent in the boundary was a lighting effect and it appeared to be essentially Ag and/or Pd-containing.

(d) The higher Fe and Ni returns shown in the grain boundary determinations, notably in EP2 and EP11B, probably resulted from electron probe positioning on the frontier of braze metal and parent metal.

(e) One very interesting feature of the analysis related to the ratio of Fe:Ni. This ratio was 1.38:1 for the untreated parent metal. Further, while neither Fe nor Ni were detected in the brazing alloys used, both elements were found in the dark and the white constituents in the solidified braze metal side of the frontier. Fe progressively increased in the dark phase from 0.5:1 ratio to Ni in the Pd-free alloy (AG7) to 2.49:1 in the alloy containing a nominal 25% Pd (PDS). In the white braze constituent, the ratio of Fe:Ni similarly rose from 1.29 to 1.85 and was following the increase in Pd. In general in both phases the ratio for parent metal was exceeded but it appeared that the significance of Ni was less than Fe, other than in the instance of the straight Ag-Cu eutectic alloy where it predominated.

(f) Under comments on the Auger/XPS examinations consideration was given to the possible formation of PdCu at 64% and PdCux at 37.4% Cu, adding that while these compounds age-harden this effect is enhanced if Ag is also present. The microprobe analyses showed there was an adequate presence for the formation of such compounds.

(g) The column (% Pd+Cu) was included in the Table as this proved pertinent to the work done at Link Analytical and will be discussed later.

6.8.2-Inter Or Transcrystalline Penetration

-104-
Using K alpha lines the specimens were spot-analysed for 100 secs. 15KeV, x4000 magn. at 31 positions, with individual spectrum charts obtained for each position viz. EP2-8 positions checked; EP3-10; EP11B-8 & EP5-5 positions. In making the analysis the principle followed was to start at the frontier and work along 2 separate grain boundaries into the core of the specimen, noting the distance from the frontier that each spectrum was recorded. Whereas the elements, Fe, Ni, Cu and Ag+Pd were found to a greater or lesser extent in the grain boundaries, with the latter two decreasing with distance, when the electron beam was concentrated in the centre of grains neither Cu, Ag nor Pd were detected, 3 spots having been checked viz. EP2 at 10 and 12 microns from the frontier, EP3 at 10 microns from the frontier.

From these observations it was concluded that the mode of failure was intercrystalline if the Ag-Cu eutectic was used as the brazing alloy for Ni-Fe alloys both with or without being modified by a Pd addition.

6.8.3-Effect Of Palladium On Distances Travelled By Other Constituents

Penetration of constituents was measured as described in the last section by tracing progress through grain boundaries and noting the distance in a direct line from frontier to core of specimen. While it cannot be regarded as a finite measurement, indicative figures are obtainable for the intensity of (a) Cu and (b) Ag+Pd by counting the number of graph paper squares beneath (a) and (b) peaks of the spectrum traces, as obtained from the S.E.M computer and substituting in the following formula:- (it was not possible with the equipment available to determine separate peaks for Ag and Pd). Fig.27 illustrates the method.

Intensity of Metal= Max. Number Squares Under Peak x Full Scale Deflection
Maximum Possible Number Of Squares

Comparison was then made of distances penetrated by the different alloying constituents of the filler alloy. Consideration was also given to the ratio of Fe to Ni by counting the number of squares under these metals peaks. In the spectrum Cu is expected to interfere with the intensity of Ni peaks with a consequent impact on the resultant Fe:NI ratio, hence a higher Ni peak should be returned in the absence of Cu. While results from a consideration of the Fe:NI ratios were not immediately significant these are given as follows, together with Cu & Ag + Pd intensities:

<table>
<thead>
<tr>
<th>Specimen No:</th>
<th>Dist. to frontier:</th>
<th>Ratio Fe:NI</th>
<th>Intensity of Cu:</th>
<th>Intensity of Ag + Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP 2</td>
<td>5 microns</td>
<td>3.07:1</td>
<td>1.6</td>
<td>1.82</td>
</tr>
<tr>
<td>&quot; 13</td>
<td>2.94:1</td>
<td>0.16</td>
<td>N.F. (Not Found)</td>
<td></td>
</tr>
<tr>
<td>&quot; 19</td>
<td>2.93:1</td>
<td>0.16</td>
<td>0.32</td>
<td></td>
</tr>
</tbody>
</table>
An examination of these results brought forward the following deductions:

(a) Cu and Ag (or Ag+Pd) penetrated to similar depths, around 19 microns, for specimens made with both the Ag-Cu eutectic and the 4.53% Pd-containing alloys, (EP2 & EP3) with the max. concentration within 7 microns of the frontier.

