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THE FORMATION OF BRITTLE PHASES IN BRAZED ZIRCONIUM JOINTS

by

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DECLARATION

While registered as a candidate for the degree of Doctor of Philosophy, the author was not registered for another award of the CNAA or of a University during the research programme.

In connection with the research, the author undertook advanced studies in Deformation Theory in partial fulfilment of the requirements for the degree.

ABSTRACT

THE FORMATION OF BRITTLE PHASES IN BRAZED ZIRCONIUM JOINTS

by J C Bassett

The purpose of the study was to investigate the metallurgical interactions that occur during the brazing of zirconium with Ag-28Cu filler, with particular reference to their effect on mechanical properties. The ultimate aim was to provide information that would aid in the production of tougher brazed zirconium joints than are currently being obtained.

The investigation was carried out in a number of stages:

1. A general literature survey of the metallurgy of brazed joints.

2. Zirconium brazed lap joints were made using either vacuum furnace or high frequency induction brazing. Interalloying was studied by optical and electron microscopy, X-ray diffraction and electron microprobe analysis. Interface layers were produced consisting of Cu_4Zr, $CuZr_2$, $AgZr_2$ and Cu, distributed in a mixture between two sub-layers. Induction brazing produced high quality joints with interface layers thinner than those in vacuum brazed joints; a link between heat-up rate and wetting was observed.

3. Butt joints for mechanical testing were produced to optimum conditions. Instrumented impact testing showed that the toughest joints were those brazed with a reactive copper filler, although in all joints most of the energy absorbed was due to fracture initiation energy.

4. The greater toughness of the reactive copper brazed joints was due to a lack of flaws of any kind in their microstructure, which consisted of a eutectic of CuZr and $CuZr_2$. In contrast, interface layer Ag-28Cu brazed joints contained shrinkage cracks and interfacial voids, along which fracture occurred.

CONTENTS

I INTRODUCTION

1.1 BRAZING - HISTORY, PRINCIPLES AND SCOPE

In the last three or four decades the ancient technology of brazing has been rejuvenated, and the factors responsible for this new lease of life are the application of scientific principles, new processes and equipment, and the availability of a vast number of new filler alloys in many different forms.

The earliest recorded use of brazing dates back to the 3rd millenium B.C. in Ancient Egypt. For example, the copper fittings on the canopy of the sarcophagus of Queen Hetep-Heres were brazed using silver, a method still used today; and by the 2nd millenium B.C. brazing was being widely used in jewellery. Later developments saw the introduction of alloy fillers around the 11th century A.D., in China and India. These fillers were brasses, from which the term 'brazing' is derived.

The modern definition of brazing is a process carried out at a temperature above 450°C, but below the melting points of the materials being joined, with a molten filler metal which is distributed through the joint-gap by capillary penetration; below the purely arbitrary temperature of 450° the same process of capillary joining is known as soldering. The feature of capillary penetration distinguishes brazing from the braze-welding method (in which a joint is achieved purely by the building up of a fillet) and is the key to the rapid production of a quality joint. How effectively it occurs is related to the degree to which the filler will 'wet' the base material: wetting may be thought of as the ability of a liquid to flow over a solid and adhere to it under the force of gravity, and it plays a central part in the brazing process.

Traditionally, the role of brazing has been in basic manufacturing industry, but its application in this sphere may be contracting. Consider, as an example, the electric kettle: originally brazing found extensive use in the manufacture of these items, but since they are increasingly being made from injection-moulded plastic and by other methods the need to join metal is becoming a thing of the past in kettle manufacturing, and this pattern has been repeated elsewhere. On the other hand, in advanced technology engineering brazing has never been more popular, and in the aerospace and nuclear industries in particular the process is increasingly specified for its versatility and cleanliness. Joints may be made without distortion or gross metallurgical changes in the base metal; and dissimilar metal combinations joined relatively easily, a task usually impossible by welding. Parts may be joined which are delicate and of awkward geometry. Brazing is very popular in space vehicle construction: the Apollo Command Module, the Viking Mars lander and the Space Shuttle all embodied many brazed joints.

1.2 THE REACTIVE METALS

The reactive metals titanium, zirconium and beryllium have made the transition from laboratory curiosities to important engineering materials since the end of the last world war. A combination of high strength, lightness and excellent corrosion resistance make titanium and its alloys ideal materials in aircraft construction, marine engineering and chemical plant, whilst zirconium is principally used in the nuclear industry. Beryllium finds application in both the nuclear and aerospace industries on account of its low density and stability in radioactive environments.

Zirconium itself is a common and widely distributed element in the earth's crust, and its principal ore is the silicate, zircon, of which the richest deposits are in the USA and Australia. Although its existence has been recognised earlier, it was not until 1824 that the metal was isolated, by Berzelius, and one hundred years later van Arkel and de Boer devised a technique of producing ductile zirconium. Further work by Kroll led to the current production process which bears his name.

Both the van Arkel (or Iodide) process and the Kroll process are based on the intermediate formation of a zirconium halide and its subsequent reduction - by thermal dissociation in the van Arkel process, and by chemical reduction (using magnesium) in the Kroll process. High cost inhibited large scale production, until the arrival of atomic power caused renewed interest in the metal as a material for the construction of nuclear reactors. Zirconium has a high melting point, excellent corrosion resistance, and a low neutron-capture cross-section, all important factors when considering nuclear reactor construction. As a result remarkable progress was made in the development and production of a wide range of zirconium alloys.

1.3 REASONS FOR RESEARCH BEING REPORTED

In industry, fabrication of zirconium, titanium and beryllium is frequently by brazing for the reasons previously discussed, but there are difficulties. Due to their chemical reactivity they form brittle intermetallic compounds with most filler metals, resulting in joints with inferior mechanical properties as a result of the intermetallic formation between base and filler metal. This problem has long been recognised, but there seems to be no complete cure. Most work carried out on the subject has been empirical, usually correlating joint strength reduction with the extent of intermetallic formation; a fundamental study of the problem would be worthwhile.

At the Atomic Weapons Research Establishment, the collaborators on this research, brazed joints are made in a variety of combinations involving reactive metals, and there is concern with respect to their impact strength. The system principally of interest is a beryllium to Monel 400 joint, and this research project was initiated to investigate the problems of brazing beryllium and the other reactive metals. However, beryllium itself could not be used in the investigation due to its toxicity, and instead zirconium was chosen as a proxy. Both metals form intermetallic compounds and low melting-point eutectics with other metals. Also, there are situations where brazed zirconium joints are specified.

1.4 AIMS OF THE WORK

The aims of this investigation are as follows:

1. To develop a means of producing brazed zirconium joints suitable for mechanical testing.
2. To generate a better understanding of the formation of intermetallic compounds in brazed zirconium joints and their subsequent effects on joint toughness and general soundness.
3. To explore ways of producing stronger joints in zirconium.

II LITERATURE REVIEW

2.1 GENERAL

The purpose of this section is to review the fundamental theory and practice of metal brazing technology, and the mechanical properties of a brazed joint, with particular reference to reactive metal brazing. Existing literature relevant to the investigation being reported is not very extensive, and much of the information presented here is derived from reviews of past and present industrial practice, with only a proportion from published accounts of formal scientific investigations.

2.2 FUNDAMENTALS OF WETTING AND FLOW

2.2.1 Liquid - Solid Interaction

In the Introduction reference was made to the importance of wetting in brazing and soldering. In order to better understand the wetting process and the role it plays in a brazing operation, the forces involved in the simple case of a liquid coming into contact with a solid surface must be examined in detail. When such a situation arises, changes involving the surface free energies of both liquid and solid occur. The overall free energy change that occurs is called the work of adhesion. W_{adh}, which is given by the Young-Dupre equation:

$$W_{adh} = \gamma_S + \gamma_L - \gamma_{S/L} \tag{1}$$

where γ_S is the surface free energy of the solid, γ_L that of the liquid, and $\gamma_{S/L}$ that of the solid-liquid interface. Surface free energies, which derive from unsaturated atomic bonds, are expressed in units of Jm^{-2}, and are numerically equal to their corresponding surface tension forces (expressed as Nm^{-1}), so that the two may be regarded as equivalent. Arising from this analogy is the Young Wettability Equation (Eq.2, Fig 1) which represents the balance of the three surface tension forces involved in the system:

$$\gamma_S = \gamma_{S/L} + \gamma_L \cos \theta \tag{2}$$

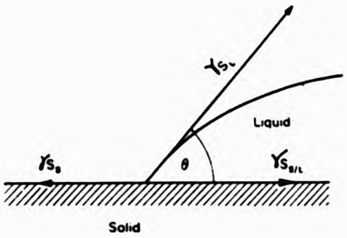

Figure 1: Configuration of forces at equilibrium

Under conditions of stable chemical thermodynamic equilibrium, wetting will occur when a drop of liquid is placed on a solid surface whose surface free energy/tension is greater than that of the liquid and an interface forms. Partly under the influence of gravity, the interfacial area will then continue to extend until the state of equilibrium represented by Equation (2) is attained; this process is called flow. From Equation (2), the specific interfacial free energy $\gamma_{S/L}$ is equivalent to γ_S reduced by a quantity equal to $\gamma_L \cos\theta$; in turn, this degree of reduction is equivalent to $\gamma_S - \gamma_{S/L}$, which can be regarded as the driving force for wetting. It follows that for an increase in the driving force the contact angle, θ, must necessarily reduce; clearly θ is a direct reflection of the degree of wetting, and may be measured to assess this. Thus one can broadly expect a liquid of low surface free energy to wet only a solid of high surface free energy, but the value of $\gamma_{S/L}$, which depends on the mode of interaction between the two, can radically alter the picture - an important point in metallic systems. If a reaction occurs at the interface, the specific free energy change, dG per unit area, will contribute to the driving force for wetting by reducing $\gamma_{S/L}$:

$$\gamma_S - (\gamma_{S/L} + dG) = \gamma_L \cos\theta \qquad (3)$$

If the overall force for wetting (expressed on the LHS of Eq.(3)) exceeds the surface tension of the liquid, physical equilibrium is no longer maintained: the contact angle will reduce to zero and spreading occurs, ie the liquid surface and interfacial area continue to extend as long as a supply of liquid is available.

In nature, high surface free energy (0.2 - 2.0 J/m²) substances include atomically clean metals, whilst metal oxides and glasses have somewhat lower values, in the order of 0.1 - 0.2 J/m². Low free energy (about 0.05 J/m²) surfaces are typically of carbon-based substances like grease and wax, which have a particularly inhibitory effect on wetting if they are present on the surface of a part to be brazed. Metal oxide surfaces also have insufficient free energy to be wetted by filler metals (in general) and since a layer of oxide is present on all metals to a greater or lesser extent, it follows that for a successful braze, the oxide layer must either be removed or be capable of being penetrated by the filler metal. How this occurs is discussed in Section 2.2.4.

2.2.2 A Free Energy Approach to Wetting

Alternatively, wetting may be viewed via a purely thermodynamic approach using the familiar free-energy equation:

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

Where G is the Gibbs free energy, H is the enthalpy, S the entropy of the system and T the temperature in kelvins. A system represented by Equation (4) is always attempting to lower its free energy (ie ΔG negative) and in liquid-solid interaction this could be effected by the liquid wetting the solid. The entropy (S) always tends to increase during the physical-chemical process, thereby providing a large negative contribution to the value of ΔG, as would raising the temperature (T).

Ultimately the value and sign of ΔG depends on the magnitude of ΔH; if there is some kind of physical-chemical affinity between the atoms of the filler and base metal, heat is liberated and ΔH is negative, so increasing the likelihood of wetting. If there is no affinity and ΔH is positive, wetting is unlikely; but raising the prevailing temperature may alter the value and sign of ΔH, as well as increasing the $T\Delta S$ term - thus making ΔG negative and inducing wetting to occur. However, it may happen that the base metal is wetted at the brazing temperature but on cooling passes through a temperature range in which $\Delta H \geq T\Delta S$. In this case, if the filler is still molten, wetting will no longer be maintained; this may provide one explanation for the phenomenon of dewetting, in which after initial wetting there is a pronounced increase in the contact angle and the liquid retracts into a globule. More generally, however, dewetting is usually attributed to a build-up of impurity atoms at the filler/base metal interface as a result of inadequate surface preparation, or to the formation of low surface free energy intermetallic compounds.

2.2.3 Capillary Flow

The ability of a molten metal to fill a joint-gap and surface imperfections therein by capillary flow is closely allied to its ability to wet the base metal. Capillary flow will only occur if the contact angle is less than 90°, and the lower the angle the greater become the forces for capillary action, but good wetting is not the only condition for flow. Viscosity is also important: filler metals close to a eutectic composition generally have lower viscosity than those with wide solidification ranges.

The vertical height H to which a liquid will rise between two parallel plates of separation d is given by:

$$H = \frac{2\gamma_L \cos\theta}{\rho\, dg} \qquad (5)$$

where ρ is the liquid density. The velocity of the flow V at any height (h) is given by the Poiseuille formula:

$$V = \frac{\gamma_L\, d \cos\theta}{4\eta h} \qquad (6)$$

where η is the viscosity. These deductions broadly describe the behaviour of a filler in a joint gap, but they take no account of interactions between filler and base metal. In practice these interactions often have a dominant effect on brazing behaviour; they include (1) alloy formation between liquid and base metal, (2) erosion and dissolution of the base metal by the filler metal, (3) formation of intermetallic compounds and (4) diffusion of filler atoms into the base metal. These phenomena can change viscosities, solidification points, joint gaps, surface energies, etc.

2.2.4 Principles of Oxide Removal

The need for a filler metal to penetrate the base metal oxide film has already been pointed out in Section 2.2.1. How this occurs is not fully understood, but a number of mechanisms have been proposed and it is likely that in any given brazing process all will be involved to some extent, with one predominating according to the conditions prevailing. Broadly, three categories of oxide removal are recognised based on the method of brazing used:

(i) Flux action Fluxes are substances used to promote wetting in torch or ordinary furnace brazing operations. They are thought to act primarily by chemical dissolution and wastage of the oxide film: once clean metal is exposed under the molten filler, wetting will occur spontaneously, and flow will be aided by the tendency of the filler to undermine the oxide film and lift it off. During the process oxygen diffuses through the flux to the metal surface, so there is a continuous oxide removal-re-oxidation cycle.

(ii) Vacuum/inert gas brazing The primary function of a vacuum or inert gas atmosphere is to prevent further oxidation of the base metal to occur. Traditionally, the mechanism though to account for oxide removal in these processes is that of chemical dissociation of the oxide under the very low partial pressure of oxygen; in some literature graphs of dissociation pressure versus temperature for various oxides are offered as a means for deciding brazing conditions. However, whilst thermal dissociation may occur in low-stability metal oxides (eg gold, platinum) more stable oxides would require absurdly low pressures (of the order in outer space) even at elevated temperatures. Clearly another mechanism must account for oxide removal.

In fact, there are three phenomena which may account for oxide removal in vacuum/inert gas atmospheres. The first is mechanical disruption of the oxide by the filler metal, in which the molten filler seeps to the metal through defects in the oxide film, and subsequently undermines it; such defects could be created by thermal cracking during heat-up. Secondly, a liquid reservoir could be created under the oxide by diffusion of filler atoms through it. Finally, some metals such as zirconium, titanium, copper and iron actually dissolve their own oxide at elevated temperatures.

(iii) Brazing in a reducing atmosphere This is the most clearly understood mechanism since it is based on firmly established chemical principles. An atmosphere (usually hydrogen or some other reducing gas) is employed to chemically reduce the metal oxide in a furnace. For reduction by hydrogen the general chemical equation is:

$$MxOy + yH_2 = xM + yH_2O \qquad (7)$$

2.2.5 Physical Metallurgy of Brazing

The main difference between wetting in metallic and non-metallic wetting systems is the potential for alloying in the former, which may lead to the formation of either a solid solution or an intermetallic compound.

The subject has been the focus of some disagreement over the past four decades; the generally held view is that some degree of alloying is an essential pre-requisite for wetting to occur in metallic systems, but this is debatable. In 1951, Bailey and Watkins (1) tested a large number of metallic combinations and concluded empirically that mutual solubility, or the formation of intermetallic compounds, was a necessary condition for good wetting. Schatz (2) went further and postulated that the free energy of alloying provided the driving force for wetting, but did not explain this connection. In 1966, however, R J Klein Wassink (3) showed theoretically that while wetting is indeed associated with interalloying, the alloying energy does not provide the driving force; instead both alloying energy and wetting are concomitant effects dependent on the same atomic properties.

The view that mutual solubility is an absolute necessity for wetting is also opposed by H H Manko (4). Asserting that no "alloying" of any kind occurs in non-metallic systems, he cites the work by Jordan and Lane (5), who found that liquid sodium is capable of wetting solid tantalum and niobium without any alloying reactions occurring. It is worth pointing out here that the surface free energy of liquid sodium is very low, only about one-tenth that of tantalum and niobium - suggesting that the condition for wetting (that γ_S should be high compared to γ_L and $\gamma_{S/L}$) is satisfied by the low value of γ_L rather than by a lowering of $\gamma_{S/L}$. Manko cites the existence of many other wetting systems which have not alloying reactions. The claim that alloying is a pre-requisite for wetting is without foundation.

There is no doubt, however, that in most systems alloying is crucial in lowering interfacial free energy to promote wetting, and the aforementioned work by Klein Wassink provides a clearer insight into the subject. From atomic structure considerations he invoked the quantity W, which is given by:

$$3(E_{AB} - \frac{E_{AA} + E_{BB}}{2}) = 3W$$

where E_{AA} is the bond energy between two A atoms, E_{BB} that between two B atoms, and E_{AB} that between an A and a B atom. 3W may be thought of as representing the overall exchange in bond energy, per pair of atoms A-B, caused by the formation of bonds between unlike atoms when they are mixed, in this case by being brought into intimate contact across an interface. Remembering that bond energies are negative, it can be shown that both the interfacial free energy ($\gamma_{S/L}$) and the enthalpy of mixing (H_m) are proportional to the same quantity W.

Solubility between two elements depends on the entropy of mixing (S_m) as well as the heat of mixing. Mixing occurs when $dG<0$ (where $G = H_m - TS_m$). If H_m has a high positive value, then the term TS_m is insufficient to make $dG<0$ and wetting will not occur, because $\gamma_{S/L}$ will be too high. Such a metal combination has a high value of W. When H_m is small the TS_m, or mixing entropy, term will promote alloying since W, and hence $\gamma_{S/L}$, are small. When H_m is negative, alloying may be excessive, causing erosion of the basis metal to occur. Although the foregoing argument is limited to solid solution systems, it probably still applies, in a qualitative sense, to systems in which intermetallic compound formation occurs.

The above considerations can also explain why the addition of a component to a brazing alloy can often have a dramatic effect in improving its wetting ability on a particular basis metal. For example, the wetting of silver on ferrous metals is very poor, but a small amount of palladium considerably improves it. This is because $E_{Pd - Fe} < E_{Ag - Fe}$; when palladium is added to silver the relatively high-energy Ag-Fe bonds at the interface can be replaced by lower energy Pd-Fe and Pd-Ag bonds. Since palladium is soluble in most metals many brazing alloys containing it have been developed.

A further point in Klein Wassink's work concerns the effect of liquid surface area geometry on joint filling. In the case of lead-tin solders, wetting is promoted by the tin, although maximum wetting (ie the lowest value of θ) occurs with alloys of only 60% tin. Measurements of γ_L of the system show that addition of lead lowers γ_L, whilst calculations indicate that addition of tin lowers $\gamma_{S/L}$; although increasing lead content raises $\gamma_{S/L}$, this is overcompensated by the decrease in γ_L until 40% lead is reached. If the solder penetrates into a gap, however, different circumstances prevail. The change in surface free energy/cm^2 in this case is given by $\gamma_S - \gamma_{S/L}$, and γ_L has little influence because the surface area does not change; maximum penetration of lead-tin alloys is thus at 100% tin. Clearly, simple "spread of a drop" wetting tests may not be sufficient to predict the real joint-filling capacity of a filler alloy.

To summarise, wetting will occur when a high value of γ_S is combined with low values of γ_L and $\gamma_{S/L}$. In non-metallic systems wetting results from the fact that γ_L is generally much smaller than γ_S; there is no "alloying" to lower $\gamma_{S/L}$. Thus water will readily wet the high free energy surface of glass, but will not wet the hydrocarbon-rich surface of an apple. In metallic systems, however, γ_L is generally not much lower than γ_S, and alloying is required to reduce the value of $\gamma_{S/L}$ to effect wetting. Hence systems where there is no potential for alloying generally do not display wetting, but exceptions can occur when the value of γ_L is very low compared to γ_S - such as the example of liquid sodium on niobium previously discussed.

2.2.6 Intermetallic Phase Formation

Intermetallic compounds are intermediate phases whose properties vary from metallic to typically non-metallic. Their bonding is rarely truly metallic in character, and they tend to have more or less fixed chemical compositions. Physical properties are typical of non-metals: they are very hard and strong, but with little or no capacity for plastic deformation, making them brittle materials; they have high melting points and generally poor electrical conductivity. Broadly, there are two ways in which intermetallic formation can occur in a brazing operation as a result of alloying between filler and basis metal:

(i) the melting point of the filler and the brazing temperature are above those of the compounds and any associated eutectics between them. In this case the compounds will solidify in the filler metal on cooling.

(ii) the melting point of the filler and the brazing temperature are below those of the compounds and their eutectics. This is the more common situation: during brazing, the compounds will most likely solidify simultaneously with their formation as a stable interface layer between the basis metal and the filler, provided that the layer is in equilibrium with the liquid.

The latter situation, in which the reactants are separated from one another by continuous layer reaction product, is quite a common one in materials technology, and may be compared with high temperature oxidation. Because it is by far the more common mode of intermetallic formation in capillary joining, it deserves special attention. A recent theoretical study of interface-layer type reactions has been made by V I Dybkov (6), in which a theory is proposed to account for interface layer growth. Existing models of an interface layer growing by the diffusion of reactants through it predict parabolic growth-rates, which, for single-compound layers at least, are observed experimentally. Their magnitude can be determined by two possible processes: the rate of diffusion of reactants through the interface layer, and the rate at which they react on reaching the reaction interface. Dybkov's criticism of existing theories is that they take no account of the latter process, which his is claimed to do. For single-compound layers the chemical reaction process is only significant in the initial stage of growth, when the layer is very thin, and diffusion through the layer is virtually instantaneous. That this stage is usually not measurable in practice is the justification for neglecting the chemical reaction step.

For multi-compound layers, however, the situation is much more complicated. Many deviations from existing "diffusional" theories occur, principally:

(i) Usually only some portion of the growth rate curve is close to a parabola. Initially it is linear.

(ii) From diffusional theory any number of compound layers may be present (as predicted by the phase diagram) which are expected to grow simultaneously. In practice the number observed is one to three, at the most four; they grow non-uniformly.

(iii) According to diffusional theory a compound layer, once formed, will remain, but this is not the case. Often a layer may disappear.

The relationships that Dybkov describes to model multi-compound layer growth continuously transform into each other to give an overall relationship which is very complicated. Fast chemical reactions taking place at the interfaces between different phases are shown to be ultimately responsible for restricting the number of compound layers growing. The growth of a new layer is sequential, not continuous: a new layer will only form when one of the initial phases is completely depleted by chemical reaction.

The model can also take into account the simultaneous dissolution, as well as formation, of an interface layer by the liquid, which could occur in a brazing operation. In such a case logarithmic rather than parabolic kinetics would be expected, and one example of this could be in the brazing of titanium Ti-6Al-4V alloy with silver-based fillers, studied by M S Tucker and K R Wilson (7), in which all growth rates were found to be logarithmic. In contrast, conventional, parabolic growth kinetics in the solid state are exemplified by the growth of aluminium-copper intermetallics, in the diffusion annealing of Al-Cu couples (8), by J A Rayne and C L Bauer. Growth of all phases could be described by the expression:

$$W = Kt^{\frac{1}{2}}$$

Where W = phase width, t = time and K is a temperature-dependent constant.

2.3 BRAZING TECHNOLOGY

In this section the practice of brazing is reviewed with particular emphasis on vacuum and induction brazing, since these are the most important processes in reactive metal brazing.

2.3.1 Process and Procedures

Brazing processes are customarily designated according to their sources of heating. Those currently of industrial significance are as follows.

(1) Torch Brazing is accomplished by heating with a gas torch, normally in conjunction with a flux. The fuel gas is usually propane, town gas or acetylene, and burned with either air or oxygen. Filler metal is either pre-placed or fed in by hand. Although torch-brazing is a versatile process, suited to fabrication, production-line and repair work, its use in advanced-technology engineering is not favoured. Many "new" metals cannot be readily joined by torch brazing; additionally, the finished product requires extensive cleaning, there is a risk of gas absorption (and subsequent embrittlement) in some metals, and the possibility of entrapment of the corrosive flux is considered too great a risk.

(2) Furnace Brazing is usually used in conjunction with a controlled atmosphere often obviating the need for a flux. Most production brazing is done in a reducing atmosphere (see Sec 2.2.4) commonly of pure hydrogen, hydrocarbons or cracked ammonia. However, some metals are prone to absorption and compound formation with these gases, and consequently inert atmospheres (usually argon or vacuum - reviewed later) are often favoured. Inert atmospheres suffer from the

disadvantage that the partial pressure of oxygen can build up around the joint due to oxide decomposition, and even with a flowing atmosphere oxygen purging may not be effective in pockets where the flow is stagnant. Vacuum can avoid these problems, but is less convenient in some respects. An important concept in furnace brazing is that of the atmosphere dew point. As Equation (7) showed, any water vapour present can react with the metal to form metal oxide. To avoid oxidising conditions, atmospheres with low water vapour levels are required, and the amount of vapour is measured by the atmosphere dew point, in °C.

(3) Induction Brazing Reviewed later.

(4) Resistance Brazing works by passing a current across the joint: the high resistance causes rapid heating and melting of the filler metal.

(5) Dip Brazing Salt bath brazing involves dipping the assembly (with filler pre-placed) into a vat of molten salt, which acts as a flux, as well as melting the filler. An alternative form of the process is molten metal bath brazing, in which the pre-fluxed parts are immersed in the molten filler, which flows into the joint.

(6) Infra-red Brazing utilises a high-intensity quartz lamp as the heat source. Exceptionally rapid heat-up rates may be obtained this way.

Besides the above processes there are a number of variations of brazing based upon metallurgical subtleties. They are chiefly used in the aerospace and nuclear industries, and include the following processes.

(i) Diffusion Brazing involves the completed joint being heat-treated to partly or wholly diffuse the filler metal into the base metal; greatly improved strength and raised melting points may be obtained this way.

(ii) Eutectic Brazing may be used to join two dissimilar metals which have a low-melting eutectic between them. The parts to be joined are pressed together and heated above the melting point of the eutectic; diffusion between the two metals will cause the formation of the liquid eutectic which acts as the filler. An example of this process is the brazing of zirconium to steel alloys: the joints are reported to be strong but brittle (9).

(iii) Active Metal Brazing is used for brazing ceramics. A reactive metal is incorporated in the filler: it acts as a reducing agent, converting metal oxide in the surface of the ceramic to pure metal, over which the filler can flow.

Whatever approach is adopted, a feature common to all is the necessity for clean, oxide-free surfaces to ensure sound joints of uniform quality. It is imperative that all grease, dirt and thick oxide scale are removed before brazing, and to this end both mechanical and chemical means of pre-treatment may be used. Mechanical methods include filing, wire brushing and grinding; chemical pre-treatment can be quite complex, and usually involves a process of grease removal (by solvent cleaning, vapour degreasing, etc) followed by pickling with suitable reagents.

For fluxless, controlled atmosphere brazing, the cleaning pre-treatment is of particular importance since fluxes partly make up the cleaning process. Cleaning must be more thorough, and if brazing is not to follow cleaning within about two hours the cleaned components should be preserved and protected. Indeed, the use of "clean rooms", as in the micro-electronics industry, may even be used to guard against contamination.

2.3.2 Vacuum Brazing

Vacuum brazing emerged around thirty years ago as a tool for the production of space hardware, but is nowadays much more widely applied. Nevertheless the high quality results which may be obtained from the process still make it a favoured tool in the aerospace and nuclear industries.

Vacuum is very effective in purging fine capillary gaps. In addition, the risk of gas absorption is virtually eliminated, and very low dew-point (around -90°C) atmospheres may be obtained routinely. Oxygen levels compare favourably with ultra-pure argon atmospheres. The main disadvantage of vacuum-brazing is the risk of volatilisation of high-vapour pressure elements in either filler or base metals, but this can be avoided. High vacuum pumping equipment generally consists of a combination of mechanical and vapour diffusion pumps which provide an operating vacuum in the region of 10^{-3} N/m^2 - 10^{-7} N/m^2 in most furnaces; the maximum tolerable pressure for successful brazing depends on a number of factors, but in general is around 10^{-1} N/m^2.

Commercial vacuum-furnaces are of two kinds - hot-wall and cold-wall. Hot-wall furnaces consist of a sealed retort, or tube, containing the work load, with a conventional furnace outside the vessel; heating and cooling rates are relatively slow with this configuration, which consequently is now used only for small scale production and laboratory work. Larger industrial furnaces are of the cold-wall type, which embody the heating elements, with reflector shields, inside the vacuum chamber.

At the present, vacuum brazing furnaces are limited to batch-type or semi-continuous production, but it seems that fully continuous furnaces will become available over the next few years.

2.3.3 Induction Heating

The principles underlying induction heating have been known for about one hundred years, and its use as a method of brazing is well established. It is a clean, very cost-effective process in which heating is usually developed directly in the work-pieces and, because it is relatively fast, factors such as oxidation, distortion and grain growth in the base metal of the work-pieces can be minimised.

The theory of induction heating is that of a power transformer. When a metal work-piece is placed in a coil supplied with alternating current, the two are linked by an alternating magnetic field, so that a current is induced in the metal, heating it up. The coil itself is water-cooled and remains cold.

The density of the induced current is greatest at the surface of the work-piece, reducing as the distance in from the surface increases. This phenomenon is called the 'skin effect' and the 'skin depth' is the depth into the work-piece in which 90% of the total energy is induced. Two factors determine the value of the skin depth - the material itself (specifically its resistivity and relative permeability) and the frequency of the heating current, which is typically about 200-500kHz for many machines. For most of the applications of induction heating the skin effect is a positive advantage, but where through-heating is required a deeper skin depth may be more desirable. Mains frequency (50Hz) machines may be used for this purpose.

The efficiency with which a metal may be heated in an induction coil also depends on its resistivity and relative permeability. Metals which are magnetic, and/or have high resistivity are heated best, and the following formula can be used to calculate the induction heating efficiency of a metal:

$$\eta = \frac{1}{1 + \frac{\rho c}{\rho w} \cdot \frac{1}{\mu w}} \qquad (\quad)$$

where η = efficiency; μw = permeability of the work-piece
ρc = resistivity of the coil metal
ρw = resistivity of the work-piece metal

Some calculated efficiencies are:

Steel (below the Curie point, 750°C)	97%
Steel (above the Curie point)	71%
Zirconium	84%
Copper	50%

The rate of heating is also dependent on the operating frequency: the magnitude of the induced current is directly proportional to the frequency. Besides using an increased operating frequency (which may require more expensive equipment) heating rates may be increased by using a model with greater power output, but his is often not as simple as it seems, and the specification choice for an induction heater can be a complicated decision.

Coil design is a very important factor, as it strongly influences the heat-up characteristics of the work-piece. Output power is distributed per turn of the coil, so that the induced current may either be localised and concentrated, or spread out and weaker. Equally important is the couple. which is the gap between the work coil and the work-piece. By varying the couple from close (small gap) to loose (wide gap) the heat input may be raised or lowered.

Properly applied, induction heating can offer a variety of improvements over more conventional means of brazing, but there are disadvantages. Tooling and coil configuration have to be adapted to each fresh application, robbing it of some of the flexibility of furnace brazing. Jigging and fixturing can be an awkward problem; obviously, any metal parts of a jig inside the magnetic field will heat up, and even if this does not cause warping of the jig it could still create a 'shadow' effect on the work-pieces. Non-metallic jig materials may be used to avoid this difficulty, but there may be other problems of manufacture and mechanical properties.

An area where induction heating technology has definitely lagged behind furnace brazing is that of temperature control. Modern electric furnaces now incorporate sophisticated microprocessor-based controllers as a matter of routine, but in most induction heaters temperature control is nothing more sophisticated than a knob to control the power admitted to the coil. Close-loop control methods (involving infra-red cameras, fibre optics, etc) are available but the equipment is expensive, and still not generally recommended for brazing.

2.3.4 Miscellaneous Considerations

2.3.4.1 Filler Metals

For satisfactory use as a filler, a metal or alloy should be able to:

(1) Wet and flow over the base metal and form a strong bond with it

(2) Demonstrate suitable properties to permit its distribution by capillary action in properly prepared joints.

(3) Retain its composition and homogeneity when molten under the brazing conditions to be encountered.

(4) Produce a joint that will meet service requirements, principally strength and corrosion resistance.

(5) Melt at a temperature which is appropriate to the process used and the metal to be brazed.

Filler metals may be either a pure metal (eg copper) or, more usually, an alloy, the latter of often a eutectic or minimum melting point system. Small alloying additions may often be made to improve properties such as wetting and corrosion resistance. For merchanised brazing filler metal is supplied in a form designed for pre-placement in the joint; such 'preforms' include rings, washers, discs etc.

2.3.4.2 Joint Design

Many variables are to be considered in the selection of a joint design - principally the fabrication process and the strength requirements. Although there are many permutations of joint design there are two basic kinds: the lap joint and the butt joint. In general, the former is to be preferred on the grounds of mechanical stability, a subject discussed further in the next section (2.4).

Given the right filler metal, a properly designed and produced joint will possess high-strength and good resistance to impact loading. The most important point in reaching this objective is the elimination of stress concentrations, by ensuring the formation of proper fillets and by incorporating smoothly radiused transitions in the design.

When considering the design of a joint and any associated jigging, it is important that attention is paid to the effects of the filler melting. Preforms should never be placed between two components unless the latter are free to fall together, or will be pushed together as the filler melts, otherwise voids may form and fillets will be poor. Voids may also form if any entrapped air is not free to escape from the filler. When calculating the volume of the filler metal to fill a particular gap it is a good idea to add 25%, to ensure good fillets, etc.

2.3.4.3 Joint Gaps

The specification and provision of a particular joint clearance in a braze is an integral part of the overall design of a joint, and an important one too, since the joint clearance (the distance between the mating surfaces of the joint) generally has a potent effect on the mechanical properties of the joint. Typical curves of joint strength versus joint clearance for a braze show the strength ascending with decreasing clearance to an optimum value, after which the strength drops off rapidly when very small clearances are obtained. However, the optimum clearance with respect to mechanical properties may not be the clearance eventually selected, as a number of other factors must be taken into account. These are chiefly the potential for capillary action (which is a function of filler viscosity, joint gap etc - see section 2.2.3); intermetallic phase formation, and joint gap changes at temperature when dissimilar base metals are involved. Both a high filler metal viscosity and intermetallic phase formation require increased joint clearance.

The method of fluxing also has an important bearing on joint clearance. When mineral fluxes are used, filler metal cannot force out the molten flux when clearances are very small; gas-phase fluxes (ie atmospheres) suffer no such problems, however, and consequently joint clearances may be made smaller, with correspondingly increased joint strength.

2.3.4.4 Dissimilar Metal Combination

Many dissimilar metal combinations may be brazed - in fact this is one of the prime advantages of the process. The foremost consideration to be made is the effect of differential thermal expansion when ring and plug type joints (or those of a similar geometry) are brazed. It is an invariable rule that the base metal having the greater co-efficient of thermal expansion is used as the female joint-half, so that the filler will be left in a state of compression rather than tension on solidification. Other factors have to be considered too: the filler metal has to be compatible with both base metals, and attention must be paid to the increased likelihood of galvanic corrosion.

2.3.4.5 Residual Stresses

The creation of residual stresses, joint distortion and cracking is a much less serious problem in brazing than in welding processes. Nevertheless the problem can occur, and causes include:-

(1) The use of jigs or joint designs which constrain natural expansion and contraction.

(2) The use of materials of too hard a temper.

(3) Excessive heating/cooling rates.

(4) Selection of a filler metal not compatible with the base

2.4 MECHANICAL PROPERTIES OF BRAZED JOINTS

2.4.1 General Considerations

The mechanical properties of brazed joints constitute a very important but by no means firmly understood aspect of brazing technology. The response of a brazed joint to stress is complicated (by virtue of its being a heterogeneous body), affected by a wide range of factors, and consequently not readily amenable to analysis. As a result the subject is a rather vague body of knowledge: there is a tendency for views and conclusions expressed in the literature not to concur, and empirical investigations of joint strengths tend to be divorced from theoretical treatments. Theoretical work has largely been confined to stress distribution in joints under elastic strain, since their behaviour under plastic strain is considerably more difficult to analyse;

unfortunately it is their plastic behaviour and UTS which are more of interest, particularly in view of the important ability of most brazed joints to undergo some localised plastic deformation to re-distribute stress. A review of recent theoretical approaches to joint stress behaviour has been made by R M Trimmer and A T Kuhn (9).

2.4.2 Factors Affecting Joint Strengths

A commonly held view is that the strength of a brazed joint is primarily determined by the filler metal strength; indeed there are national standards (eg DIN 8525) which quote filler strengths as a tentative means of predicting joint strength. However, although it may be important in some brazing systems (10), filler metal strength probably plays a minor role generally; Schwartz (11) dismisses its importance completely. The factors having a dominant effect on joint strength are listed below:

(1) Composition and mechanical properties of the base metal.
(2) Joint configuration.
(3) Joint clearance.
(4) General quality of brazing and joint design. The importance of good fillets and smooth transitions has been discussed in Section 2.3.4.2.
(5) Type of stress system.
(6) Metallurgical changes due to interaction between filler and base metal, as described in Section 2.2.3.

Items 2 and 5 are clearly interactive. Butt joints are weak in tension, lap joints suffer in fatigue (9); impact loading, under which brazed joints seem endemically weak, is particularly pernicious. Item 6 tends to be overlooked in reviews, but can be very important: diffusion between filler and base metals can account for outstanding mechanical properties (12), while the formation of intermetallics may have the reverse effect.

2.4.3 The Response of Joints to Stress

The butt joint loaded in tension is probably the most commonly investigated system. From a theoretical approach, based on thermodynamics and interatomic forces, Milner and Apps calculate the work required to remove a layer of braze metal from the base metal (13). The exercise is probably of little practical use, but does show that under tensile loading a butt joint with a filler metal of lower strength than the base metal will fail inside the filler itself. Generally, this seems to be the case in practice.

An important factor in relation to the tensile strength of brazed joints is the effect of constraint, encountered when the filler is much softer than the base metal - the usual case. When such a joint is pulled in tension the soft layer of filler metal reaches its yield point long before the hard base metal stock, but is prevented from contracting plastically by virtue of being bonded to the base metal, as shown in Figure 2:

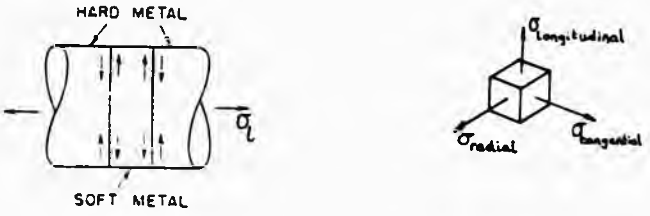

Figure 2(a) The stress configuration in a butt joint in tension, and
(b) The stress distribution in an element of the filler.

The result is a state of triaxial tension: in addition to the longitudinal stress imposed by the loading, the effect of constraint gives rise to a tensile radial stress and a tensile tangential stress in the filler. As one approaches the filler/base metal interface inside the filler, the hydrostatic component of the stress system is increased at the expense of the shear component, progressively raising the yield strength of the material by reducing its ability to fail by plastic deformation.

The effect is clearly least along the centreline of the joint (where the effect of constraint is experienced least) but may be increased there by reducing the joint clearance. The result of this will be to raise the minimum yield strength of the filler and hence increase the tensile strength of the joint; and in the limiting case of zero joint clearance, the strength of the joint will, in theory, approach the brittle fracture stress of the filler metal. In practice, the strength of the joint might be limited by the yield stress of the base metal before this point is reached.

It is this effect of constraint which is thought to account for the observed variation of joint strength with clearance, and why the preferred failure site is along the centreline. It has been studied by

N Bredzs and H Schwartzbart (14), whose results showed that joint strength reached a maximum and then rapidly dropped off at very small joint gaps, but this was attributed to the effect of contact between base-metal asperities. Lautenshlager et al, as quoted by Trimmer and Kuhn, have derived a relationship for the strength of butt joints taking into account the effect of triaxiality due to constraint.

Similar considerations do not apply to lap joints, which are designed to be loaded in shear, as there is no effect of constraint, although ring-and-plug joints may be exceptional. Extensive work in West Germany shows that there are optimum joint gaps, but for reasons of joint-filling rather than any inherent mechanical effect. A more important factor is the length of overlap of the joint: stress analysis and empirical results show that most of the load imposed on a lap joint is taken up by the ends of the joint, and increasing the overlap beyond a certain length (about three to four times the thinnest member of the joint) simply creates a body of filler in the middle which carries no load. Thus unlimited increases in the shear strength of a lap joint may not be obtained.

An important aspect of the strength of brazed joints which receives little attention is impact loading resistance, or "toughness", a term usually used in relation to homogeneous materials. All work on the subject seems to be largely empirical, and an example is that by E Lugscheider et al (15). In this work, 10mm square-section notched stainless steel joints, brazed with gold-nickel alloys, were tested for impact strength at various temperatures. Toughnesses of up to 230J were obtained, which may be regarded as very good for brazed joints. Evidence of diffusion of filler metal atoms into the base metal was found, and fracturing occurred in the fillers. The highest toughnesses were found in joints in which hardening of the adjacent base metal had not occurred - minimising the "notch effect".

2.4.4 The Effect of Intermetallic formation on Joint Soundness

As described in Section 2.2.6, intermetallic compounds are generally hard and brittle, and their formation in a joining operation usually has a detrimental effect on joint soundness. This is particularly true when a non-uniform stress - such as that generated under impact loading - is applied, since intermetallic phases do not have the ductility to allow a re-distribution of stress, and failure occurs at comparatively low loads.

Practical experience of intermetallic phase formation, in joining operations as diverse as flash-butt welding, friction welding and vacuum brazing, shows that intermetallic formation is accompanied by a general deterioration in mechanical properties, the degree of which depending on the extent of brittle phase growth. In investigations of each of the above joining processes, the tensile strengths of joints produced declined in proportion to the degree of intermetallic formation. Only in the work on flash-butt welded Al-Cu couples by Rayne and Bauer (8) was the effect on impact strength assessed: it was found to drop off very rapidly with increasing intermetallic phase-width, and joints with very thick intermetallic layers often broke during handling.