(b) In the case of the 9.92% Pd alloy (EP11B) there was little penetration of Cu beyond 10 microns but Ag+Pd was evident to approx. 15 microns from the frontier. The major concentration of both metals remained within 5 microns however.

(c) With the 25.81% Pd-containing alloy (EP5) it was apparent that while no Cu was detected beyond 5 microns from the surface of the Ni-Fe parent metal, some Ag or Ag+Pd had diffused via grain boundaries to a depth of circa 5 microns, with traces to 14 microns.

(d) The broad conclusion was reached that the progressive increase in Pd content not only reduced the effects of penetration by Cu and or Ag but additionally these constituents were concentrated in layers closer to the frontier probably in cracks or grain boundaries. It was not possible to be more
Fig. 27
SEM Spectra demonstrates intensity calculation

Link Systems Ltd X Ray Analysis
specific at this stage due to the inability to quantify the amounts of Ag and Pd respectively but later determinations at Link proved this not to be Ag but Pd.

(e) A comparison of Cu intensities in the case of EP2 & EP3 revealed that the former was stronger than EP3 which contains Pd.

6.8.4-Back scattered X-Ray Photographs

The specimens which had been presented for electron microprobe analysis and spot analyses had all been etched, with the intentions of assisting location of the electron beam and by black & white photographs demonstrating regions of interest. The microscopist, however felt that there was a danger that atoms of Cu, Ag and or Pd could have been removed during etching, possibly leading to spurious conclusions, especially as at higher magnifications grain boundaries appeared as deep fissures. Clearly this view would have to be kept in mind, particularly when x-ray maps were being made.

In a first assessment of the effects of etching and as a preliminary to mapping, back-scattered polaroid x-ray photographs were taken of the frontiers of specimens EP2 & EP3. Whereas the photograph showed slight "muzziness" at the frontier between braze filler and Ni-Fe parent in the case of the Pd-containing alloy, what had been thought to be deeply etched grain boundaries were shown to be cracks in the parent metal in the case of the EP2 Pd-free specimen at x1500 magn.

Commercial brazers had reported that stress-cracking was not always found after brazing and initial impressions before results were available from statically loaded high temperature strain evaluations were that this work was being conducted with a batch of rod which was not prone to cracking. The appearance of cracking now noted called into question whether cracks are not always present but because they are not always seen by naked eye the conclusion has been reached that many batches of Ni-Fe low expansion alloys are not prone to stress corrosion.

6.8.5-Dot, Spot Or X-Ray Mapping For Cu, Ag+Pd, Fe & Ni

All the etched specimens, EP2, EP3, EP11B and EP5 were mapped at 25KV, x1500 magn. but as returns were weak, possibly due to loss of crystal boundary atoms as anticipated by the S.E.M. microscopist, mapping of the etched samples was repeated with a higher count rate at 20KV, x2000 magn. The latter conditions were also applied to the unetched specimens after repolishing.

Etched specimens had been swabbed with 5% nitric acid for 20-30 seconds followed by a 1 second wipe with 50% nitric acid-50% glacial acetic acid. Mapping resulted in 5 photographs for each specimen, namely a general view, Cu map, Ag+Pd map, Fe map and Ni map.

Maps from etched versus unetched specimens:
The repeat etched specimen maps resulting from higher counts were clearer, hence more meaningful than the first ones made at 25KV - the latter were therefore disregarded from further consideration.
Comparing the General View Maps obtained from unetched with etched specimens confirmed that detail had been lost in the etching process and further examinations were concentrated towards maps gained from the unetched samples, with the exception of EP5 where both etched and unetched-type maps confirmed the absence of any constituent which could have been etched away.
To assist in evaluating depth of penetration of individual constituents, 'overlays' were made by photocopying prints from the unetched specimens onto transparencies, available for examination by light box or overhead projector.