A point emerges here which does not seem to have been noted. Intermetallic compounds are high-strengh materials; the deterioration of impact strength with increasing intermetallic phase-width is understandable, given the complex nature of impact stresses; but the same should not be true for uniform tensile strength, in the same way as the strength of a chain is not affected by the length of its links. The suggestion is that the brittleness of the intermetallics is not the only factor directly responsible for the deterioration in mechanical properties.

In fact, the conclusion of Rayne and Bauer was that thermal cracking played an important part, adducing the presence of cracks in and around the $CuAl_2$ phase where failure usually occurred. As noted in Section 2.2.6, intermetallics have little capacity for plastic deformation, and will tend to crack rather than flow under high thermal stresses. Similarly, J Ruge et al (16), working on the friction welding of copper to titanium, found the presence of extensive cracking in the Cu-Ti intermetallic material produced. This was particularly true when a jumbled mixture of intermetallic phases and base material had crystallised out of a common melt, creating deep cracks and between phases. Glenn et al (17) correlated the tensile strength of vacuum-brazed beryllium to Monel joints with brazing parameters, and noted the tendency for failure to occur in one particular Be-Cu phase; although no evidence of thermal cracking was reported the brittle phase exhibited cracking when micro-hardness tested.

In conclusion, the deterioration in mechanical properties experienced when intermetallics form is caused by the formation of a brittle layer in the joint, and by the defects associated with its formation.

2.4.5 Mechanical Testing - Instrumented Impact Testing

The properties of brazed joints most commonly tested to make and evaluation of joint soundness are tensile, shear and impact strength, the last being especially important in this investigation.

Traditionally, the behaviour of materials under impact loading has been characterised by the use of Izod and, latterly, Charpy testing. The advantages of the Charpy test are the ease of specimen preparation, speed and low cost. However, the information derived from the test is rather limited and of purely comparative value; furthermore the Charpy test measures only the total energy absorbed, which in fact is the aggregate energy of the separate processes of crack initiation, crack propagation, and, in a ductile material, shear lip formation. To improve this situation, and provide a better insight into the load-time fracture characteristics of a material, a test has been developed called the instrumented impact test. The equipment comprises a normal impact tester with a strain gauge mounted on the hammer: when the hammer strikes the specimen, the strain gauge senses the deformation of the specimen (which is reflected by the deformation of the hammer) and the resulting signal is recorded on an oscilloscope in the form of a load-time curve. A schematic representation of such a curve is shown in Figure 3.

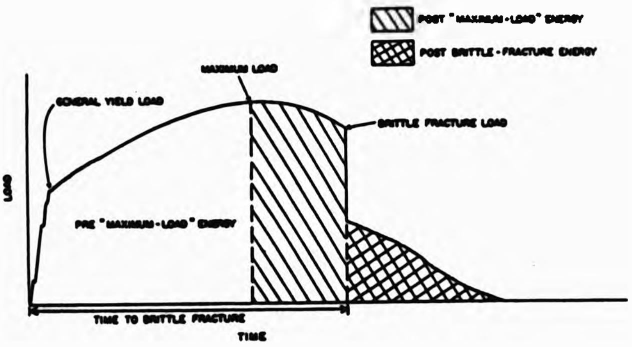

Figure 3: Idealised load-time instrumented impact curve

Figure 3 is the sort of result one would expect from a material displaying a mixed ductile-brittle fracture. The point of "maximum load" marks the formation of a crack, which undergoes stable growth until the "brittle fracture load" is reached, whereupon the crack propagates almost instantaneously. Thus the area under the curve up to maximum load is identifiable with initiation energy; and that up to the brittle fracture load as propagation energy. Post brittle-fracture energy is the energy absorbed by the shear lip formation. Provided various parameters of the tester are known, the load-time curve can be converted to a load-extension one, and the fracture energies calculated by measuring the area under the curve.

The physics of instrumented impact testing is complicated, and theories have been developed which permit further analysis of the information gained from it. In practice the load-time curves obtained are not as simple as that shown in Figure 3. One feature which invariably occurs is an initial discontinuity called the initial loading peak, which has nothing to do with the deformation of the sample, being caused by its inertia as it is accelerated from rest to the velocity of the pendulum. Its height is governed by the factor Z, the acoustic impedance of the material. Errors in curve interpretation can occur when a very brittle specimen is tested as its curve may be totally inside the inertial loading peak. This situation is illustrated in the examples of various schematic curves in Figure 4.

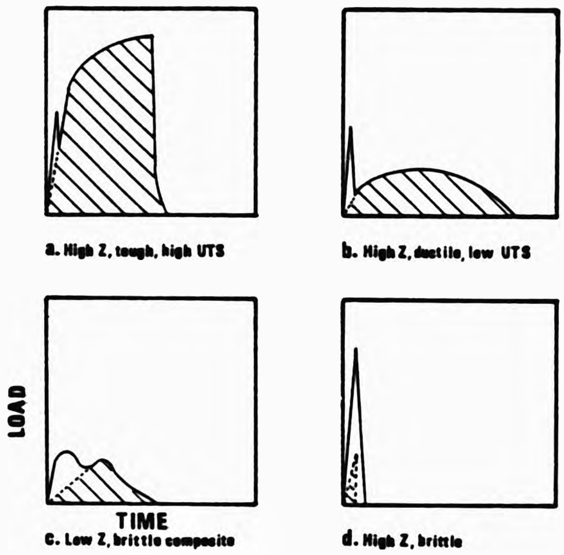

Figure 4: Schematic examples demonstrating the interrelationship of impedance (Z) and mechanical properties for various materials.

Another feature which occurs are series of oscillations, which appear following rapid changes in deflection rate (eg, at the onset of general yielding). Beyond the load-time curve of the sample the trace oscillates widely, due to vibration in the tester; this part of the trace is ignored.

2.5 THE METALLURGY AND BRAZING OF THE REACTIVE METALS

2.5.1 Physical Properties and Metallurgy

Although beryllium, titanium and zirconium are similar in respect of their chemical reactivity, beryllium stands out in having different physical properties and metallurgy to titanium and zirconium, which closely resemble each other. A Group II metal, atomic number 4, beryllium is the lightest engineering metal, with a specific gravity of only 1.8. Melting point is 1,285°C. The principal characteristic of its mechanical properties is its very high Young's modulus, making it vulnerable to fracture by thermal or residual stresses. Beryllium forms intermetallics with most metals with which it has some solubility, but not with the following: Ag, Al, Ga, Ge, In, Si, Sn.

Titanium and zirconium are both Group IVa transition metals with atomic numbers of 22 and 40. Melting points are 1,725°C and 1,800°C. The strength:weight ratio of zirconium is good, and exceptionally good in titanium, which is why its use in high-performance aircraft construction is so widespread. The metallurgy of titanium and zirconium is characterised by an allotropic transus in each metal from

HCP to BCC (the higher temperature form), at 883°C in titanium and 862°C in zirconium. The phase diagrams of titanium and zirconium are sometimes analogous to iron-based systems, having eutectoid transformations; like iron, the higher temperature allotropes can not be retained at room temperature by quenching, but may be by alloying. Metals not forming intermetallics with titanium are: V, W, Y, Zr, Sc, Re, Pu, Nb, Mo, Hf and Cd. Zirconium does not form intermetallics with V, U, Ti, Th, Sc, Pu, Nb, Mg, Hf and Ce.

2.5.2 Phase Diagrams

The phase diagrams of some of the binary systems relevant to the investigation are shown in Figures 5 - 9.

The zirconium - copper phase diagram illustrated in Figure 7 dates from 1953 and shows the presence of five intermetallic compounds; the zirconium-rich end of the phase diagram is strongly reminiscent of the Fe-Fe$_3$C system, with a eutectic and eutectoid. Compared to later versions of the Zr-Cu phase diagram however it seems to be over-simplified: Figure 8 is the latest (1986) version, containing many more intermetallics, and without simple stoichiometries. For example, ZrCu$_3$ is replaced by Cu$_{51}$Zr$_{14}$. Of the silver-zirconium phase diagram there is some uncertainty, but it is known that there are two intermetallics, AgZr and AgZr$_2$, as shown in Figure 9.

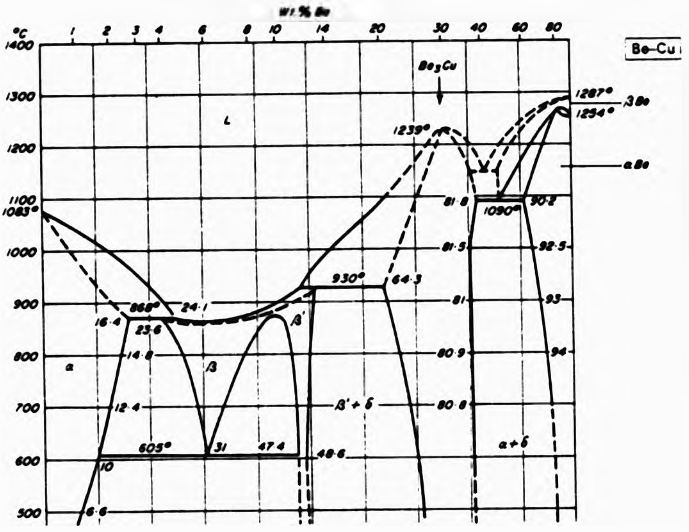

Figure 5: The beryllium - copper phase diagram

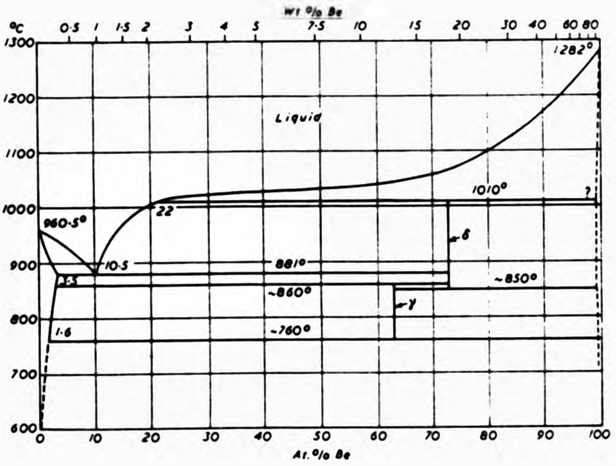

Figure 6: The beryllium - silver phase diagram

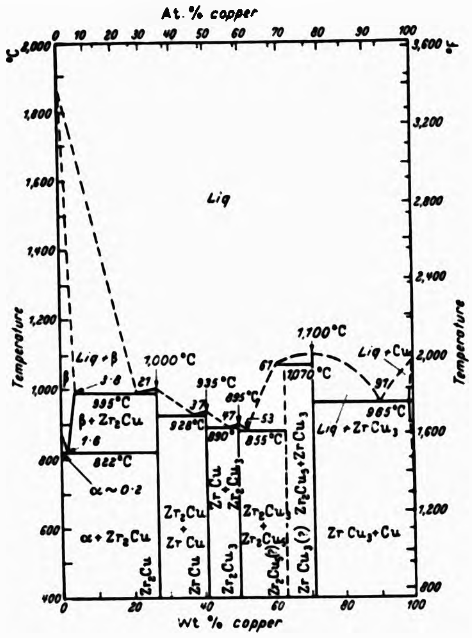

Figure 7: The zirconium - copper phase diagram (old version)

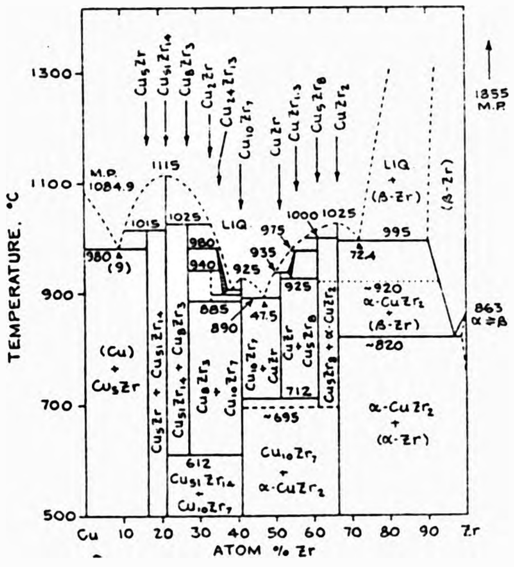

Figure 8: The zirconium - copper phase diagram (1986)

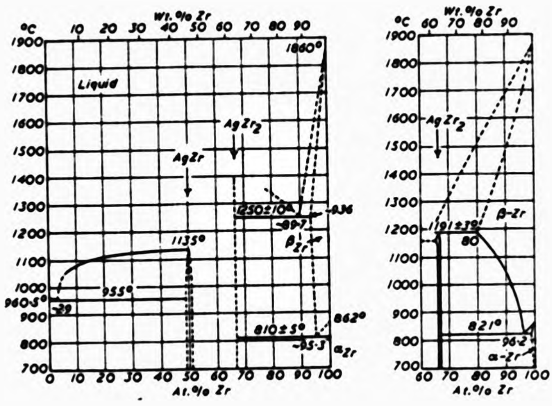

Figure 9: the zirconium - silver phase diagram

2.5.3 Brazing of Beryllium, Titanium and Zirconium

As explained in Section 2.3.4, a filler metal must fulfil several requirements - wet the base metal, melt at a reasonable temperature, etc. In brazing the reactive metals, the problem of intermetallic formation could, in theory, be solved by using filler metals which do not from intermetallics with the base metal. In practice this is usually not possible without endangering the other requirements, although modification with a further alloying addition may restore optimum properties. Instead, the usual approach is to use an intermetallic- forming filler and adopt a brazing procedure which keeps compound formation to a minimum; or, possibly, the base metal could be coated with a 'barrier' metal, but this approach does not seem favoured. The following paragraphs describe some of the filler metals which have been developed for reactive metal brazing.

2.5.3.1 Beryllium

The list of metals with which beryllium does not form intermetallics includes aluminium, silver and silicon, all of which (especially the first two) are important as brazing fillers. Unfortunately the wetting characteristics of silver, aluminium and Al-Si on beryllium are poor (18) and although their use has been reported they are usually used in combination with other, intermetallic-forming elements. A popular example is silver-copper eutectic (Ag-28Cu), which melts at 778°C. Its use has been mentioned in Section 2.4.4.

Beryllium is not an easy metal to braze. It is particularly difficult to wet, and precautions must be taken to guard against its fracture during the brazing heat-treatment. It may be furnace or induction brazed, and best results are obtained using purified argon atmospheres.

2.5.3.2 Titanium

Early work on furnace brazing titanium made use of copper and silver fillers, but they were not very successful. Both caused the formation of brittle intermetallics, and copper brazed joints were severely eroded due to the formation of low melting point eutectics. Later development produced alloy fillers such as Ti-48Zr-4Be, which is particularly successful - zirconium does not form brittle compounds with titanium (the system Ti-Zr has a melting point minimum at 1540°C, with complete solubility) and the small proportion of beryllium added to lower the melting point will form compounds internally, in the filler.

2.5.3.3 Zirconium

The brazing of zirconium is very similar to that of titanium, although the development of filler metals for zirconium has been directed towards corrosion resistance (for use in reactors). The list of metals not forming intermetallics with zirconium is similar to that for titanium, and consists of reactive rare-earths (eg yttrium), radioactive metals like thorium and uranium, and refractories such as niobium. None are suitable as fillers singly, but as alloying additions they offer promise, and again fillers based on Zr-Be and Ti-Zr-Be are reported to be successful. Generally, filler metals based on zirconium itself give the best results for brazing zirconium and its alloys (19) in terms of wetting characteristics, joint soundness and corrosion resistance.

A method was reported for zinc-coating zirconium parts for brazing by prior hot dipping in molten zinc chloride (20), but even though brazing would be facilitated it seems to have remained a laboratory curiosity - probably due to poor heat and corrosion resistance of the joints.

Like titanium, but unlike beryllium, zirconium is most successfully brazed in vacuum atmosphere. Torch brazing for any of the reactive metals is out of favour, but furnace and induction brazing are both used for zirconium. The latter is particularly effective as it can minimise filler/base metal reaction.

III EXPERIMENTAL

3.1 GENERAL

The brazing system of interest to the contractors is beryllium to Monel 400, using Ag-28Cu eutectic as a filler. For the purpose of this investigation zirconium to zirconium, again using Ag-28Cu filler, was decided on as a suitable analogous brazing system from which information could be derived, and possibly applied to the prototype system. There is, however, a major difference in beryllium and zirconium brazing using silver-copper filler - namely that beryllium will form intermetallic compounds only with the copper, whereas zirconium will react with both copper and silver.

The aims of the investigation, as explained in the Introduction, were to elucidate the formation of intermetallic compounds and their subsequent effect on mechanical properties in brazed zirconium joints, and to devise ways of producing tougher brazed joints in zirconium. These objectives constituted a very broad brief, and it was evident from the start that a variety of problems would have to be overcome. Expertise would have to be built up in producing good joints by both vacuum and induction brazing, for which there was no experience at hand to draw on. Joint design was another problem: although there are tentative standard joint designs, they tend not to be used, probably because the suitability of a brazed joint design often depends on the brazing method used. A standard joint design would have to be specified for the investigation.

Although Be-Monel 400 was the system on which attention was originally focussed, another of interest is titanium-318 to stainless steel, using a filler of gold-nickel (Au-18Ni). Thus, as a parallel exercise, further contract work was undertaken with undergraduate project students, in which the brazing of titanium was examined with particular reference to the re-heat characteristics of Ti-318-steel -joints (21). Information from this work complemented and stimulated work in the main programme, and is presented as an integral part of it. In this section, the procedures that were developed to produce joints and test them are described, and the experimental programme explained.

3.2 MATERIALS AND EQUIPMENT

3.2.1 Metals

Zirconium - commercial purity (99.8%) plate and rod. Annealed.
Titanium - commercial purity (99.6%) plate.
Titanium - 318 alloy (6% Al, 4% V, Bal.Ti) plate.
Stainless Steel - En58E (304)(18.5% Cr,, 10% Ni, 0.8% Mn. Bal.Fe).
Ag-28Cu - eutectic filler (vacuum grade). Melting point 778°-780°C (Johnson Matthey Ltd). See Figure 9A.
Au-18Ni filler - Melting point 950°C (Johnson Matthey Ltd).
Copper - commercial purity filler. Melting point 1,083°C.

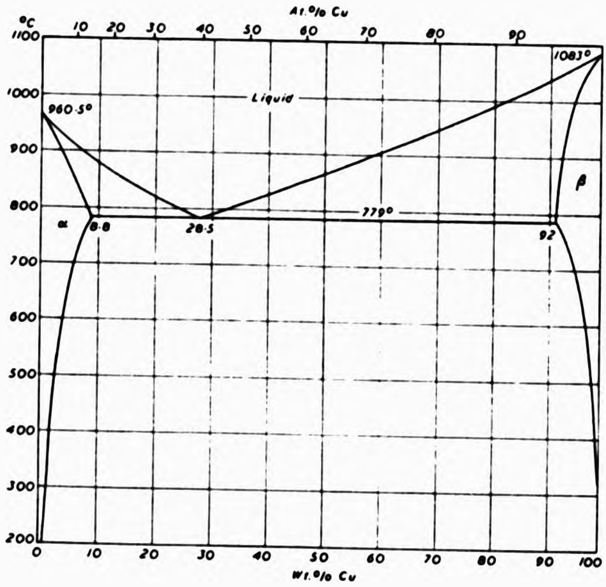

Figure 9A: The Ag-Cu phase diagram. Note eutectic at 28% Cu

The various metal combinations used in the study, together with their experimental purposes, are as follows:

Table 1: Metal Combinations

Type	Base Metals	Filler	Process	Purpose
Lap	Zr-Zr	Ag-Cu	VB	Metallography
Lap	S/S-S/S	Ag-Cu	VB	Metallography
Lap	Zr-Zr	Ag-Cu	RFB	Metallography
Lap	Ti-Ti	Ag-Cu	BV	Re-melting
Lap	Ti318-S/S	Au-Ni	VB	Re-melting
Lap	Zr-Zr	Cu	RFB	Re-melting
Butt	Zr-Zr	Ag-Cu	VB	Mechanical testing
Butt	S/S-S/S	Ag-Cu	VB	Mechanical testing
Butt	Zr-Zr	Ag-Cu	RFB	Mechanical testing
Butt	Zr-Zr	Ag-Cu	RFB	Metallography
Butt	Zr-Zr	Cu	RFB	Metallography
Butt	Zr-Zr	Cu	RFB	Mechanical testing

NB: VB = vacuum brazing; RFB = radio frequency induction brazing.

3.2.2 Joint Design

Two kinds of joints were needed for the experimental programme - small-scale lap joints for metallographic examinaton, and a more elaborate design for mechanical testing. The lap joints consisted of 10mm x 15mm coupons cut from 2mm thick plate, with a shim of filler placed between them. A mild steel clip held the assembly together during handling and brazing. More thought went into the design for joints suitable for mechanical testing: these had to be compatible with the contractors' testing equipment, suitable for brazing by both furnace and induction heating, and be cheap and easy to machine. The design eventually selected was a 55mm long, 10mm diameter cylindrical butt joint with a concentric 5mm diameter hole, making, in effect, a thick-walled tube. There were several reasons for this design: it was the geometry best suited to induction heating (bearing in mind the "skin effect"), allowed flexibility in the type of brazing pre-form used, was easy to handle, and permitted more effective purging. Each 27½mm joint-half was machined by parting off from a length of 10mm diameter stock in a lathe, and facing the brazing surfaces; burring was removed using a fine flat file on the outside, and a needle file in the central bore. The only critical dimension was the external diameter, obtained by specifying a suitable tolerance in the stock, and by this procedure high-quality joint-pieces could be produced in large quantities. Although zirconium is a difficult metal to machine, better results were obtained with it than with the stainless steel.