**EP2 (Ag-Cu eutectic braze)**
The general view, Fig.23, showed a silver coloured grain boundary constituent which filled sub-cutaneous cracks below the Ni-Fe surface. The maximum crack length noted was 41.6 microns. The Cu map revealed that Cu was present around boundaries extending into the core but was not found in the crack. Ag was not only surrounding crystals at the frontier but was also in the crack. Absence of Fe from fissures confirmed the cracking in that map. The Ni map although less distinct was similar to Fe. The maximum depth of interference due to the brazing was up to 3.5 microns from the frontier.
The broad conclusion reached at this time was that both Ag and Cu penetrated the Ni-Fe.

**EP3 (Ag-Cu + 4.53% Pd braze)**
The general view, Fig.24, showed that the Cu-rich phase was spread more uniformly along the frontier than observed in the EP2 specimen. There had been some penetration via boundaries and fissures. There was cracking but this was less intense than noted with the earlier specimen, with the longest crack 30.9 microns.
The Cu map confirmed that this metal had penetrated around boundaries and voids. Ag + Pd mapping proved that this constituent had similarly run around boundaries and voids. Both Fe and Ni maps showed the presence of small cracks before molten brazing alloy flowed inwards to fill them. The depth of interference beneath the frontier was 4.1 microns.
The inference from this examination was that the addition of Pd modified the structure but insufficiently to prevent stress corrosion effects, questioning the claim\(^{(26)}\) that as little as 1% Pd can improve the range.

**EP11B (Ag-Cu + 9.92% Pd braze)**
The general view, Fig.25, revealed some 'distortion' of structure along the frontier of braze and Ni-Fe (a similar 'blurred' appearance was noted in the optical examinations). As with optical microscopy there appeared to be a further increase of the Cu-phase concentration in the braze at its frontier with the Ni-Fe when compared with EP2 and EP3 respectively. There was also the lighter phase between the Cu-phase and parent metal as with the optical examination. However there was no significant penetration of parent metal by the braze alloy. Cu, Ag + Pd, Fe and Ni maps confirmed the absence of deep penetration or cracking.

It appeared from this evaluation that whereas 4.53% Pd, as added to EP3 was insufficient to eliminate stress cracking, the addition of 9.92% Pd is adequate for this purpose, confirming observations made previously upon completion of the load-at-temperature tests.

**EP5 (Ag-Cu + 25.81% Pd braze)**
The frontier noted in the general view, Fig.26, was somewhat similar to that of EP11B except that it appeared to take the form of a ripple rather than a distortion; this effect extended approx. 4.9 microns into the core of the specimen. The Cu, Ag + Pd, Fe and Ni maps failed to indicate the presence of penetrating brazing alloy through grain boundaries and no cracks were found. This examination also supported the view that crack propagation, noted when the Ag-Cu eutectic is used by itself to braze Ni-Fe, is progressively reduced on
increasing the amounts of Pd in the filler alloy. 

Comments on EP3 included consideration of whether cracks noted had arisen at, or before, brazing temperature was reached. Stress cracking is usually overcome, if it results from earlier fabrication processes, by heat treatment for a prescribed period below the solidus of the brazing alloy. This procedure took place in the cases of EP1 through EP4 where it is earlier recorded that they were soaked for 12 mins. at 750°C before raising to brazing temperature. Such a soak should have prevented cracking as a result of relieving in-built stresses. That cracks had occurred showed that some other effect had taken place in the cases of EP2 and EP3 as they were absent from EP5. Later information showed that to achieve maximum dimensional stability pre-heating with this alloy should have taken place in the range 800-1000°C, i.e. within the range of temperature used for the brazements. Taking into account the results of the strain-at-temperature tests again led to the conclusion that cracking took place at the time the alloy melted and was a stress corrosion-type effect.

6.8.6-Evaluation Of Specimens At Link Analytical Ltd.