Two kinds of pre-forms could be used in conjunction with this type of joint: either rings made from wire filler, or flat washers stamped out of sheet. The latter type was preferred, as it was thought it could give better control over the joint gap size.

3.2.3 Vacuum Brazing Equipment

For vacuum-furnace brazing, a hot-wall tube furnace and a top-loading cold-wall furnace were available. The tube furnace was used for brazing lap-joints, and was a 3-zone model manufactured by Severn Science Ltd, capable of operating at temperatures of up to 1100°C. Three independently controlled heating zones gave a continuous hot zone of 150 millimetres, and the Eurotherm 820 master controller ensured temperature control to within ± 5°C. Logic-conrolled vacuum equipment provided a vacuum of about 10^{-3} Pa to 10^{-4} Pa.

55mm butt joints were brazed in the AWRE cold-wall furnace. Manufactured by Vacuum Generators Ltd, this furnace was computer controlled and provided a vacuum of 10^{-3} Pa to 10^{-4} Pa. Since the joint design was a relatively simple one, joints were required to be fully jigged to maintain co-axiality, and for this purpose a mild steel jig was designed and constructed. This is illustrated in Figure 10. Up to twelve joints at a time could be brazed in the jig, and the tolerances allowed zirconium or steel joints to be brazed at temperatures of up to 900°C. After brazing and subsequent cooling, the upper part of the jig could be removed to allow easy removal of the joints; this was usually done after briefly immersing the jig in an ultrasonic bath, to overcome stickiness.

Figure 10: Vacuum brazing jig for 55mm butt joints

3.2.4 Induction Brazing Equipment

A 4kW, 500kHz Radyne radio-frequency heater was available for the work on induction brazing and, as in the vacuum-brazing programme, provision for brazing lap joints and 55mm butt joints for mechanical testing was required. After extensive development work, apparatus for this purpose was conceived and constructed.

The facility designed for brazing lap joints is shown in Figure 11. The joint assembly was placed on a silica glass pillar, located at the centre of the two-turn coil, and enclosed in a chamber made from Pyrex tube. Atmosphere control was provided by a purge of argon through the chamber, exhausting through a narrow sleeve.

The difficulty of controlling the temperature cycle of the process, in the absence of sophisticated equipment, was resolved by exploiting the natural heat-up characteristics of a specimen located in the work-coil. As the rate of heat loss from the specimen approached equilibrium with that of the heat gain, a near stable "plateau" temperature was attained which, by adjusting the power control, could be made to coincide with a suitable brazing "window" of temperature and time. Sample heating cycle curves were recorded using a platinum/platinum-rhodium thermocouple, spot-welded to a dummy test-joint and connected to a chart recorder. Examples of such curves are shown in Figure 12.

There were, however, difficulties with this approach. The sample curves obtained were consistent but with a systematic error; closer representations were made by making a correction based on the measured time of melting of a shim of filler in a trial braze. Secondly, even the lowest power output in the coil could not prevent excessive temperature rise in the heat-up curve, represented by Curve A in Figure 12; joints brazed thus were found to be over-heated. However, maintaining the flow of argon at a high rate throughout the brazing cycle had the effect of creating a sharp levelling-off of the temperature rise, represented by Curve B. This curve seemed close to

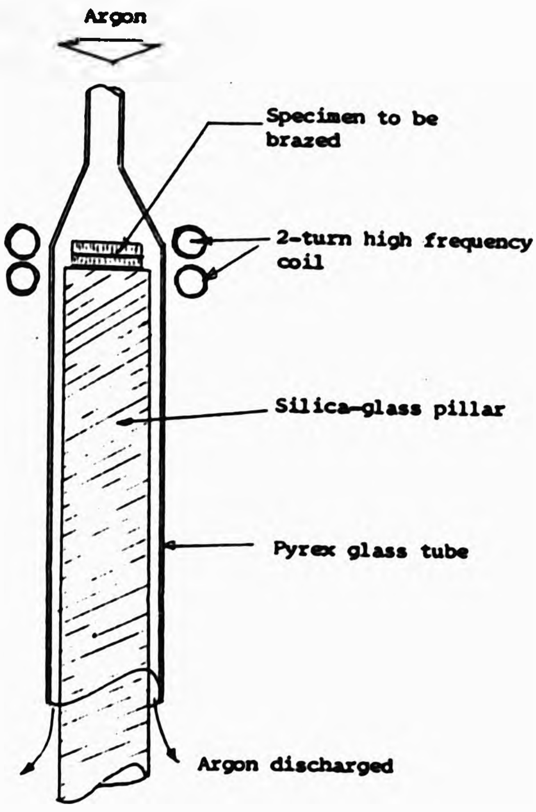

Figure 11: Apparatus for induction brazing lap joints (x½)

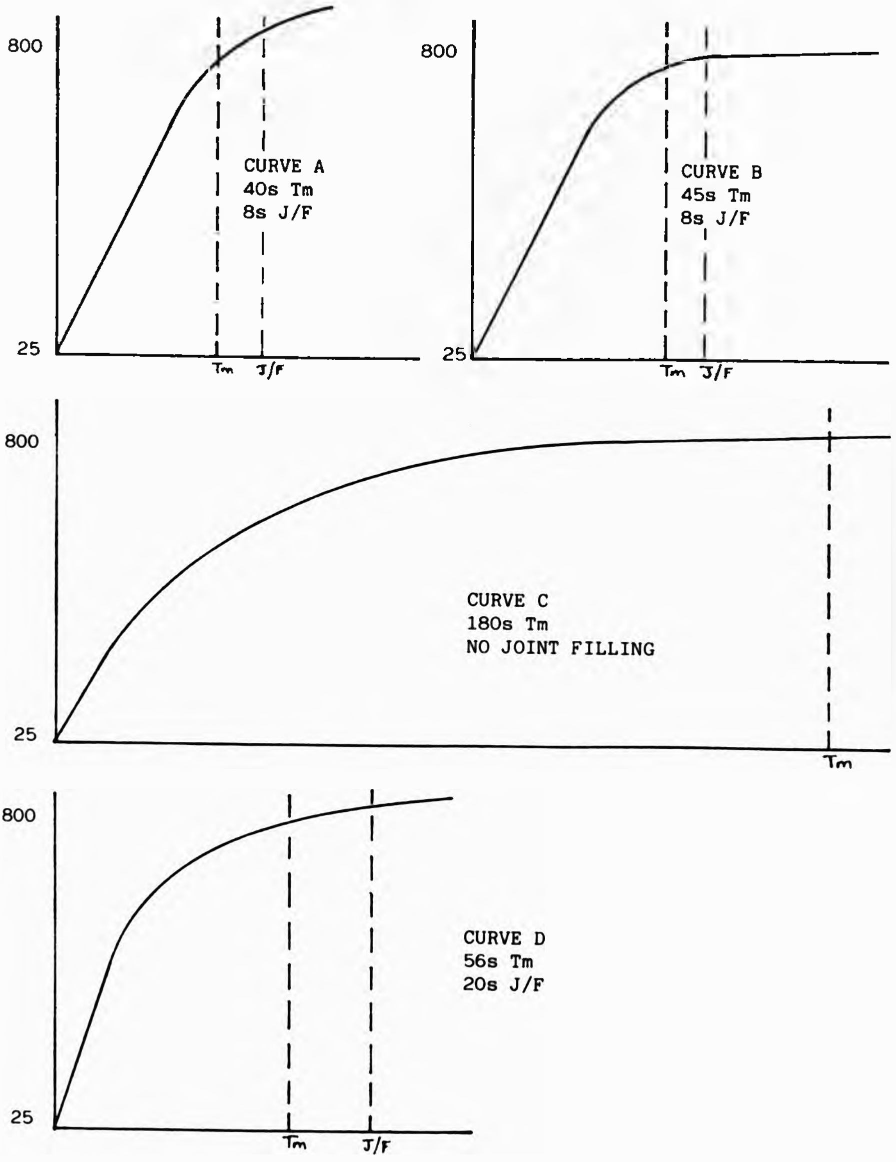

Fig. 12: Induction heating simulation curves. The vertical dotted lines represent time to melting (Tm) and time for joint filling (J/F).

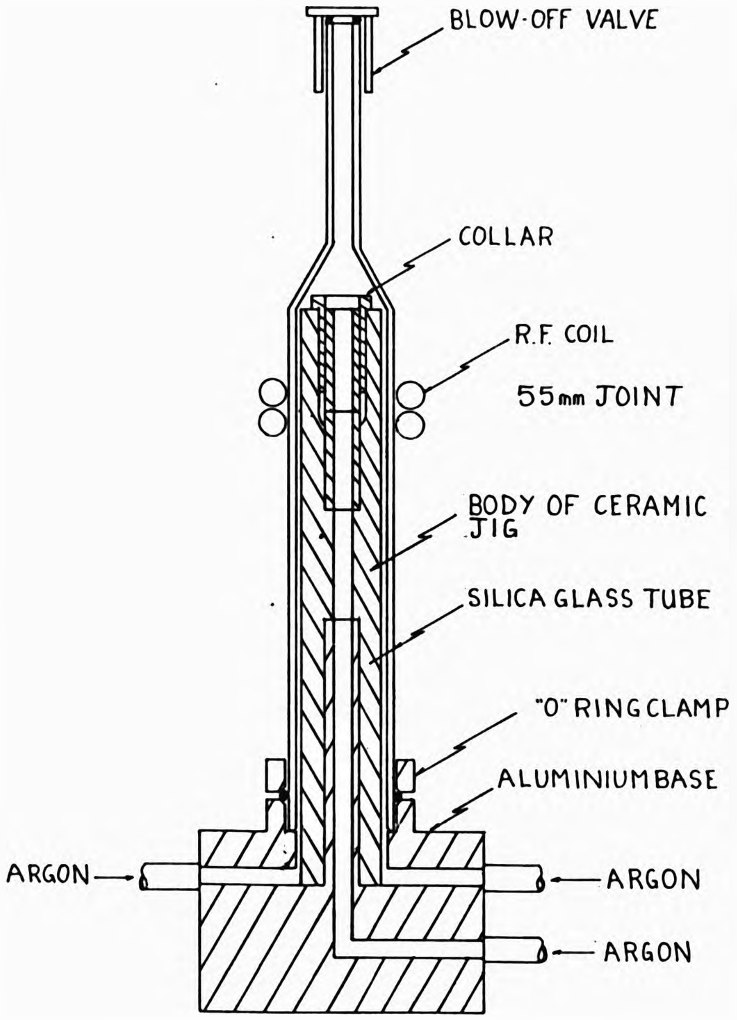

Figure 13. Induction brazing facility for 55 mm joints.

an ideal, producing joints of exceptional quality, but another problem arose. Frequently wetting could not be obtained; either the braze would proceed very successfully or not at all. Eventually, this behaviour was traced to the positioning of the filler shim in the joint: shim placed near the edge of the joint wetted, but shim in the middle of the joint exhibited complete non-wetting (180° contact angle). Since the rate of heating was much higher at the edges of the joint (due to the "skin effect") this suggested that wetting was associated with the rate of heating through the melting-point - a conclusion substantiated by further experience.
Successful experience of induction brazing lap joints led to the development of a scheme for brazing 55mm butt joints, a more complicated task. As in the programme for vacuum brazing butt joints, full jigging would be necessary; but the use of steel as a jig material was out of the question for the reasons outlined in Section 2.3.3, and after some abortive experiments with glass and copper it became clear that only a ceramic jig would suffice.

The ceramic chosen was silicon nitride, a material possessing good toughness and machineability, and excellent resistance to thermal shock; tolerances may be made as close as ± 5mm. A design for the jig was prepared, and made up by A E Developments Ltd (now T&N Technology) of Rugby. Trial runs with the new jig, enclosed in a glass tube, showed that a simple argon flow down the chamber was not an effective purging procedure: the system was therefore modified so that the chamber was initially vacuum pumped down to 1.3 Pa, before argon under pressure was admitted. The flow was directed upwards, through the

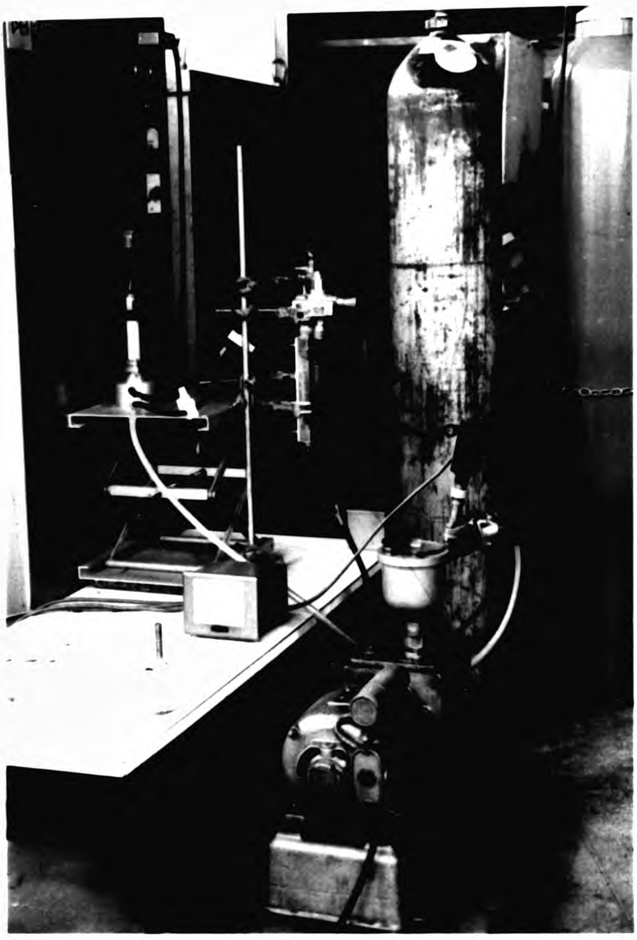

Figure 14: Facility for induction brazing butt joints

Figure 15: Same. Close-up of jig

central bore of the joint as well as over its exterior, exhausting via a blow-off valve at the top of the vessel. Removal of the joint after brazing was facilitated by a removable collar in the jig. The complete facility developed for brazing butt joints is illustrated diagrammatically in Figure 13, and pictorially in Figures 14 and 15.

Temperature control was by the same method as for lap-joint brazing, but, because of the relatively high thermal mass of the joint, long flat, thermal cycles could easily be obtained (Curve C, Figure 12). Unfortunately, joints brazed to this condition were not wetted and filled even with extending brazing times, in keeping with the conclusions from lap-joint brazing. Raising the power output gave rise to more rapid cycles which did result in properly filled joints, but were less of an approximation to the ideal as Curve B. Consequently, the joints produced were of slightly inferior quality to the best lap-joints. Curve D represents the best compromise curve that could be obtained: a better one would have required more sophisticated equipment.

A final point is that stainless steel lap-joints could be brazed very successfully, but butt joints could not. This was because the high heat capacity of stainless steel did not allow sufficiently rapid cycles to overcome non-wetting, even with the highest power output available.

3.3 METALLOGRAPHY AND BRAZING PRE-TREATMENT

3.3.1 Metallographic Preparation

Like titanium, the metallographic preparation of zirconium presents certain problems, the principal one being its capacity to flow and smear during polishing; consequently special procedures are needed to obtain good results. Electropolishing may be used, but the most convenient method was found to be chemical polishing. After grinding on silicon carbide paper, and lightly polishing on diamond paste, the specimen was immersed in a polishing solution of 45% HNO_3, 15% HF, 40% H_2O for 20 seconds, and subsequently etched using an etchant of 1% HNO_3, 20% HF, 79% H_2O. Care had to be taken as the reaction was vigorous; thin sheets of zirconium even ignited occasionally. Figure 16 is a micrograph of the 2mm zirconium plate used, prepared by the chemical polishing method.

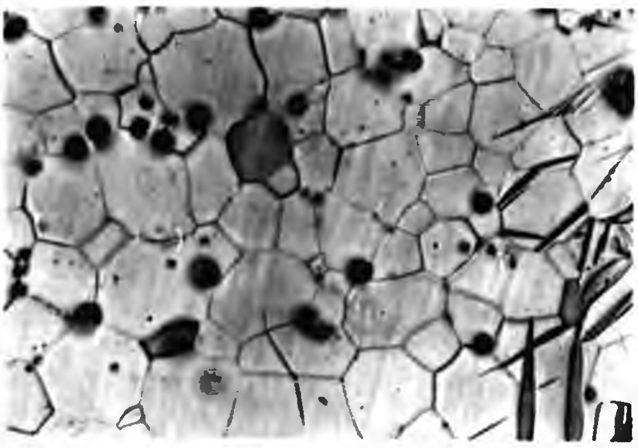

Figure 16: Zirconium plate, X 195. Note deformation twins around a hardness identation. Etched $HNO_3/HF/H_2O$

More conventional techniques could be used for brazed zirconium joints, since only the braze area was normally of interest. For examination of the Ag-Cu filler and intermetallic layers, mechanical polishing and etching using acidified $FeCl_3$ solution gave excellent results, whilst joints in which large scale interalloying had occurred were prepared using the procedure already described for zirconium sheet. The preparation of specimens for electron microscopical examinations required modifications to the procedure. In the as-polished condition, specimens were found to be contaminated with a flowed layer of zirconium, which naturally distorted results; etching removed the contamination, but analysis indicated that preferential dissolution of zirconium had occurred. The problem was resolved by lightly polishing after etching, and subsequent light re-etching. Good, consistent results could then be obtained.

3.3.2 Brazing Pre-treatment

A standard pre-treatment procedure was established for both zirconium and stainless steel joint surfaces to ensure the best condition for wetting. Joint surfaces were first abraded on fine silicon carbide grit paper and then cleaned ultrasonically in acetone (as were the filler pre-forms). After drying they were treated with a pickling solution, rinsed in distilled water and dried, again using alcohol and acetone; subsequently the joint-pieces were only handled using tweezers. Pickling solutions used were 10%HF, 30% HNO_3, 60% H_2O for zirconium; and 3.8% HCl, 0.35% HF, bal, H_2O to 100cc for the stainless steel.

3.4 EXPERIMENTAL PROGRAMME

3.4.1 Vacuum Brazing

The experimental programme began with a phase of vacuum brazing work, the aim of which was to establish the general efficacy of this method for producing zirconium joints and, more specifically, to investigate the effect of brazing temperature and time on wetting behaviour and joint microstructure. Accordingly, vacuum brazing runs were carried out at various temperatures up to about 900°C, and for durations of up to 30 minutes. Each run incorporated a wetting test sample, consisting of a shim of Ag-28Cu filler on a thin-gauge coupon of zirconium and a standard lap-joint for sectioning and metallography; microhardness tests were also carried out.

Joints were also made in En58e stainless steel, again using Ag-28Cu, for comparison and future reference.

3.4.2 Induction Brazing

In Section 2.3.3 reference was made to the rapidity of heating cycles obtained with induction heating, suggesting that the process could offer advantages in reactive metal brazing, by reducing interaction between filler and base metals. To test this proposal work was carried out on the induction brazing of lap-joints, using the apparatus described earlier, so that a comparison could be made against the manufacture of joints by the more conventional vacuum-brazing process: particular attention was paid to joint-filling characteristics and the degree of intermetallic formation in sectioned joints. Trial runs established a "standard" heat up curve (Curve B, Fig 12) in which time to filler melting point (778°C) was about 45 seconds, with a further 5-10 seconds at a brazing temperature of about 800°C. Other types of heating cycle were possible: experiments were carried out using cycles of very short duration - about 3 seconds from room temperature to filler melting point, plus 2 seconds to maximum temperature (880°C) and joint filling. Curves of this cycle type resemble a sharp peak.

3.4.3 Analytical Work

In order to better understand the results of wetting and spreading during vacuum brazing, analytical work on the microstructures obtained was undertaken; the principal tools used were scanning electron microscopy (SEM) and associated energy-dispersive analysis (EDS), and X-ray diffraction (XRD).

SEM has a number of advantages over optical microscopy: not only may magnifications be greater, but the depth of focus obtained means that topographic features such as cracks and voids are readily discernable. Image brightness depends on the atomic number of the element (or elements) being scanned, so that different phases may be distinguished on that basis. For surface element analysis EDS may be used in three ways.

(i) X-ray dot map - qualitative only.

(ii) Line scan. Can be semi quantitative, but affected by surface topography.

(iii) Point analysis. Fully quantitative: compositions (in Wt.%) calculated from characteristic X-ray intensities via the Cliff-Lorimer equation which, for a two- component system is:

$$\frac{CA}{CB} = K_{AB} \frac{I_A}{I_B}. \qquad (\;\;)$$

where $C_{A/B}$ is the wt.% of element A/B, K a constant, and $I_{A/B}$ the intensity of element A/B.

The equation may be extended for higher order systems, though the procedure is more complicated and less reliable. All three EDS modes were used in this investigation.

Unlike EDS, XRD can identify compounds rather than just element wt.%. The procedure followed in XRD work was to break open the joint of interest and subject the broken surface to X-ray diffractometry; the peak intensities and characteristic "d" spacings of the spectrum produced were then correlated with the spectra of known compounds, although there was no guarantee that the compounds present would already be listed.

3.4.4 Re-Melt Behaviour of Brazed Joints

As a parallel project the microstructures and re-melting characteristics of titanium-brazed joints were investigated. Interest in the re-melting temperatures of brazed joints arose from concern that low melting eutectics could form between the base metal and the filler metal or, in a dissimilar metal combination, between the base metals themselves, thus reducing the service temperature to which the joints could be exposed.