In reviewing results, as previously indicated, a major feature causing concern was the inability of both Auger and SEM spectra to differentiate between Ag and Pd. The electron probe analysis equipment was able to analyse the amounts of each element but there could be no certainty of whether these were separate or combined such as Ag + Pd, Cu + Pd or as a combination of the 3 elements. In discussions with Link Analytical Ltd. they advised that they had developed a system capable of differentiating between the different atomic numbers and they requested our co-operation. As a result of their request specimens EP10 and EP11A were prepared and provided in the "as polished" state for evaluations. Link stated that traditional x-ray mapping has largely been superseded by digital mapping but this technique itself had limitations, notably overlapping peaks cannot be mapped, background subtraction is impossible in regions of the spectrum where peaks of interest are close together and low level intensities in maps cannot be reliably interpreted as genuine features. Their latest development has been the "On-Line Quantitative Programme" where fast processing routines with digital mapping are claimed to produce images which are a true reflection of x-ray intensity from individual elements. Link quoted advantages of Quantitative Elemental Mapping as:

(a) Elements whose peak energies overlap in the spectrum can be mapped.

(b) Background effects are automatically eliminated by digital filtering throughout the energy range.

(c) Rigorous statistical significance tests can be applied to maps of low concentration to reveal true low concentration areas.

(d) Unstable samples which exhibit image drift can be automatically tracked and maps corrected.

In sect.6.8.3, Ag+Pd was treated as a single element for comparing penetration distances into the Ni-Fe parent metal; Surrey were therefore pleased to co-operate with Link by providing samples containing these elements, in particular to support their claim (a) above.

For this phase of the investigation Link used a Cambridge S200 Microscope with their AN 10000 X-Ray Microanalysis System. The microscope conditions were
x2050 magnification, 20kV accelerating voltage, 25mm working distance and a 35° x-ray take off angle.

Maps were collected at 128 pixel resolution for 1.5 secs. dwell per pixel, therefore each map took 128 x 128 x 1.5=6.82 hrs. (to avoid loss of instrument time Link usually set up at the end of the day leaving collection processes to automatically take place over night). Maps were processed using special routines to set intensity to zero if the level was below 2 o for that element. To correct for any drift in the image during acquisition a tracking analyser was used.

In interpretation of maps a reminder was given that the higher the atomic number the greater the intensity at the micrograph e.g.: Fe=26, Ni=28, Cu=29, Pd=46, Ag=47.

Link conducted profile analyses for principal elements at 20 spot positions, from braze metal to core at approx. 1.5 micro-millimeter intervals on EP3 and EP5. In addition to providing slides and graphs depicting changes in concentrations of the different elements they gave photographs marked with a (+) for each place analysed. Link also prepared maps for all four "as polished" specimens labeled, EP2 (0% Pd), EP3 (ca.5% Pd), EP11A (ca.10% Pd) and EP5 (ca.25% Pd). The last 4 are considered later but the graphs are retained with the data obtained from them being listed in the Tables which follow.

6.8.6.1-Profile Analyses

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<th>%Pd</th>
<th>%Fe</th>
<th>%Ni</th>
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Point 7 corresponded to the frontier: max. penetration by Pd+Cu = 18.1 μm. The ratio of Fe:Ni approximates to 1:1 (from points 3 to 6).

Comments on EP3 analysis

(a) Variations of totals from 100% can be due to excluding minor impurities from the analysis e.g. Mn & Co, both known to be present, to errors in reading the graphed results (taking to nearest 0.5%) and to slight wander of the electron beam. For this exercise they are regarded as insignificant and no attempt has therefore been made to normalise results.
(b) Point 7 was right on the frontier and also at the edge of a crack running into the specimen, which accounts for the high Ag and Cu returns at this point. Similarly cracks or fissures were noted at points 10, 12 and 16.
(c) Disturbed metal (muzzyiness) as a result of alloying and penetration was noted on the photograph to extend from the frontier for ca. 18 μm, this is compared with sect.6.5.1, A/XEP4.SP6 which indicated a depth of penetration of c.12.7 μm; and sect.6.8.3 which showed that main penetration was between 17-22 μm.
(d) The analysis showed that if there had been no cracking it was likely that Ag and Cu would not have penetrated so far into the Ni-Fe alloy but this was not quantified.

EP5 (PDS alloy) Profile Analysis

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<th>Point No.</th>
<th>Distances-μm</th>
<th>%Ag</th>
<th>%Cu</th>
<th>%Pd</th>
<th>%Fe</th>
<th>%Ni</th>
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<td>(b) to frontier</td>
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<td>(b)</td>
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-111-
Point 12 corresponded to the frontier + max. penetration by Pd was 4 μm. The ratio of Fe:Ni (points 3 to 11) varied from 2 to 3:1.

Comments on EP5 analysis

(a) The effect of Pd is again noted as reducing penetration into the parent metal with limits noted of nil for Ag, 2.7 for Cu and 4 micro millimeters for Pd, indicating that there is 4% times as much penetration with the 5% Pd alloy as is experienced with the 25% Pd braze alloy; also that as with EP3, Pd and Cu ingressed further into the core metal than Ag.
(b) In both studies Cu and Pd progressed further into the structure of the metal than Ag, bearing out earlier Auger work where it was found from mapping that a Cu map almost filled the window in the case of the Ag-Cu eutectic, whereas the addition of 4.53% Pd as EP4, substantially reduced the spread of Cu.

6.8.6.2- Maps For EP2, 3, 11A & 5

It will be recalled that the original specimens were halved by slitting wheel to give a cross section as nearly as possible to the centre line after polishing and etching. This meant that the other halves as provided to Link would have less core but more braze material for microscopic examination and therefore surfaces would not necessarily be "mirror images" of specimens discussed in earlier sections. In fact there was good correlation of results and as a result of the Link analyses maps became available of a general view plus Pd, Cu and Ag for each specimen. (As EP2 did not contain Pd the fourth position mapped there was for Ni)

EP2 (Fe/Ni+B.S.1845:1984-AG7 braze alloy)-Fig.28
The Ni map showed the same type of cracking noted earlier in the dot map (sect.6.8.5). There were also some grain boundaries evident. There was a trace of Cu in the crack and Ag was also detected. Cu and Ag were present in similar amounts along the frontier with neither appearing to agglomerate. The general view colour map high-lighted the cracking, with braze alloy running through cracks and boundaries. While the photographed dot maps of 6.8.5 have been discussed they are not reproduced as the work at Link offered improvement on quality of prints and in any case was an advance on the earlier work.

EP3 (Fe/Ni+B.S.1845:1984-PD1 braze alloy)-Fig.29
Cu was more concentrated in the form of globs in the brazing alloy along the frontier with parent metal than seen with AG7 alloy. There appeared to be a fine but intermittent layer of Ag between the globs and the frontier suggesting that while other elements had alloyed with the parent metals Ag had been rejected. The Ni-Fe material had been penetrated to the same depth as EP2 with the surface broken up into a succession of sub-cutaneous cracks rather than the continuous lines found in the earlier specimen. There was a preponderance of Ag found in these cracks.
The Pd and Cu maps were of great interest as they were virtually identical, proving that these 2 elements had preferentially alloyed to leave Ag at the frontier and in cracks and crevices. This showed that the modified Link system could satisfactorily separate Pd from Ag. Sect.6.8.6.1. had shown that percentages of Cu and Pd had penetrated the specimen to a similar extent and the disturbed metal seen in the photographs just below the frontier confirmed alloying of these elements with the Ni-Fe parent metal, supporting the view that while stress corrosion resulted in the attack found with AG7 and PD1 it could
be inhibited with higher percentages of Pd in the brazing alloy. The maps gave further support to the view that if the Ag–Cu eutectic was used alone Cu will attack the Ni–Fe to give rise to intergranular weakness as a result of stress corrosion at brazing temperature. Taking into account the Auger results this further suggested that Cu separating from the brazing alloy is the reason behind the failure of low expansion Ni–Fe alloys having residual internal stress.