A rig was constructed to measure re-melting temperatures, utilising a 4kW Radyne heater with a 5-turn coil in which the lap-joint was suspended. Argon was used to provide a protective atmosphere, and the joint held under tension by a weight attached to it.

A variety of joint combinations were tested including titanium, titanium using Ag-28Cu filler, and titanium-318 alloy to En58e steel using Au-18Ni - the system of principal interest. Finally, zirconium joints were tested. Maximum temperature obtainable in the rig was about 1600°C.

3.4.5 Mechanical Testing

The mechanical testing programme was the longest and most important part of the investigation, and entailed the production of 55mm butt joints by vacuum and induction brazing, and their subsequent testing.

Having established the relationship between brazing conditions and joint microstructure, the logical next step was to impact test joints brazed to these conditions, so that a quantitative picture of the effect of intermetallic formation on joint soundness could emerge. As the testing procedure was non-standard, and therefore not comparable with any published data, some form of reference toughness was needed against which the toughness of zirconium joints could be compared: this role was fulfilled by a series of En58e steel joints, vacuum brazed using Ag-Cu filler. No embrittlement reaction occurs in this system under normal brazing conditions. The steel joint series also provided a control. The experimental schedule can be summarised thus:-

Vacuum brazing of zirconium and steel joints: effect of brazing time (and increased intermetallic thickness); effect of overheat.

Induction brazing: (i) Ag-28Cu zirconium joints, brazed to optimum conditions (Curve D, Fig 12), for comparison with vacuum brazed joints; (ii) copper-brazed zirconium joints, brazing temperature about 1100°C; including effect of joint gap through pre-form thickness variation.

The copper-brazed series was not envisaged originally; interest in copper-brazed zirconium joints (using RF heating) arose during process development as a result of their robustness.

All joints were tested in an Izod mode on an Amsler instrumented impact tester at AWRE; traces of the load-time profile were recorded and toughness noted. Technical problems meant that integration of the curve could not be done, and toughnesses were recorded conventionally.

Some as-brazed joints were sectioned for metallography, and broken joint pieces retained for analysis.

Finally, a series of Ag-28Cu and pure copper induction-brazed zirconium joints was subjected to 3-point bend testing to provide results complementary to the impact testing result. Some of the joints were deliberately overheated during brazing.

3.4.6 Fracture Analysis

In the final phase of the experimental programme analytical work was undertaken to rationalise and explain the results of mechanical testing. Techniques used included SEM fractography, TEM (transmission electron microscopy) and further SEM and EDS work.

IV RESULTS

4.1 VACUUM BRAZING

In this section the results are presented of work on wetting Ag-28Cu filler on zirconium, the metallography of zirconium and stainless steel lap-joints, and microhardness testing.

4.1.1. Wetting and Flow Tests

Wetting and flow tests were conducted over a range of temperatures from 780 - 900°C for about ten to fifteen minutes 'brazing' time. From these results three regimes of wetting behaviour, according to the temperature of the process, could be discerned.* They are exemplified by the specimens shown in Figure 17.

Figure 17: Variation of wetting/flow behaviour with temperature (x2)

The regimes may be characterised thus:-

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* See Appendix A1

(a) 780-850°C (Fig 17(a)): Normal behaviour. Wetting adequate; rate of filler melting and flow sluggish, particularly at lower temperatures. In the example shown a "cap" of impurities has formed on the surface of the solidified drop.

(b) 855° ± 5°C (Fig 17(b)): at about 850 - 860°C, just below the transus temperature of zirconium, there is a transition from normal wetting behaviour to one marked by rapid erosion of the zirconium base metal and the gross precipitation of reaction products. Flow characteristics were rather poor. In all the specimens heated above this transition temperature the zirconium coupon (0.13mm thick) was penetrated by the melt.

(c) 880 - 900°C (Figure 17(c)): At still higher temperatures the wetting angle is reduced, the rate of flow very rapid and accompanied by equally rapid dissolution of the zirconium; the specimen in Figure 17(c) was cooled just before it disappeared into a single globule of molten metal. Unlike the granular appearance of the melt in Figure 17(b), the surface of the fused metal is smooth, suggesting that large-scale precipitation of reaction product is not occurring at the brazing hold temperature.

These results suggest that a good product will not be obtained if brazing is carried out above about 850°C - the transition to "overheat" conditions.

4.1.2 Metallography of Joints*

4.1.2.1 Effect of Brazing Time

A series of lap-joints was made at a temperature of 780°C using brazing times of 7, 9, 11, 13 and 25 minutes respectively. Experience showed that a 'warm-up' time of about four minutes was necessary to bring the filler to its melting point of 778°C; thus the true brazing times were estimated to be 3, 5, 7, 9 and 21 minutes. All the joints displayed poor joint filling. Only filler shim directly in contact with the zirconium plates melted, suggesting that heat transfer by radiation was not as effective as that by direct conduction from the base metal.

Metallography of sectioned joints showed that the silver-copper filler in each joint was separated from the zirconium by an interface layer, the thickness of which depended on the duration of the brazing time. Figures 18 and 19 are photomicro-graphs of the 3 minute and 21 minute joints respectively.

Closer inspection of the interface layers, particularly of the 21 minute joint, shows that they consist of two sub-layers: a thick one next to the filler, and a thin one next to the zirconium (NB the interface on the left of each micrograph has a shadow caused by a polishing artifact).

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* See Appendix A3

The structures of the eutectic filler are interesting: in the 3 minute joint non-equilibrium conditions have caused the filler to solidify partly as a 'divorced eutectic', with areas of pseudo-primary copper-rich β-phase embedded in silver-rich α-phase. In contrast, the structure of the filler in the 21 minute joint appears to consist of genuine primary silver-rich phase, surrounded by eutectic cells; the overall depletion of copper indicates that the interface layer grows primarily by the reaction of the copper component of the filler with the zirconium base metal.

At higher brazing temperatures, still within the 'normal' range of up to 850°C, the interface layers were observed to become more irregular and diffuse, with much reaction product apparently being precipitated discretely in the filler, but with enough remaining as a continuous barrier between filler and zirconium base metal. Alternatively, the "precipitation" may be evidence of breaking-up of the layer, through dissolution by the liquid.

4.1.2.2 Microhardness Testing

Microhardness tests using a Vickers tester with a 50g load were carried out on the joint illustrated in Figure 19. For each location the average of five readings were taken and the following results obtained:-

(i)	Zirconium base metal	198 VPN
(ii)	Silver-copper filler	217 VPN
(iii)	Interface layer	1020VPN

Figure 18: Vacuum brazed, 3 minutes (x 195)

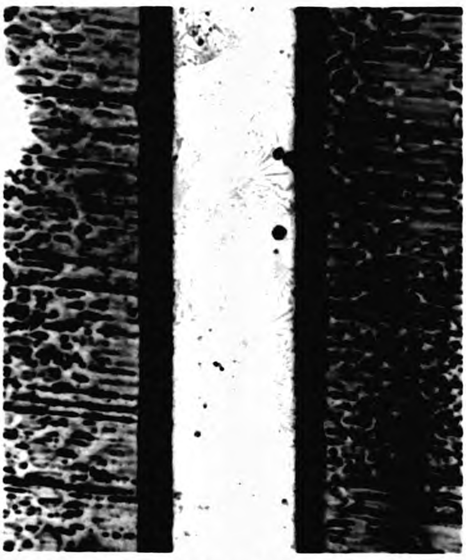

Figure 19: Vacuum brazed, 21 minutes (x 195)

The results fully confirm that the interface layer is an intermetallic phase.

4.1.2.3 Joint Microstructure at 'Overheat' Temperature

Having fully investigated the joint microstructures associated with the type of wetting exemplified by Figure 17(a), joints brazed above the transition temperature of 855°C were similarly evaluated. Accordingly, a joint was brazed at 860°C for ten minutes. Joint filling was quite poor, despite the high temperature, and even to the unaided eye erosion was discernable - as in the equivalent wetting test of Figure 17(b).

Figure 20 is a micrograph of the joint. The structure is very different to that of the lower-temperature joints. The silver-copper filler has reacted almost completely (there is a small residue of silver at the centre) showing that silver is reacting with the zirconium, if not as vigorously as the copper, and most of the braze area consists of a mass of coarse intermetallic phase reaction product. These features reflect the observations on the greatly enhanced erosion/reaction rate noted for the specimen in Figure 17(b).

4.1.2.4 Stainless Steel Joint Microstructure

For comparison purposes, joints were brazed in En58e steel using Ag-28Cu filler for various times and temperatures. Joint

Figure 20: Structure of 860°C braze (x 195)

Figure 21: Stainless steel braze (x 475)

microstructure displayed no variation; Figure 21 illustrates a joint brazed at 800°C for 10 minutes. As one might expect, there is no interface layer observable; the silver-copper filler retains its typical eutectic structure. Wetting of Ag-28Cu on steel was no better than on zirconium.

4.1.2.5 Fracture Path

Preliminary photomicrography was carried out on zirconium lap-joints broken in a vice. Figure 22 is a joint brazed at 780°C for 21 minutes and subsequently broken.

Figure 22: Fractured Joint (x 195)

The preferred path for fracture appears to be the zirconium/interface layer junction. Joint microstructure is clearly seen in this micrograph.

4.2 INDUCTION BRAZING

4.2.1 Reason for Use

Although the initial vacuum brazing programme had been successful in yielding a basis understanding of the Zr-Ag-Cu brazing system, from a practical point of view the results were not impressive; slow melting of the filler, inadequate joint filling and excessive intermetallic compound growth were the main criticisms. For these reasons radio- frequency induction heating was turned to as a means of producing better brazed joints.

4.2.2 Wetting Tests*

Wetting tests were carried out using the apparatus described in Section 3.2.4. Compared with those obtained by vacuum furnace brazing, the results showed an immediate improvement, characterised by rapid and uniform melting, short joint-filling time and minimised intermetallic compound formation. Figure 23 is a micrograph of a sectioned wetting test.

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* See Appendix A2

Figure 23: Sectioned wetting test (x 195)

Contact angle in the test illustrated by Figure 23 is about 20° - similar to that in vacuum brazed examples.

The peculiarities of wetting behaviour encountered in induction brazing work have been briefly mentioned previously (Section 3.2.4). To recall, whether or not wetting occurred appeared to depend on the heat-up rate of the base-metal workpieces through the melting point of the filler. It was observed that when wetting did occur, the filler initially melted and contracted into a globule; after a few seconds of 'incubation time' the globule then wetted the base metal, giving the results exemplified by Figure 23. When the heat-up rate was not high enough the molten globule would simply remain in that state, despite reacting with the zirconium where in contact with it.

4.2.3 Metallography of Joints*

4.2.3.1 Normally Brazed Joints

Initial attempts to produce brazed lap-joints resulted in 'overheated' microstructures comparable with that of Figure 20. Eventually a 'standard' heat-up curve of 45 seconds plus 5-10 seconds brazing time was developed, and this produced the excellent results illustrated in Figures 24(a) and (b). Despite the considerably reduced interface layer thickness (compared to vacuum brazed joints), these joints were completely filled by the Ag-28Cu eutectic; a typical joint is illustrated in Figure 25. Observe that the microstructure of the filler is strongly dendritic: this is a result of the very non-equilibrium conditions imposed by rapid cooling.

4.2.3.2 High Temperature Brazing

In the Experimental section (3.2.4) reference was made to very short high temperature heating cycles which could be obtained by induction brazing. The duration of these cycles was about 5 seconds, including about 2 seconds brazing time, reaching a temperature of about 900°C. A this temperature wetting was almost uncontrollable, and comparable witht the regime experienced by the specimen in Figure 17(c). However, the short brazing time prevented extensive base metal dissolution. The microstructure of a joint brazed thus is shown in Figure 26.

*See Appendix A3

Figure 24(a): Induction brazed lap joint (x 195)

Figure 24(b): Same as above (x 475)

Figure 25: An induction brazed lap joint

Figure 26: Induction brazed, high temperature joint microstructure (x 195)

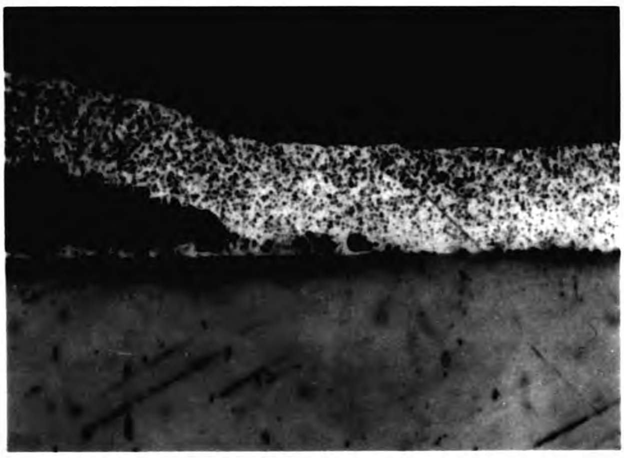


Figure 27(a): Failure in an induction brazed lap-joint.
Note voids ahead of crack (x 195)

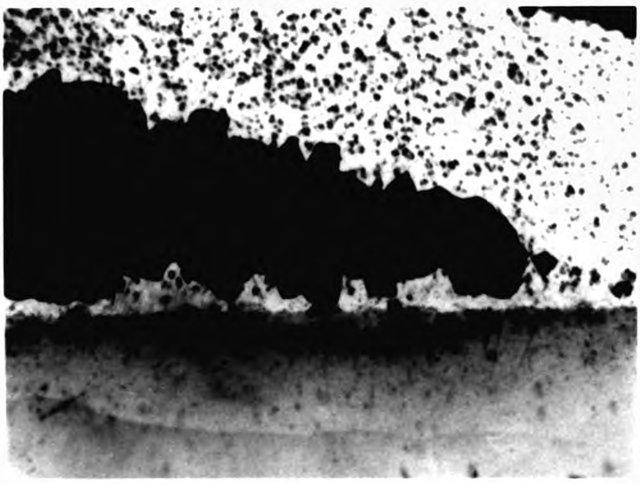


Figure 27(b): Same view (x 475)

The microstructure bears no resemblance to the original eutectic structure. It has inter-alloyed completely, and consists of needles of intermetallic compound embedded in a matrix. At this stage the absence of an interface layer (which seemed to provide a clear fracture path) suggested that this type of joint might have improved mechanical properties.

Notice that the structure of the zirconium itself has changed, indicating that it has passed through the transus temperature of 863°C.

4.2.3.3 Fracture Path

An induction brazed lap-joint was broken and examined to ascertain the fracture path. The joint itself was brazed with a vanishingly-thin interface layer, obtained at the expense of complete joint filling. Figures 27(a)(b) show that fracture occurred largely through the ductile filler. Observe the voids formed ahead of the crack - suggesting failure by microvoid coalescence (MVC).

4.3 ANALYTICAL WORK*

4.3.1 SEM Micrography

SEM micrography was undertaken on all the microstructures obtained so far.

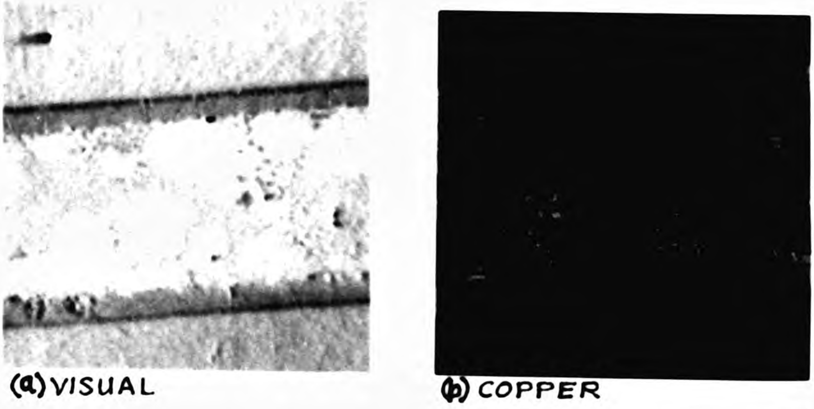
Micrographs of normal interface-layer joints revealed little that optical micrography had not (except for the occasional transverse crack

*See Appendix A5

Figure 28(a): SEM micrograph of an overheated joint (x 400)

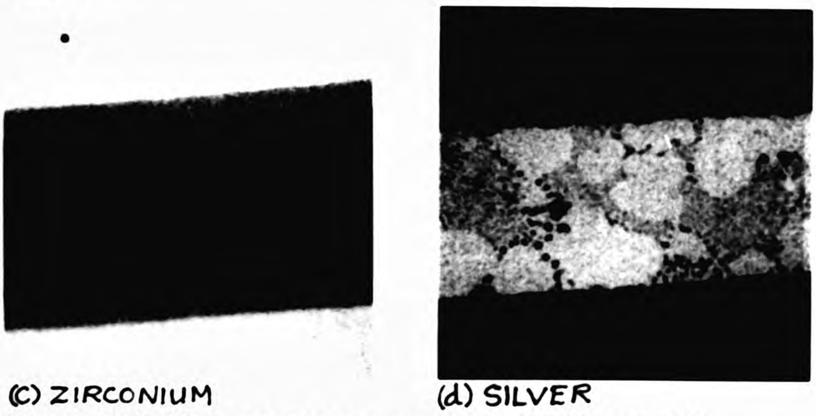
Figure 28(b): Same view (x 1000)

Figure 29: SEM View of an induction brazed high temperature joint. (x 1000)



(a) VISUAL

(b) COPPER



(c) ZIRCONIUM

(d) SILVER

Figures 30 (a-d): X-ray dot maps of a brazed Zr joint (x 400) in the intermetallic layer), but those of overheated joints were striking. Figures 28(a)(b) are examples taken of the joint previously illustrated in Figure 20: widespread solidification cracking has occurred between the precipitated crystals and their surrounding matrix, as well as transgranular cracking through both phases. Also present, though not seen in these views, were deep fissures running right across the braze. A joint brazed with so many defects would be unlikely to have acceptable mechanical properties. The order of solidification of the three phases appears to be:

Precipitated crystals > matrix > residual silver-rich phase

Closer examination of the matrix shows that it is a eutectic.

SEM examination of the high-temperature induction brazed joints, previously illustrated in Figure 26, showed the presence of deep transverse fissures, as in the 'overheated' joints. As a result of this discovery practical interest in this type of joint faded; Figure 29, a SEM micrograph, is a typical example of this type of microstructure. The plate crystals appear to be a silver-zirconium phase.

4.3.2 EDS Analysis

4.3.2.1 Linescans

EDS linescans on polished sections were found to be easily distorted by surface irregularities. X-ray dot maps, point analysis and EPMA (electron probe microanalysis) were more productive.

4.3.2.2 X-ray Dot Maps

These were carried out for zirconium, copper and silver on a normal interface-layer-joint, and reproduced in Figures 30(a)-(d). They show that copper is the dominant element in both interface layers (confirming earlier conclusions) and that the outer, thinner layer, contains zirconium and copper only.

4.3.2.3 Point Analysis

EDS point analysis was carried out on the interface layer joint depicted in Figure 30(a) and the overheated joint in Figure 28, in order to determine the composition of the intermetallic phases.

Calculated compositions are:-

(i) Interface Layer Joint (normal braze temperature):
Thick layer (next to filler): 58%Cu, 20.5%Ag, 21.5%Zr
Thin layer (next to zirconium): 63%Cu, 4.5%Ag, 33%Zr
The Ag-Cu filler contained a trace of zirconium (<1%), suggesting some dissolution of the intermetallic phase, as suspected from metallographic work.

(ii) Overheated Joint:

Residual Silver:	6%Cu, 89.5%Ag, 4%Zr
Crystals:	10.5%Cu, 39%Ag, 50.5%Zr
Matrix:	32.5%Cu, 25.5%Ag, 42%Zr

4.3.3 EPMA

Electron probe microanalysis was carried out on the intermetallic layers in a normal temperature, interface layer-joint to determine whether or not the compositions of the interface layers were uniform across them. Figure 31 reproduces the zirconium, copper and silver profiles across one side of the joint, and shows that the zirconium concentration is markedly uniform across the thick layer, increasing slightly through the thin layer. Likewise the silver concentration is mainly constant in the thick layer, decreasing to zero at the interface of the thin layer. Copper dominates the entire interface region.

The suggestion from the EPMA results is that both zirconium-copper and zirconium-silver compounds are present; but in this three-component system, precise identification of the compounds would depend entirely on the results of X-ray diffraction of fracture surfaces.

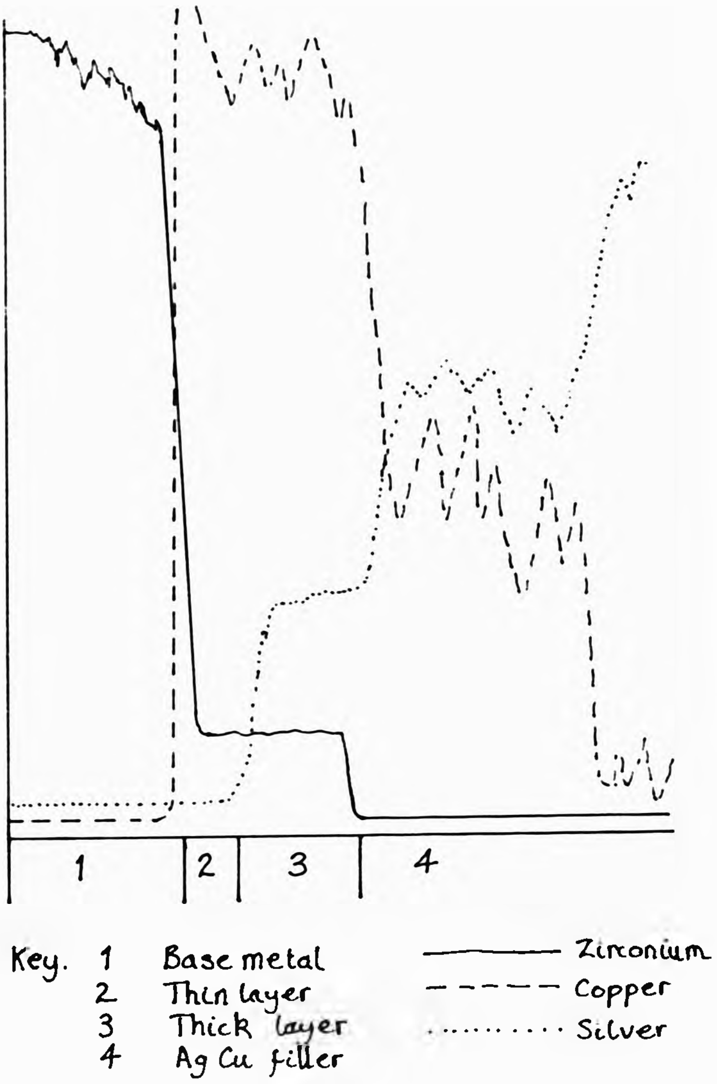


Fig. 31: EPMA profiles for Zr, Cu and Ag across the interface of a zirconium brazed joint.

4.3.4 X-Ray Diffractometry

In an attempt to identify the compounds being formed, X-ray diffractometry (XRD) was undertaken of the fracture surfaces of interface-layer-joints, overheated joints, and the high-temperature joints obtained by rapid-cycle induction brazing. Tables 2 (a, b, c) list the results, in terms of peak intensities and calculated 'd' spacings, of XRD work on each type of joint, together with the 'd' spacings of the compounds with which the results were correlated. 100% intensity peaks are marked by asterisks.

The results for the high temperature joint indicate conclusively the presence of Ag-Zr (which work by the contractors confirmed), and that the zirconium base metal has been detected; the zirconium reflections match almost identically an XRD run on pure zirconium, although the results for the latter did not closely resemble the data listed in the X-ray diffraction files. It is surprising that no copper compounds have been detected, yet were likely to be present, considering the number present in the Cu-Zr phase diagram. Another anomaly is the very high intensity of the peak corresponding to a 'd' value of 1.644 Å.

To conclude, it does not seem that XRD has provided conclusive, exhaustive information on the compounds present. Unreliability is due to the large number of possible compounds present, their physical condition and the lack of complete data file information.

Table 2(a) XRD - interface layer-joint

Intensity %	'd' spacing/Å	Cu	Ag	$AgZr_2$	$CuZr_2$
25	2.575			2.512*	
60	2.443				2.429*
20	2.336		2.359		
3	2.290			2.288	
4	2.252				2.269
5	2.199				
1	2.149				
100	2.085	2.088*			
12	2.021		2.044		
30	1.992			1.996	
1	1.959			1.928	
6	1.898				1.860
		1.808		1.506	
20	1.466		1.455		1.441
4	1.430				1.429
10	1.416				1.393
15	1.335			1.363	1.342
12	1.289	1.278		1.258	
11	1.227		1.231	1.232	
5	1.173			1.147	

These results suggest that the main intermetallics forming are $AgZr_2$ and $CuZr_2$; the copper and silver detected are probably from the filler, although the XRD technique suggested that copper was present in the interface layer too. The thick interface layer was thought to account for both intermetallics as well as the interfacial free copper.

Table 2(b) XRD - overheated joint

Intensity%	d' spacing/Å	Cu	AgZr	$CuZr_2$
5	6.508		6.65	
10	2.570			
62	2.454		2.45	
43	2.422			2.416
52	2.355		2.39*	
14	2.286		2.30	
11	2.206			2.269
100	2.093	2.088*		
19	2.035			
29	2.005			
11	1.712	1.808	1.73	1.860
5	1.462			
7	1.442			1.441
9	1.421		1.40	1.429
10	1.389		1.37	1.393
11	1.339			1.342
5	1.288	1.278		
11	1.230		1.23	
3	1.212			1.219
6	1.084			1.158

The results for the overheated joint suggest that AgZr and $CuZr_2$ are the main intermetallics. Copper appears to be present, but the apparent lack of silver reflections is a surprising feature.

Table 2(c) XRD - High temperature joint

Intensity%	'd' spacing/Å	AgZr	Zr
6	6.654	6.65	
4	2.813		2.813
7	2.591		2.584*
12	2.467		2.473
6	2.448	2.45	
28	2.379	2.39*	
5	2.309	2.30	
11	2.190	2.20	
2	2.121		1.902
2	1.902		1.902
2	1.848	1.70	
100	1.644	1.65	
2	1.467		1.467
2	1.448		
2	1.396	1.40	
2	1.362	1.37	1.372
3	1.359		
12	1.314	1.32	

* 100% intensity peaks

NB: The zirconium reference data were derived from an XRD run on pure zirconium and not from files.

4.4 RE-MELTING STUDIES

4.4.1 Titanium Brazed Joints

Work on the re-melting/heat treatment of brazed zirconium joints developed from another project on the metallography and re-melting of brazed titanium joints. The microstuctures of these joints, brazed with Ag-28Cu, closely resembled those of zirconium joints described earlier.

Re-melting tests were conducted on pure titanium and titanium-318 joints (brazed with Ag-28Cu), and on titanium-318 to stainless steel joints in which the filler used was Au-18Ni. These experiments showed that re-heating rates of about 180°C/minute were sufficient to melt joints (at about the melting point of the filler), but lower heating rates - around 50°C/minute - did not have the same effect: instead the joint under test remained stable up to 1500°C, the maximum obtainable from the Radyne heater. Titanium to steel joints failed at about 1300°C when the stainless steel melted.

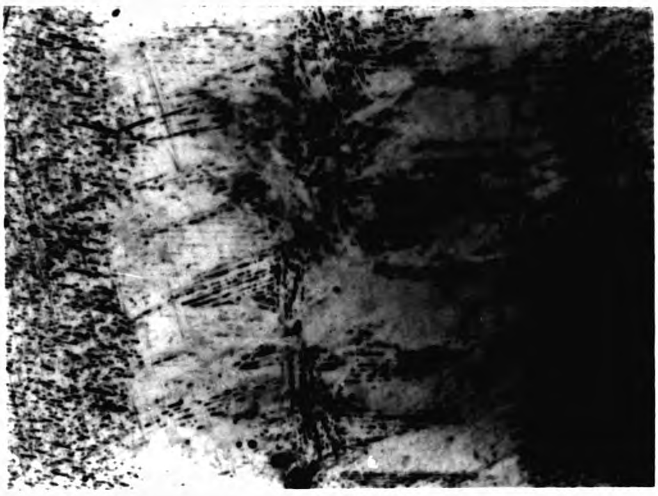


Figure 32(a): Re-heated titanium joint. Optical (x 200)
No sign of the original braze remains.

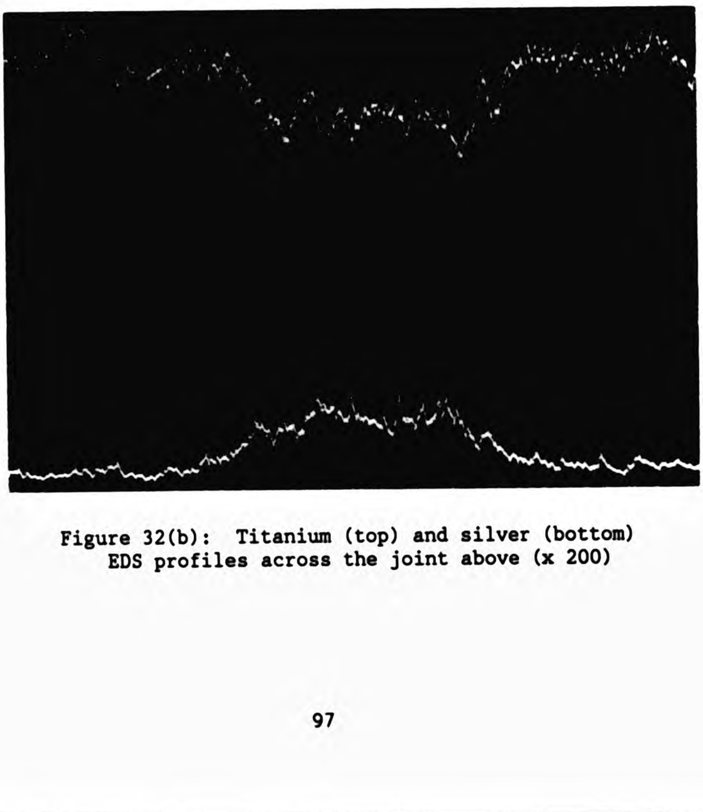


Figure 32(b): Titanium (top) and silver (bottom)
EDS profiles across the joint above (x 200)

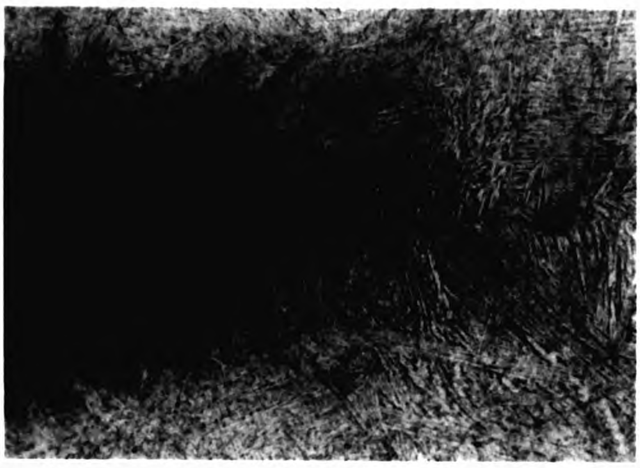


Figure 33: Periphery of a heat-treated zirconium joint
Part of the liquified core is on the left (x 95)

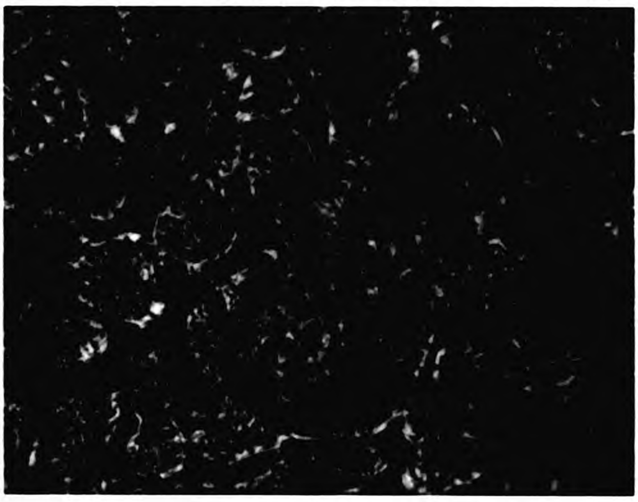


Figure 34: High magnification view of the liquefied and transformed core above. Note eutectoid transformation in the dendrites.

Work was undertaken to discover the reason for the unremeltability of these joints. Metallography revealed that large-scale solid state diffusion of the filler into the base metal had occurred; in effect the re-melting test had diffusion-welded the joints. The process was particularly efficient in the joint brazed with Au-18Ni: no trace of the gold could be detected anywhere in the joint by EDS analysis, so completely had it been distributed through the joint. Figure 32(a) is an optical micrograph of a re-heated titanium joint in which the braze area has been completely dissolved by the titanium. Figure 32(b) records the EDS profiles of silver and titanium across the joint, showing that very little silver remains in the centre of the joint.

4.4.2 Zirconium Joints

The interdiffusion results obtained from the re-heating of titanium joints suggested that similar work on zirconium joints might be worthwhile, with the aim of eventually establishing a technique of diffusion-treating zirconium brazed joints, which in turn may have a beneficial effect on joint strength. Accordingly, work began on re-heating zirconium lap-joints brazed with Ag-28Cu and pure copper. The latter filler was chosen because of possibly improved diffusion characteristics.

The results showed that, like titanium joints, they could not be re-melted by slow re-heating, but metallography of the re-heated joints showed that an entirely different process had occurred: the insides of the joints were liquefying (wholly or partly), and solidifying with a dendritic structure. Fusion was only occurring along the joint periphery, where, due to the filler dissolving into the interior of the joint, contact clearance was achieved. There was no evidence of large scale diffusion of the filler into the joints. In copper-brazed joints, heat-treated at about 1100°C for an hour, recrystallisation and growth had occurred across the original interface at the edges. This effect is well illustrated by Figure 33, in which the original plane of the joint interface is marked by voids. Figure 34 shows the core of the joint: the liquid has solidified as a zirconium-copper analogue of white cast iron (the $Zr-Zr_2Cu$ system is analogous to the $Fe-Fe_3C$ system). It consists of primary dendrites of zirconium plus eutectic. The zirconium dendrites (originally primary β-zirconium) have transformed to the α $Zr-Zr_2Cu$ eutectoid constituent - a Zr-Cu analogue of pearlite.

A natural progression from this work was to produce diffusion treated zirconium butt joints for mechanical testing by re-heating in a vacuum furnace. Unfortunately the effects that occurred in lap-joint heat treatment could not be reproduced in butt joints. Due to some unknown reason, associated with the different joint geometry, the peripheral sealing-up did not occur, with the result that the semi-molten braze leaked out during heat treatment; even very thin braze alloy pre-forms (0.025mm) were too thick for the zirconium to dissolve. Unfortunately, lack of time curtailed further developments of this promising line of work.

4.5 MECHANICAL TESTING

This section presents the results of mechanical testing of 55mm butt joints and the process variables involved in brazing them. Each butt joint brazed is identified by a Joint Number.

4.5.1 Vacuum Brazed Joints

Vacuum brazing of zirconium and stainless steel joints with Ag-28Cu filler was carried out using the furnace and jig described in Section 3.2.3. Trial brazing runs at relatively low temperature (780-790°C), undertaken to establish optimum conditions, were plagued by the poor joint filling noted in earlier work; it was hard to say whether wetting had occurred at all. Eventually the brazing temperature had to be raised to 810°C for a duration of ten minutes to ensure complete joint filling. This was more or less in line with the practice adopted by the contractor for brazing beryllium-to-monel joints. Figure 35 is a SEM micrograph of Joint 56 which was brazed to these conditions; note the extensive intermetallic formation - most of it precipitated in the filler rather than as a compact layer.

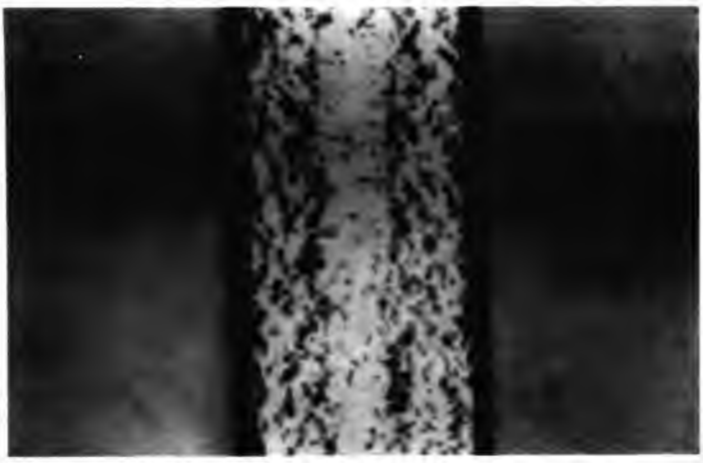


Figure 35: SEM micrograph of Joint 56 (x 500)(zirconium)

The following Tables 3 and 4 record the brazing process variables and fracture energies (in joules) recorded from impact testing zirconium and stainless steel vacuum brazed joints. Figures 36(a),36(b) are representative load-time curves (drawn from originals) of Joints 57 and 60, derived from the instrumented testing technique.

The results in Tables 3 and 4 show the fracture energy of the zirconium joints to be considerably lower than that of the steel joints; none of them has equalled even the weakest steel joint, but the reason for the disparity is probably not a metallurgical one. Earlier trial work on impact testing roughly-prepared steel and zirconium joints produced more or less similar results for both. Almost certainly, the real reason for the weakness of the zirconium joints in Table 4 is poor

Table 3: Vacuum brazing - stainless steel

Joint No.	Braze Temperature/°C	Braze time/mins	Fracture energy/J
50	810	10	0.82
51	810	10	1.22
52	810	10	1.32
53	810	10	Retained for Sectioning
57	810	20	2.31
58	810	20	3.13
61	810	30	1.63
62	810	30	2.04

Table 4: Vacuum brazing - zirconium

Joint No.	Braze Temperature/°C	Braze time/mins	Fracture energy/J
54	810	10	0.00
55	810	10	0.23
56	810	10	Retained for Sectioning
59	810	20	0.20
60	810	20	0.97
63	810	30	0.41
64	810	30	0.58
65	850	5	0.27
66	850	5	0.27

fillet formation: micrographs of the rim of the braze in Joint 56 showed a concavity where a fillet should have been. The problem could probably be cured by using a thicker filler shim: the rough trial joints were brazed with excess filler.

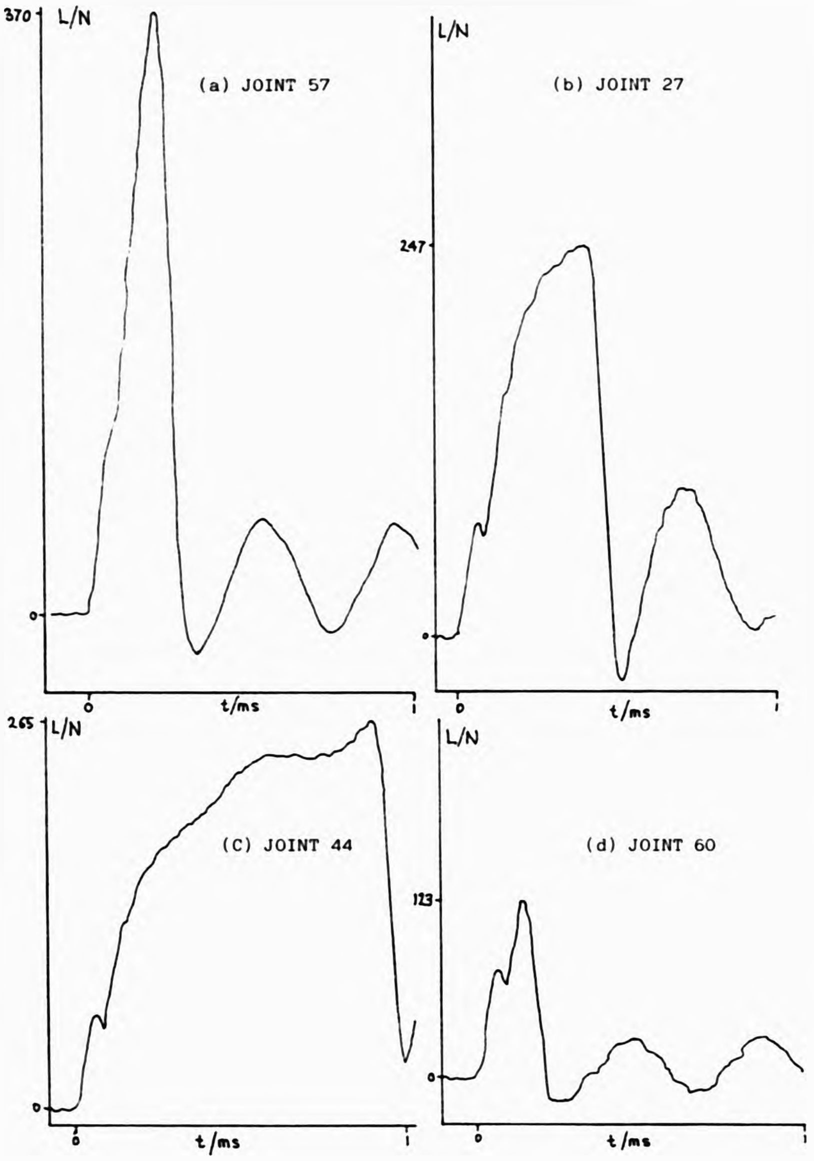


Figure 36 (a-d): Load (L) VS time (t) traces for Joints 57,27,44 and 60.

The two series - zirconium and stainless steel joints - exhibit a pattern common to both. The 10 minute runs have produced the weakest joints, and the 20 minute runs the strongest, with the fracture energy reducing to intermediate values for the 30 minute runs. There seems to be no reasons to account for this, but it may be that optimum joint filling (and perhaps, joint clearance) coincide with a 20 minute brazing duration.

The load-time traces of Joints 57 and 60 are illustrated in Figures 36(a), 36(c). In each trace the deformation behaviour of the joint is characterised by a main peak, which rises through the "crack initiation" stage to a maximum value (the load at failure) which marks the onset of "crack propagation". Unstable crack growth is marked by a rapid fall-off in the trace; in both these examples the onset of crack propagation and the point of unstable crack growth coincide. Following the peaks are the series of oscillations caused by vibrations in the hammer, and having nothing to do with the deformation of the joint.

Examination of the zirconium Joint 60 trace shows that it failed with a load of only 123 newtons, reflecting the low fracture energy, and the inertial loading peak is clearly visible. In contrast the steel Joint 57 failed at 370 newtons (higher still for joint 58, which went off the scale), but over only a very short period - about 0.3ms. The inertial loading peak is visible only as a faint 'blip' on the peak. Virtually all the fracture energy is that of initiation, given by the area under the curve up to its maximum value; propagation energy is the area under the curve following this point and is practically nil.