EP11A (Fe/Ni+B.S.1845:1984–PD2 braze alloy)—Fig.30.
The Cu globs noted in EP3 had further increased in size but the fine Ag layer between core and frontier was less evident. The Cu and Pd maps were again virtually identical except that the intensity of Cu merged into the core of the parent metal less distinctly than the Pd. A roughness was noted at the brazed metal–parent metal interface which was more pronounced than anticipated with a carefully machined specimen. Initially this was thought to be due to porosity in the braze [6.3.(b)(iv)]. However on reconsideration it was thought that there had been erosion of the parent metal and the effect was due to atoms of Fe and or Ni being removed to deposit in the solidified brazing alloy. Re-examination of Fig.25 and associated dot maps [6.8.5,EP11B] confirmed that there were blobs in the braze in that specimen and EPMA found these contained both Fe and Ni. However after etching the EP11B specimen all traces of blobs had been removed and the roughness at the parent metal was less pronounced. Fig.32 illustrates a SEM spectrum obtained from a blob prior to etching. It was concluded that in slitting the specimen [6.7.2,first para.] the slitting wheel had transported fine particles of parent metal into the softer braze alloy in which they had become embedded. In the case of the sample sent to Link this had only been ground and polished and the edge roughness was pronounced compared to EP11B which had been subjected to a number of repolishing and etching treatments to get through the Beilby layer.

EP5 (Fe/Ni–B.S.1845:1988–PD6 braze alloy)—Fig.31.
The Cu in the braze had spread even further along the frontier than in the other specimens. There were again identical pictures for Cu and Pd confirming the alloying of those metals and leaving Ag as a separate phase in the brazing alloy. Dendrites of Cu–Pd alloy were clearly identified as separate from the Ag in the braze metal zone. There were no cracks in the parent metal hence confirming once more that as the Pd content is increased so stress cracking tendencies diminish in this series.

6.9—DISCUSSION

This investigation has established that cracks arose at brazing temperature using Ag–Cu both without Pd and with a 4.53% Pd addition, although cracks were marginally less severe if Pd was present. Specimens machined from the same rod were free from cracks when higher percentages of Pd were added to the Ag–Cu alloy e.g. 9.92%. Reverting to the Electronics Industry which found the nominal 5% Pd addition acceptable compared to using AG7 alloy, presumably this was because the good gap-filling, wetting and spreading properties imparted by the Pd resulted in sealing any cracks or other discontinuities which may have occurred during the brazing cycle—although there is no evidence that the Industry was aware that cracking still persisted after Pd had been included in the composition.

Culham Laboratory, who provide a contract brazing service to all industries, reported that contacts in the Electronic Industry were currently advising them
Fig. 28.
SEM. Map. Ag-Cu Eutectic On Fe-42 Ni Alloy - EP2

Fig. 29.
SEM. Map. Ag-Cu + 4.53\% Pd On Ni-Fe - EP3
Fig. 30.
SEM. Map. Ag-Cu + 9.92% Pd - EP11 A

Fig. 31.
SEM. Map. Ag-Cu + 25.81% Pd - EP5
Fig. 32.
X-Rays Identify Fe-Ni Swarf
Within Specimen EP 11B
that cracks still arose in around 2% of instances but the alloy rod U.K.A.E.A. provided was alleged to be crack-free and in fact no crack was found visually even after going through the brazing cycles although they became evident on microscopic examination at x520 magn. The cracks were therefore very small in the case of this rod and it seemed likely that cracking can always occur with brazed Ni-Fe alloy unless sufficient Pd or some element having similar properties is present as a depressant to the corrosion-promoting mechanism.

It is believed that the fractures noted as a result of the high temperature static beam loading tests comply with the latest views on liquid metal embrittlement where reviewers 101-102 listed the main requirements for this type of failure as:

(i) loss of elongation and little or no reduction of area when normally ductile metals are stressed in contact with certain liquid metals,

(ii) crack nucleation arises at wetted surfaces of solid metal following which the liquid embrittler flows into the now-formed cracks and thence propagate,

(iii) applied stress must be of an order to bring about plastic deformation,

(iv) crack growth stops once supply of embrittling liquid ceases,

(v) metals breaking through liquid metal embrittlement fail by an intercrystalline mechanism,

(vi) embrittlement usually occurs at or just above the melting point of the embrittler,

(vii) higher strain rates tend to increase embrittlement,

(viii) embrittlement is aggravated by large grain size,

(ix) composition of the liquid/solid combination, (which influences wetting ) metallurgical state, and exposure conditions can all influence liquid metal embrittlement.