4.5.2 Induction Brazed Joints

Zirconium butt joints only were made by induction brazing, some with Ag-28Cu filler and some with pure copper filler, using the apparatus and techniques described in the Experimental section. During trial work on producing butt joints with Ag-28Cu filler, the wetting peculiarities observed in lap-joint brazing were again experienced, and solved by altering the heat-up curve, as described in Section 3.2.4. In that Section it was noted that the heat-up curve for brazing butt joints could not be made quite the same as that for the highly-successful lap-joint brazing, resulting in joints of slightly lower quality. Microstructurally, this reduction in quality was translated as increased intermetallic phase formation, though there was no compromise on the high standards of joint filling obtained.

A typical microstructure of an induction brazed joint using Ag-28Cu filler is that of Joint 24, illustrated in Figure 37. Compared with the lap-joint illustrated in Figure 24(b) the intermetallic phase-width is about 50% thicker, though still much less than the compound formation in Joint 56 (vacuum brazed).

Less development work went into the production of copper-brazed joints, which were produced using a higher rate of heating, bringing the copper preform to melting point in 60-65 seconds; a further 10 seconds was allowed to elapse to ensure complete joint-filling. Wetting and joint-filling characteristics of these joints were outstanding, and in appearance the resulting joints were exceptionally neat, with the braze

Figure 37: Joint 24, an induction brazed butt joint (x 475)

being hardly visible. Typical examples of induction-brazed butt joints using copper and Ag-28Cu fillers are illustrated in Figure 38.

Tables 5 and 6 present the results of impact testing induction brazed joints, with representative load-time curves of Joints 27 and 44 illustrated in Figure 33(c), 33(d). The results of bend-testing a selection of induction brazed joints are presented in Table 7; some of these joints were deliberately overheated to simulate various conditions. The microstructure of the copper-brazed joints is interpreted in Section 4.6.

The results of the Ag-28Cu brazed joints given in Table 5 show a fair degree of scatter, despite being brazed to the same conditions, but their average fracture energy compares well with that of the 20 minute stainless steel joints in Table 3. However it is the copper brazed joints in Table 6 that have performed really well, with fracture energies of around 5.5 - 9.5J, although there seems to have been a quality assurance problem in the series. The variation of preform thickness has produced no discernable results.

As in the load-time traces of the vacuum brazed joints (57 and 60), the traces for Joints 27 and 44 (Figures 36(c), 36(d)) show that failure occurred almost instantaneously following the onset of crack propagation. Thus the "propagation energy" is again practically nil, and the overall fracture energy is accounted for by the energy of initiation of a crack. Loads at failure are 247N for Joint 27, and 265N for Joint 44.

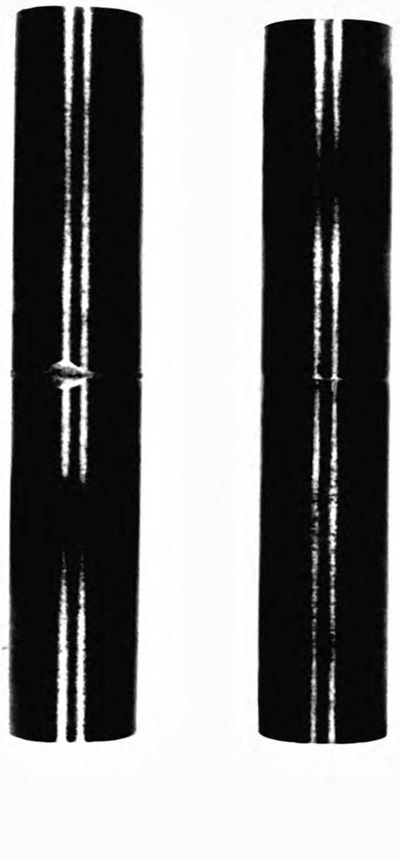


Figure 38: Induction brazed butt joints. The one on the left was brazed using Ag-28Cu filler, that on the right using pure copper

Table 5: Induction brazing - Ag-28Cu brazed joints

Joint No	Fracture energy/J	Remarks
24	Retained for sectioning	
26	2.42	
27	2.92	
28	1.81	
29	2.04	
30	0.37	Poor joint filling

Table 6: Induction brazing - copper brazed joints

Joint No	Preform thickness/mm	Fracture energy/J	Remarks
40	0.1	0.75	Incomplete melting
41	0.1	6.08	
42	0.1	3.54	Brazing irregularity
43	0.025	5.85	
44	0.05	9.52	
45	0.1	Retained for sectioning	

Table 7: Slow bend testing

Joint No	Filler	Load to failure/kN	Remarks
31	Ag-28Cu	2.9	Overheated
32	Ag-28Cu	2.9	Overheated
33	Ag-28Cu	4.0	Normal braze
34	Ag-28Cu	3.8	Normal braze
46	Pure Cu	5.2	Poor brazing
47	Pure Cu	4.0	Poor brazing
48	Pure Cu	7.0	Normal braze
49	Pure Cu	8.0	Normal braze
50	Pure Cu	0.5	Overbrazed(1)

(1) Brazed for excess time to simulate a furnace braze.

The slow bend testing did not proceed in the way it was intended. Originally, the purpose of the work was to calculate the fracture skin-stress using beam theory, but due to the geometry of the test the joint was constrained from bending freely, with the result that it was squashed slightly as well as bent; consequently the loads applied were much higher than for simple bending, and the figures presented in Table 7 are purely comparative. Even so, the tests provided a good measure of the robustness of the joints tested.

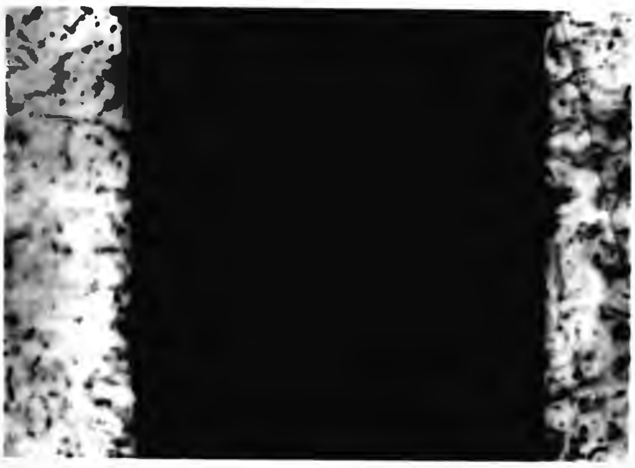


Figure 39: Braze area of Joint 45 (x 475)

4.6 FRACTURE INTERPRETATION

4.6.1 Analysis of joint 45 Microstructure

Following the outstanding performance of the induction copper-brazed joints in Table 6, metallography and EDS work was undertaken on Joint 45 to elucidate its microstructure.* Figure 39 is an optical micrograph of this joint.

The microstructure of Joint 45 is fully interalloyed, and the braze appears to consist of a eutectic plus a primary phase. There are no signs of uncontrolled erosion. These features contrast with the results of early attempts to furnace braze zirconium with pure copper, which produced joints characterised by gross erosion and cracked, jumbled microstructures reminiscent of the 'overheated' structure of Figure 20.

EDS was carried out on the microstructure to determine its composition. The results were:-

Primary phase: 75% Zr, 25% Cu. This corresponds to the compound Zr_2Cu (74%Zr, 26% Cu).

Matrix: 58% Zr, 42% Cu. This corresponds to ZrCu (59%Zr, 41%Cu)

Thus the microstructure in a eutectic of two intermetallics, Zr_2Cu and ZrCu. Overall hardness of the braze area was 1000 VPN.

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*See Appendix A5

4.6.2 Fracture Path

A number of the broken joint pieces obtained from mechanical testing were sectioned for metallographic examination, with the aim of locating the preferred fracture paths.

In the vacuum brazed zirconium joints using Ag-28Cu fillers the preferred location of the fracture was around the thin, copper-rich layer next to the zirconium, as illustrated by the fracture of Joint 60 in Figure 40; this type of fracture had previously been seen in Figure 22. In contrast, the induction-brazed (with Ag-28Cu) joints in Table 5 broke partly through the filler itself, as shown in Figure 41.

The stainless steel joints broke partly through the interface and partly through the filler, whilst the copper-brazed joints in Table 6 showed a vague tendency to crack near the intermetallic-zirconium interface, but along no clearly-defined fracture path.

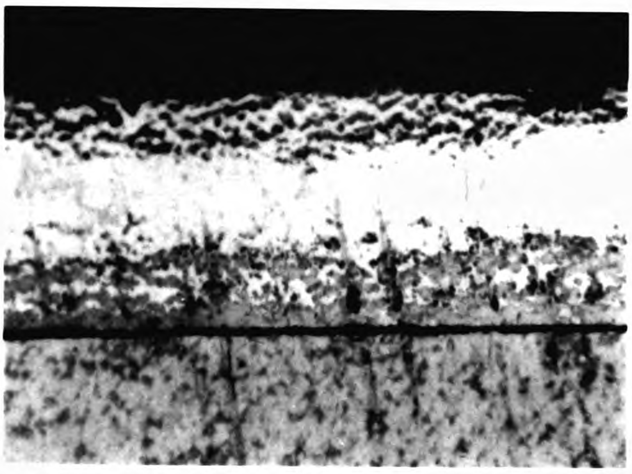


Figure 40: Optical micrograph of Joint 60.
Note fracture location around dark-etching thin layer (x 475)

Figure 41: Optical micrograph of Joint 27, showing failure through the filler.

4.6.3 Fractography

The fracture surfaces of Joints 64 and 44 are illustrated macroscopically in Figure 42.

Figure 42: Fracture surfaces of Joint 44 (left) and 63 (right)(x 2)

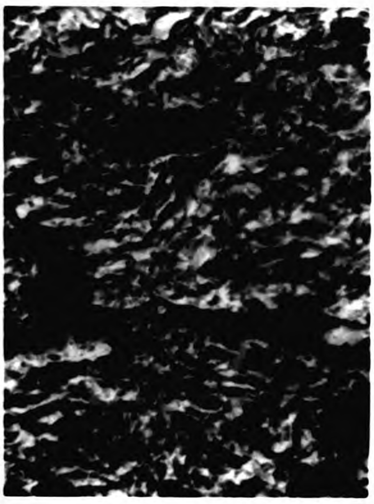


Figure 43: The fracture surface of induction braze (Ag-Cu) Joint 27 (x 2000)

Figure 44: Fracture surface of induction brazed (Cu) Joint 44.(x 2000)

Figure 45: SEM view of stainless steel joint 57 fracture surface (x 200)

Figure 46: SEM view of above (x 3000)

Notice that the copper-brazed Joint 44 has a finer fracture surface than the crystalline, typically brittle-fracture surface of Joint 64. However, under SEM examination none of the zirconium joint surfaces displayed any features that could be interpreted as evidence of ductile fracture - with the possible exception of some areas in the induction - brazed Table 5 joints; granular, facetted surfaces with cracks were the norm in all these joints. (See Figs 43 and 44).

The stainless steel joint surfaces, in contrast, displayed features which could be readily interpreted and tied in with the observations in Section 4.6.2. Figures 45 and 46 illustrate the surface of Joint 57, and show that the joint failed partly by the filler simply plucking away from the steel surface (on which the original abrasion striations are still clearly visible), and partly by failure through the filler itself, which has broken with the cup-like appearance typical of a ductile fracture.

4.6.4 Interface Examination

Since fractures in the zirconium joints were usually confined to the base metal/intermetallic phase interface area, SEM and TEM investigations were carried out on the interface areas to ascertain the presence of any defects which could promote failure.*

Figures 47 and 48 illustrate the interface area of Joint 56. Notice the small voids at the juncture of the thin and thick intermetallic layers. Likewise the TEM micrograph in Figure 49 appears to show a

*See Appendix A5

discontinuity of some sort at the same point. In contrast, there appears to be no similar discontinuity of any kind in the TEM micrograph of the induction copper brazed Joint 45 in Figure 50; the transition from base metal to intermetallic seems perfectly featureless.

Figure 47: SEM view of Joint 56. Observe the voids along the juncture between the two intermetallic layers (x 2500)

Figure 48: Higher magnification view of above (x 5000)

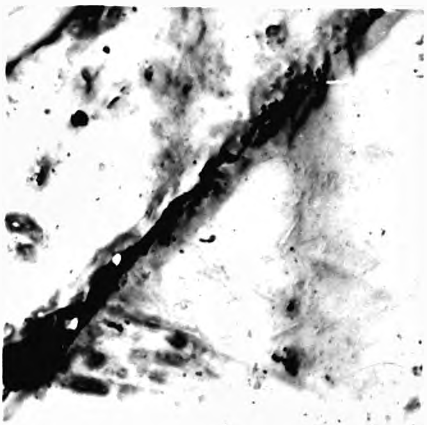


Figure 49: TEM view of the interface area in Joint 56.
Note evidence of rupture (x 2500)

Figure 50: TEM view of the interface in Joint 45.
The interface appears featureless (x 2500)

V DISCUSSION

The Discussion section consists of four main topics in which the results are evaluated and their significance discussed, from a practical as well as a scientific point of view.

5.1 WETTING AND JOINT FILLING

In the Literature Review, the point was made that a brazed joint will only be mechanically sound if it has been properly filled in the brazing operation, making the wetting/joint filling characteristics of the system all-important. In view of the wide variation in the quality of joint filling experienced in this investigation, the subject deserves special attention.

The principal result to emerge from the work on small-scale lap-joint brazing (Section 4.2.3) was that while the wetting and joint filling of zirconium (and stainless steel) joints by Ag-28Cu eutectic were generally mediocre, dramatic improvements in joint filling could be obtained by using radio-frequency induction heating rather than conventional furnace brazing; furthermore, these improvements seemed to stem not from a lowering of the contact angle in the completed braze but from other factors. In the following paragraphs an attempt will be made to explain these observations.

In a furnace-brazing operation the two factors which may be varied to induce complete joint-filling are temperature and time. Unfortunately these are the factors promoting increased intermetallic compound formation; in practice therefore, the brazing of a reactive metal is a compromise between joint filling (taking priority) and the need to keep compound formation to a minimum. The development work on brazing 55mm butt joints showed that quite a high degree of superheat - 30°C above filler melting point - had to be accepted for joint filling to be achieved.

Raising the temperature in this way to force through joint filling does, however, bring problems of its own. The inevitable increase in compound formation will clog-up the joint channel, and the reservoir of liquid filler available for joint-filling will be depleted by the reaction. Furthermore, since in this case one component (copper) is leaked preferentially from the filler, the composition of the filler will go off-eutectic into the "mushy" state, increasing its viscosity; the viscous forces add to the liquid surface tension forces raising the contact angle and increasing the resistance to capillary flow (22). These hindrances actually necessitate a temperature increase to overcome them: thus a vicious circle is created. The situation may be ameliorated to some extent (as experience showed) by increasing the joint clearance, and thereby the amount of filler. However, both responses - raising the process temperature and increasing joint clearance - are essentially "brute force" solutions leading, respectively, to increased compound formation and wider than normal joint gaps, both of which contribute to a deterioration in mechanical properties of the joint.

On the other hand, induction heating seems to offer the best of both worlds in terms of joint filling and the avoidance of compound formation.

Compared to the sluggish melting-wetting-joint-filling cycle of furnace brazing it is exceptionally rapid. Because of the short heating time compound formation is minimised, and the problems of interaction, described above, largely eliminated. This reasoning partly explains the improvement in joint-filling characteristics, but not entirely, as the improvement seems to stem ultimately from the rapid melting-wetting-flow-cycle associated with induction brazing. This point needs to be explained. The high quality of induction brazing is usually attributed to the fact that the heat is generated in the work-pieces themselves: whereas in furnace brazing, heat transfer is by the impingement of radiation onto the workpieces; a relatively inefficient process, as experience showed. As a result, so this reasoning implies, the temperature of the braze area lags behind that of the environmental temperature of the furnace chamber. Yet this cannot be the case: in a modern vacuum furnace the control thermocouple is placed on, or even inside, the article being brazed. Given this situation there seems no reason why a furnace brazing run should take 10 minutes, and an induction brazing run 10 seconds.

An answer may lie in the apparent dependence, during induction brazing, of wetting and joint-filling on the heat-up rate of the process. Recall from the results that, upon melting, the filler initially retracted, and after a period of "incubation time" wetted and filled the joint; the length of incubation time decreased with increasing heat-up rate (Section 3.2.3). If this procedure also occurs in furnace brazing, the long brazing time required could be explained by the slow heat-up rate associated with furnace brazing.

Returning to the induction brazing results, one must consider whether the incubation time is genuinely dependent on the heat-up rate itself, or whether it is linked to the final hold temperature, associated with a particular heat-up rate, experienced by the braze; this is difficult to answer for certain, but the general impression is of a combination of the two. Although hold temperatures could not be determined precisely, it seems that the effect of a rapid heating rate is to bring the filler quickly up to a higher-temperature hold, avoiding a dwell just above the melting point where wetting, if it occurs at all in the time observed, does so only after a protracted incubation time.

The question then is why wetting does not occur just above the melting point (or, put another way, why the incubation state tends to permanence), and a pertinent investigation into wetting mechanisms is that by J M Cohen, J E Castle and M B Waldron (23). Studying the wetting of Au-18Ni on Jethete steel, the authors found that flowing filler was preceded by a halo of sub-oxide flow of the filler; to account for oxide penetration, a mechanism involving the formation of defects in the oxide due to silica production was invoked. Prior to penetration by the molten filler there was an 'induction period', but this is probably not identifiable with the 'incubation time' noted in the current study; sections of non-wetted 'reject' joints revealed that the fused filler had bonded to and formed an intermetallic layer with the zirconium base metal, so penetration must occur with relative ease. Instead, the temperature dependent rate determining step is the wetting and flow of the filler by sub-oxide flow (or some other mechanism), following penetration. To describe the free energy changes associated with sub-oxide flow, Cohen et al use the equation:-

$$\Delta G = \gamma_{L/O} + \gamma_{L/M} - \gamma_{O/M} \tag{9}$$

Where $\gamma_{L/O}$ is the free energy of the liquid filler/base metal oxide interface, $\gamma_{L/M}$ that of the liquid/base metal interface, and $\gamma_{O/M}$ that of the oxide/base metal interface. The authors assert that once penetration occurs flow is spontaneous, ie ΔG is large and negative, but in the current study it may be that, at the filler melting point, the free energy terms are finely balanced, and $\Delta G \approx 0$. Looking at the free energy change via Equation 4:

$$\Delta G = \Delta H - T\Delta S$$

It might be that a raised holding temperature is necessary to give ΔG negative, as discussed in Section 2.2.2.

A thermodynamic explanation for the wetting behaviour would seem plausible, but there are objections. During low heat-up rate brazing runs, wetting could not be induced from a state of non-wetting by manually raising the temperature during the hold, contrary to what one would expect from the simple explanation above; this and the apparent link between wetting and heat-up rate suggest a possible kinetic factor.

In fact, a closer rationalisation of the wetting behaviour may lie in more recent work on the thermodynamics of wetting in which a kinetic factory is considered. Referring to Equation 3:-

$$\gamma_S - (\gamma_{S/L} + dG_R) = \gamma_L \cos\theta.$$

Sharps et al (24) consider the specific free energy of reaction - dG_R per unit area - to be a dynamic quantity whose magnitude at any given instant is dependent on the rate of reaction, which is transient. This is a radical departure from the classical thermodynamic approach adopted by, say, R J Klein Wassink (3), which considers only the energy difference between the final state and the initial state. The theory behind Sharps' assertion is set out in an earlier paper by the same group (25). It seems that at the first instant of the formation of an interface the free energy decrease of the system is solely attributable to the free energy decrease of the planar interface; but as the reaction region grows in thickness the large bulk free energy decrease will, after a certain time, reduce the overall free energy (and hence the interfacial tension) to a minimum, thereby raising the wetting force to a maximum. Thereafter the contribution of certain free-energy terms involved in the quantity dG_R will decrease and become minimal due to the diminishing chemical potential, or composition gradient, as the reaction layer thickens with time; as a result the interfacial tension will then rise to a static level of intermediate value, and the wetting force will fall off.

A further effect governing wetting behaviour is the relative rate of diffusion of reaction products compared to the flow rate of the liquid drop: if the latter is the greater, the periphery of the drop will be in contact with unreacted solid, and the large free energy change between the two will promote a transient lowering of the contact angle until mechanical equilibrium is attained; diffusion of reaction products will then proceed to the periphery, raising the interfacial free energy and increasing the contact angle. If, on the other hand, the diffusion rate of the reaction zone is greater than the flow rate, the liquid at the drop periphery will always be in contact with the reacted solid, and no transient lowering of the contact angle will occur.

From the foregoing argument it would appear that the wetting behaviour of Ag-28Cu on zirconium and on stainless steel can now be better understood. Although the metallurgy of the reaction between Ag-28Cu on zirconium is very different to that on stainless steel, Aksay et al (25) consider that the two situations - the formation of intermetallics and the formation of a solid solution in an undersaturated base metal - are similar in respect of their wetting behaviour. In the present work sections of non-wetted joints displayed intermetallic layers thicker than those in high quality wetted joints, despite no tendency for wetting; but as we have seen, what appears to provide a high initial driving force for wetting is not the ultimate extent of the reaction, but the rate of the reaction in its very earliest stages. The magnitude of this reaction (and hence the value of dG_R) would be raised in the earlier stages by a higher initial temperature - achievable by a high heating rate through the filler melting point. An insufficiently high heating rate would not induce wetting because the magnitude of dG_R would be too low.