Both the AG7 and PD1 treated Ni-Fe alloy were experimentally shown to be susceptible to this form of attack. While both alloys failed similarly there was support for commercial claims that even a small addition of Pd is helpful, in that microscopy showed that globules of Cu-rich compound found at the parent metal/braze alloy interface had spread to a greater extent in the case of the PD1 brazed metal. It was also noted that penetration into the sub-surface crystals was marginally less in the case of the PD1 alloy. The importance of stress to crack propagation was also emphasised by these tests where external loads ranging from 115 g to 1.36 kg resulted in hot-shortness whereas with lower applied loads the specimens remained ductile even though surface crystals revealed intergranular penetration, probably resulting from machining a work-hardening metal. From this it seemed that the core of the metal was inherently ductile but strain had to be sufficient to bring about crack formation hence permitting braze alloy to penetrate the parent metal. Another consideration in the failure mechanism was the question of why some braze alloys should be subject to such failure but not others and for examples, in this work no indication of failure was noted when PD2 or PD6 alloys were employed.

It was thought that in the case of the AG7 alloy, Ni from grain boundaries was taken into solution by the molten brazing alloy, leaving vacancies which were
filled by Cu atoms. The Auger Ni maps support the view that Ni had been dissolved and the Cu maps showed the depth of penetration into the core by the Cu, the depth of penetration being limited by the residual stresses resulting from the use of half hard metal, from stresses caused by machining and by the amount of available molten braze alloy.

The importance of stress to propagation of cracking is emphasised on comparing both AG7 and PD1 treated specimens. Extra loads ranging from 115 g to 1.36 kg all resulted in hot short failures compared to specimens similarly treated but with loads of 50 g or less. In the case of PD1 alloy reduced surface penetration could be related to the addition of 4.53% Pd to the composition; the penetration noted in Fig.23 (AG7) is seen to be slighter greater than in Fig.24 (PD1).

The small surface cracks noted in these two tests were not found to any extent in Fig. 25 (PD2) and were absent from Fig. 26 (PD6), although all specimens were lathe turned by the same machinist from the same rod of Fe-Ni alloy rod.

In addition to the penetration of braze alloy into the cracks apparent in the cross sections (sect.6.6.2, Figs. 20-22) the fracture surfaces revealed corrosive attack on the grain boundaries. This was particularly apparent for the Pd-free AG7 alloy. Fig. 33 (a & b) shows in detail the pits formed at the Ag-Cu eutectic-treated grain boundary and it will be noted that these are similar to the many reported incidences of grain boundary pitting and tunnelling which accompany stress corrosion cracking in aqueous solutions. A search of grain boundaries in the intergranular failure of the alloy in contact with PD1 brazing alloy did not reveal any clear example of similar pitting.

Intergranular stress corrosion cracking usually occurs in situations in which corrosion is for some reason focussed on the grain boundary.

The influence of Pd, which forms solid solutions with Ni, Fe and Cu, is to increase the general corrosivity of the braze towards the alloy. Calculations of the partial excess free energy of iron and nickel in the molten braze show a decrease for both iron and nickel as the Pd content increases, the change for iron being much greater than that for nickel.

Evidence that the selectivity of the Pd-free alloy towards Ni is lost when Pd is added can also be seen in the Table on page 103. The analysis of the dark constituent (the Cu-rich phase) in the solidified braze shows a progressive change in the Fe: Ni ratio as the Pd content is increased. Assuming that the selective uptake of Ni which occurs with AG7 alloy may be correlated with attack on the grain boundary, it follows that any alloying addition which depresses this selectivity will also destroy one of the conditions for grain boundary cracking; this is probably the role of Pd in these Pd-containing alloys.

The Auger maps were made on samples which had been broken when cold. These did not reveal any evidence of brittleness under this condition but the failure followed in part the line of penetration of braze into parent metal. It was thus possible to see, in the maps, regions where the crack passed through the braze and onwards into the substrate. The two regions are delineated in Figs.16(a) and 16(b) where maps confirm the enhanced uptake of Fe by the Pd-containing alloy in the PD1 treated as compared to the AG7 treated specimen; thus supporting the trend of the ratios of the p.103 Table. Auger analysis of both figures show that Cu is present in the crack on the alloy side of the failure, showing that although the lowest level of Pd used might have mitigated the tendency to cracking it had not completely eliminated it as, of course, was also observed in the cross-sections following the static beam loading induced failures.
6.10-CONCLUSIONS

(1) The work confirmed that Fe-42% Ni is subject to intergranular liquid metal embrittlement. Rate of strain is most important as evidenced by the comparison of the embrittled material after applying additional stress at brazing temperature with the ductile failures noted when the only stresses present came from using metal which was not fully softened and influenced by light machining stresses.

(2) Auger maps showed that there was less migration of Ni and a corresponding reduction of Cu penetration on adding 4.53% Pd to the composition. However static beam loading tests at brazing temperature proved that this amount of Pd was insufficient to totally overcome stress corrosion failures.

(3) Scanning electron and optical microscopy proved that intergranular penetration was marked with AG7 alloy. There was slightly less penetration noted with PD1 alloy, less still with the PD2 alloy and virtually no penetration with the PD6-treated specimen - in fact penetration was 4.53% greater with the alloy containing 4.53% Pd than the alloy with 25.81% Pd. Similarly the increase in Pd content was matched by an increase in build-up and spreading of the dark constituent noted at the interface of braze and parent metals. This phase contained both Fe and Ni dissolved from the substrate. The Pd addition enhanced the uptake of Fe relative to Ni: it was probably this feature that reduced the susceptibility to intergranular failure.

(4) The PD2 alloy and PD6 alloy specimens were both ductile at all temperatures proving that stress-corrosion cracking is overcome with an analysis of 9.92% Pd.

(5) No intermediate compositions were available between PD1 and PD2 to permit bracketing, hence allowing assessment of the change-over composition from susceptibility to non-susceptibility to stress-corrosion with this series of braze alloys.

(6) SEM maps proved the strong alloying tendencies of Cu and Pd; nevertheless the more important consideration was the ability of Pd to take up Fe from the parent metal, which inhibited liquid metal corrosion of the higher Pd content filler alloys. While no work has taken place here with other phase systems containing this element it is likely that similar conclusions could apply.

(7) A number of methods of attack of parent metal by molten brazing alloy have been evaluated. The pits and tunnelling found by SEM in cold grain boundaries has led to the conclusion that in the case of the Pd-free, AG7 alloy, Ni atoms are dissolved by the molten brazing alloy. Vacancies left are filled by Cu atoms as demonstrated by Auger maps. Penetration of Cu is assisted by the readiness with which it wets Ni and Fe compared to Ag which has low miscibility for the parent metal constituents. The addition of stress to a structure which has been weakened by replacing Ni with Cu atoms assists the propagation of cracks allowing the brazing alloy to flow into the cracks which have been initiated.

Both the microprobe analysis and the Link profile analysis (sects. 6.8.1 & 6.8.6.1) showed that migration had occurred of both Fe and Ni into the molten braze alloy, no brazing alloy used for this work showing presence of either constituent before melting. The addition of Pd resulted in little change in the Ni content of the brazing alloy but the ratio of Fe:Ni increased on its addition, confirming that reduction in corrosivity was accompanied by uptake of Fe into the brazing alloy.

In sect. 6.8.3 ratios of Fe:Ni were assessed at grain boundaries for all combinations using a 'squares under spectrum peak' approach. It was evident that there was no significant change. It was concluded from this that the extra Fe noted in the brazing alloy as Pd increased did not come solely from grain boundaries but resulted from a more general attack probably associated...
Fig. 33(a).
EP15. Higher Magn. Fig. 20(b)

Fig. 33(b).
EP15. Further Enlargement Emphasises Voids in Crystal Boundary, AG7 Treated Fe-42% Ni Alloy
with the well-established wetting given to alloys containing this metal. This was confirmed by the "muzziness" noted under the optical and electron microscopic examinations.

(8) An invitation was accepted to submit a chapter for inclusion in a reference book in the powder metallurgy series, currently being edited by Jenkins, I and Wood, J.V. This chapter gives the up-to-date U.K. position on brazing and is based on sections 1-4 of this thesis.

(9) A poster summarising sections 5-6 of this work was prepared for the Institute of Metals "Metals and Materials'89" conference. This presentation has been followed by a full scale technical paper which was submitted to the Institute of Metals in May 1989, and accepted.
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