During the earliest stages of growth of an interface layer mass transport is virtually instantaneous, and the kinetics limited only by the chemical reaction step: but the creation of a reaction layer of significant thickness will prevent a high reaction rate by imposing diffusional control on the kinetics. Furthermore, the separation of liquid and unreacted solid will reduce the free energy contribution to the driving force for wetting. For these reasons, it is argued, wetting could not be induced by raising the temperature once a state of non-wetting was established. The possibility should also be considered that filler/base metal reactions could occur during the slow heat-up rate in furnace brazing, thus helping to account for the sluggish joint filling observed.

The arguments advanced above pre-suppose the need for a large initial driving force to induce wetting. It must be admitted that there is no direct evidence for this; though such a force could be required to initiate sub-oxide flow, thereby inducing wetting. Certainly, the wetting behaviour of Ag-28Cu would be well worth further investigation, for practical and theoretical reasons.

A final point concerns the wetting behaviour of Ag-28Cu on zirconium at very high superheat (880-900°C), which created a condition of spreading caused by a rapid reaction in the absence of a rate-controlling interface layer, and the direct contact of liquid and unreacted solid. According to Aksay et al this situation is transient pending the establishment of full thermodynamic equilibrium, at which point the contact angle would rise. However, this condition would take some time to be attained, and for all practical purposes the contact angle would remain around zero throughout the brazing cycle. Unfortunately, microstructural details appeared to preclude this condition as a practical brazing procedure.

5.2 PHYSICAL METALLURGY

5.2.1 Ag-Cu Brazed Joints

The investigation into the physical metallurgy of zirconium joints brazed with Ag-Cu filler yielded results which, for discussion purposes, may be grouped into two broad areas:-

(1) The nature and reason for the formation of the two intermetallic layers at the interface of joints brazed at normal temperatures.

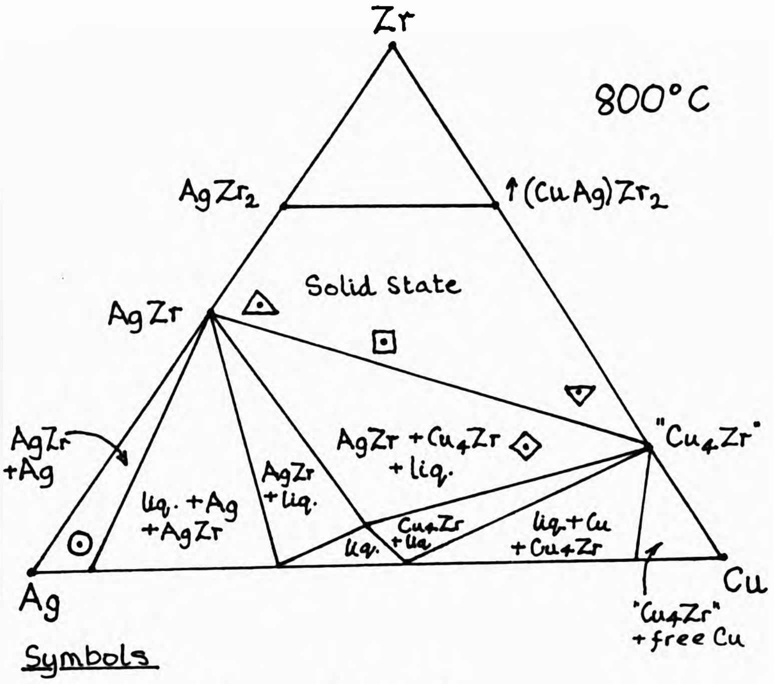
(2) At higher brazing temperatures an interface layer does not form and filler/base metal reaction is rapid. What is the cause of the transition to this regime?

When work began on joint metallography, a feature which caused some initial surprise was the absence of multi-layered interfaces. These had been expected due to the large number of Ag-Zr and Cu-Zr compounds, but V I Dybkov's work (Section 2.2.6) has explained why this was so. In fact, only two layers were present: a thin one next to the zirconium, and a thick one separating it from the filler.

In order to illustrate the Zr/Ag-Cu brazing system, a tentative 800°C isothermal section of the Ag-Cu-Zr phase diagram was obtained (Figure 51), on which the EDS compositions of the phases in both interface-layer and overheated joints have been plotted. The section is a simplified representation, although the presence of only two Cu-Zr compounds ($CuZr_2$ and Cu_4Zr) is due to these being considered the only such compounds likely to form (26).

The position of the thin interface layer is seen to lie in the solid state region near the compound Cu_4Zr, and, in fact, the EDS composition for it (Section 4.3.2.3) corresponds closely to a mixture of Cu_4Zr with a small proportion of $AgZr_2$. From XRD, a mixture of $AgZr_2$, $CuZr_2$ and free copper was recorded for the thick interface layer, although the EDS composition places it in a liquid plus solid region: this cannot be its true constitution, and a plotting or analytical error is thought to account for this anomaly. Even so, it is clear that a composition of $CuZr_2$ + $AgZr_2$ + Cu corresponds to no phase field on the section, and it could not have been created by a process at thermodynamic equilibrium. Furthermore, such a composition would not be in equilibrium with the liquid, and one would expect dissolution to occur, as suggested by metallography and the presence of zirconium in the filler.

Although attempts to measure and deduce growth kinetics were not successful, it is probable that logarithmic kinetics were prevailing, as in the analogous titanium-sterling silver system (Section 2.2.6). Growth rates of this sort represent the simultaneous dissolution as well as growth of an interface layer. It is thought that, by analogy



<u>Symbols</u>

Overheat Joints (860°C):

⊙ Ag residue

△ Ag rich crystals (AgZr)

⊡ Matrix. Liquid at >855°C?

Interface Layer Joints:

▽ Thin Layer

◇ Thick layer

Figure 51. 800C isothermal section of the Ag-Cu-Zr ternary system.

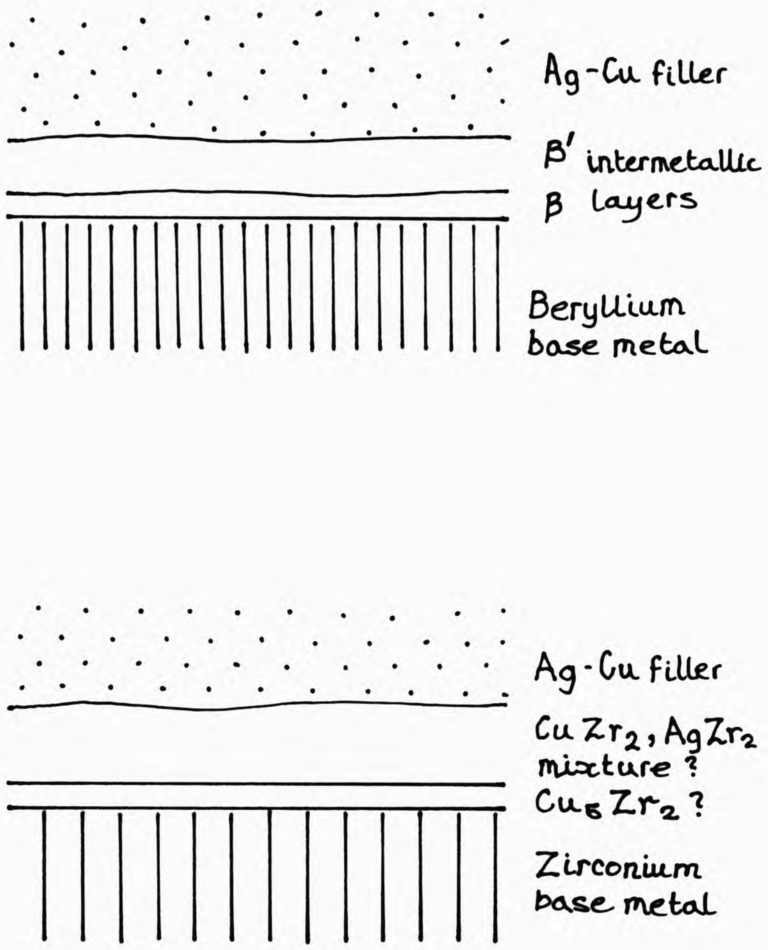


Figure 52. Physical metallurgy of Be/Ag-Cu and Zr/Ag-Cu brazed joints.

with oxidation, the latter process proceeded by diffusion of zirconium ions through the intermetallic layers to the liquid/solid reaction interface. The thick layer was itself probably decomposing too, since its composition was not in equilibrium with the zirconium base metal.

It is useful to compare the Zr/Cu-Ag brazing metallurgy with that of the Be/Cu-Ag system (Section 2.4.4), as illustrated diagrammatically in Figure 52; see Section 2.5.2 for the relevant phase diagrams. Remembering that only the copper component of Ag-Cu filler forms intermetallics with beryllium, the only interface layer observed at low brazing temperatures (790°C) is that of the Be-Cu β phase; at a slightly higher temperature (797°C), a second layer of β^1 phase appears. At very high temperatures (around 950°C) a layer of the δ phase (Be_2Cu) forms, particularly in fillet areas. There does appear to be a marked difference between the two systems. A final point is that none of the above observations on interface layer growth can be predicted from phase diagrams. As Dybkov explained, the process by which interface layers grow is dominated by kinetic factors, and thermodynamic considerations have comparatively little relevance.

The second area of interest is the transition to "overheat" conditions, experienced when zirconium joints were heated above about 850-855°C. Chaotic, deeply flawed microstructures were produced, reminiscent of the description by J Ruge et al (16) of the solidified melt in Cu-Ti friction welding. Cracks were observed to occur due to differential thermal contraction between phases, and also between the zirconium base metal and the entire solidified melt, which produced coarse transverse fissures in the braze. These features were also seen in the high-temperature induction brazed joints. A large increase in reaction rate accompanied the transition, due to the absence of a diffusion layer: kinetics were probably linear. During brazing large scale precipitation of intermetallic phase was clearly occurring, accounting for the poor joint filling under these conditions. Compositionally, the microstructure consisted of silver-zirconium precipitate in a copper-rich matrix, with a silver-rich residue of filler; the silver-zirconium compound was now not $AgZr_2$, but AgZr, as in the high temperature joints.

The question, then, is why a solid interface layer does not form, even though all the compounds, and (most probably) all their eutectics, are solid at 850-855°C. A solution is as follows. Since in lower-temperature joints the interface layer was slowly dissolving, it is argued that the overheat transition was simply the temperature at which the rate of dissolution exceeded that of growth; a solid layer would not form and inter-alloying would proceed rapidly. As the liquid became enriched in zirconium its composition reached the AgZr liquidus line, and crystals of AgZr began to precipitate isothermally, leaving the liquid copper-rich (see Figure 51). On cooling, the liquid solidifed as the matrix, consisting of Cu_4Zr with a smaller proportion of AgZr. An interesting point is that this overheat transition was not reported in the Be/Cu-Ag system (17).

5.2.2. Copper Brazed Joints

Copper brazing is a long obsolete process for joining the reactive metals. Initial attempts to copper braze zirconium produced joints characterised by gross over-reaction (not surprising, considering that liquid copper can dissolve up to 80% zirconium) and microstructures resembling the overheated type of microstructure obtained in Ag-Cu brazing. Having no practical value, this line of investigation was soon abandoned.

The use of induction rather than furnace brazing produced results of exceptional quality. As Section 4.6.1 described, the microstructure was of a eutectic, or divorced eutectic, of $CuZr_2$ and CuZr. Reference to the Zr-Cu phase diagram in Figure 7 shows that this eutectic has a melting point of 928°C; yet in the newer version of the phase diagram this feature and the compounds themselves do not exist, a point which needs explaining. It is unlikely that one is simply incorrect. Most probably, the newer one was based on experiments carried out at full thermodynamic equilibrium, whereas the first was not; even so, the latter is probably of more practical use, particularly in view of the strongly non-equilibrium conditions associated with induction brazing.

A final point is that there was nothing to be gained from brazing just above the copper melting point. In joints brazed this way the molten copper solidified isothermally, before joint-filling had been completed no doubt to the formation of the high melting point (1,100°C) compound , Cu_3/Cu_4Zr.

5.3 JOINT STRENGTHS

5.3.1 Stainless Steel Joints

For reasons which are not clear, but may be associated with an optimisation of joint-gap/joint filling variation, the strongest joints in the stainless steel series were produced by the 20 minute run, with "toughnesses" of 2.3J and 3.1J being recorded. Since no intermetallic reaction occurred in the steel joints (see Fig 21), these figures may be regarded as "benchmark" toughnesses to judge the effect of intermetallic phase reaction in zirconium joints.

The figures seem quite low, certainly in comparison with the very high toughnesses (up to 230J) obtained by Lugscheider et al (Section 2.4.3) from Au-Ni brazed steel joints. A clue to the reason for this great disparity is provided by the fracture surface micrographs of Figures 39 and 40. These show that while ductile failure through the filler (promoting toughness) has occurred in some areas, in others the filler has simply broken away from the steel surface, leaving it in pristine condition; an analogy is the disbonding of paint from a substrate. It is possible that the joint pre-treatment was not effective, but this sems unlikely, as recommended procedure was adopted and stringently applied. Brazing at a higher temperature may have helped, but the temperature used was itself fairly high.

According to theory the filler should be firmly mated to the surface by a metallurgical bond stronger than the filler itself, and this does not seem to have happened; it is as though the filler has succeeded in wetting the oxide layer, leaving it in situ. In fact this was the conclusion reached by R A Jarman et al (27) from work on the corrosion of brazed stainless steel joints. Wetting, it was argued, occurred as a result of adsorped dirt being cleared from the oxide surface, whilst Siewart (27) as quoted by Cohen (22), showed that Ag-28Cu 0.2Li wetted the oxide of 304L stainless steel via the initial diffusion of copper into the oxide surface. It seems that contrary to the discussion in Section 2.2, penetration of the oxide layer is not a universal pre-requisite for the wetting of a metal surface.

Returning to mechanical properties, the high strength of Lugscheider's joints can now be clearly understood. The fracture surfaces of these joints were entirely ductile, failure occurring through the filler. This was due to the ease of diffusion of the gold and nickel atoms into the base metal, breaking up the oxide layer and ensuring strong metal-to-metal bonding between the atoms of the filler and those of the base metal. In contrast, no such coalescence occurred in the steel joints tested in this investigation (no evidence of diffusion of either silver or copper was found) and as a result the filler was mated to the steel by a weak, electrostatic metal-to-metal oxide bond.

The load-time curve (Fig 36a) of this type of joint showed that failure occurred at a fairly high load but over a very short duration (0.3ms). This is the sort of failure typified by a brittle material, though no brittle phases were present in these joints.

5.3.2 Zirconium Joints - AgCu Brazed

This group comprised two main series of joints - vacuum furnace brazed and induction brazed. For reasons outlined earlier the former was not a success in providing quantitative information on joint embrittlement, though did at least illustrate remarks made in the Literature Review about stress concentrations and the importance of fillets.

The induction brazed joints - both those subjected to impact testing and those to slow bend testing - did provide useful information. As expected the "overheated" type of joint (Fig 28) with its cracks and other microstructural defects did exhibit impaired mechanical properties in slow bend testing compared to normally brazed joints. Impact testing of induction brazed joints (Table 5) showed "toughnesses" only slightly below the average of the best steel joints.

Microstructures of sectioned joint fractures showed a greater tendency for failure to occur in the intermetallic layer as its thickness increased. The vacuum brazed joints seemed to fracture entirely along the interface of the two intermetallic layers, but not actually through the layers, suggesting the presence of some defect associated with the interface of the layers rather than a weakness of the layers themselves. This hypothesis is supported by the evidence of SEM micrographs (Figs 47 and 48) which show what appears to be a line of voids at the interface of the two compound layers; a suggestion that these are Kirkendall pores can be discounted, since the brazing time (20 minutes) was too short for the formation of Kirkendall pores, which in any case would have formed in the base metal rather than at the interface. A more convincing explanation for the formation of these voids can be derived by analogy with oxidation and sulphidation: during the formation of a high-temperature scale by outward diffusion of metal cations (and the injection of vacancies into the bulk metal), it is quite common (29) for vacancy coalescence to occur at the metal/scale interface. Depending on its plasticity, the scale may then be unable to follow the retreating alloy surface and become locally detached from it, creating voids at the interface. The complete lack of plasticity of the intermetallic layers in the brazed joint examined would certainly promote void formation if this process applied to the growth of the intermetallic layers. More general evidence of interfacial rupturing is provided by Figure 49 (TEM). This could be due to cooling stresses, as are the transverse cracks in the compound layer observed by optical microscopy.

These microscopic defects provide very convenient straight-line fracture paths for cracks to nucleate and propagate in (see Fig 53). No doubt their magnitude increases with intermetallic layer thickness due to continued vacancy coalescence. When the intermetallic phase is very thin, the absence of significant defects will leave the intermetallic layer firmly bonded to the zirconium, causing failure through the filler by an energy absorbing ductile failure (see Fig 27). Had mechanical testing of such a joint been feasible, a higher strength than the steel joints would probably have been recorded. The vacuum brazed joints were the opposite case with 100% interfacial failure; the induction brazed joints intermediate between the two extremes.

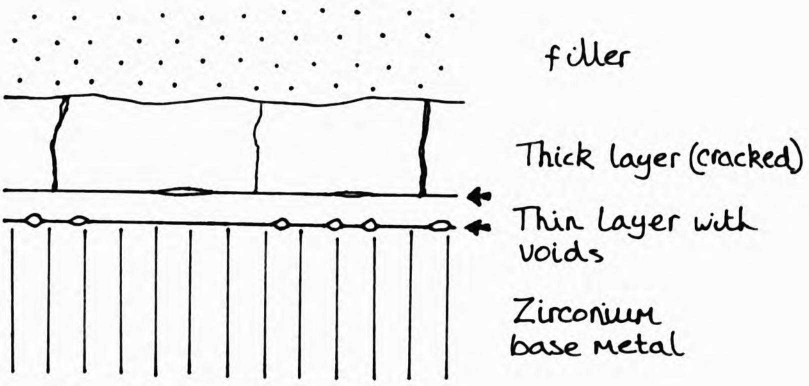


Figure 53. Schematic section of a zirconium joint brazed using Ag-Cu filler, showing cracks and voids observed from SEM analysis.

5.3.3. Zirconium Joints - Copper Brazed

As discussed in Section 5.2.2, zirconium vacuum furnace brazed joints using a copper filler were found to be of very poor quality, with gross defects and no promise of mechanical soundness. Indeed, the slow bend test (Table 7) on a simulated furnace-brazed joint (Joint 50) caused failure at negligible load. On the other hand, induction brazing using a copper filler produced the best results of all the joints tested (Table 6), although, as in the Ag-Cu brazed joints, practically all the toughness was due to initiation. There is no question of the relatively high toughness of these joints being due to ductile fracture: fractography showed nothing but a brittle fracture, and in any case the filler consisted entirely of brittle intermetallic phase. What factor was responsible for the toughness improvement?

The answer is that the formation of flaws has not occurred in the solidification of these joints. As the TEM view of the interface in Figure 50 showed, the transition from zirconium base metal to Zr-Cu intermetallic filler is completely featureless, with no defects whatsoever, and this integrity is reflected macroscopically in the neatness of these joints. Thus the results for the copper brazed joints represent a true benchmark toughness for intermetallic phase formation in a joint, with the results for the Ag-Cu joints being a "worst case", in which the effect of compound formation is exacerbated by the accompanying effect of defect formation. It is interesting to note that the copper brazed joints were stronger than the compound-free steel joints, which were brazed with a recognised (if not ideal) filler for brazing stainless steel. It seems that compound formation in a brazing system need not automatically be considered the worst soundness-determining factor.

A final point is that in this series pre-forms of different thickness were used to test the effect of joint-gap variation; as Table 6 shows, there has been no discernible effect on mechanical properties. In view of the fact that the filler was considerably harder, rather than softer, than the base metal, this is not an altogether surprising result as no effect of constraint would have been present.

5.3.4. Theory of Joint Embrittlement

In the Literature Review it was pointed out that the deterioration in joint soundness accompanying the formation of intermetallic phase cannot be sensibly explained by simply citing the brittleness of intermetallic compounds, and there is much evidence that other factors are partly or wholly responsible.

That this is so has been conclusively proved by this investigation. Solidification of the intermetallic phase in Ag-Cu brazed zirconium joints is accompanied by the formation of various defects according to the solidification mode of the compound. Thus, at overheat temperatures and above, solidification from a jumbled melt is partly isothermal and accompanied by the creation of flows resulting from cooling stresses; at lower temperatures the formation of intermetallic phase is by the diffusion controlled growth of an interface layer, a by-product of which is the formation of voids at the interface of the two sub-layers. In all the joints tested, fracture energy was more or less entirely accounted for by initiation energy; clearly, the presence of pre-existing flaws will act as nucleation sites for crack formation, markedly reducing crack initiation energy and hence reducing the overall toughness of the joint. As the magnitude of the voids increases with intermetallic phase-width, so will their stress concentrating effect; whilst the total cross sectional area available for base metal/intermetallic phase bonding will reduce. This explains the deterioration in joint mechanical properties experienced with increasing intermetallic formation.

In contrast, the straightforward eutectic solidification which characterised the copper-brazed joints was not accompanied by the creation of flaws (presumably, cooling stresses between solidified melt and substrate were insufficient to cause cracking). Consequently, these joints required a higher initiation energy for fracture.

Although the copper-brazed joints have been credited with having a degree of mechanical strength, it must be admitted that this is only under the older meaning of the word toughness: in the fracture mechanics sense, in which the stress intensity required to propagate a crack is considered, none of the joints had any toughness, since their defect tolerance under stress was negligible.

5.4 BRAZING PROCESSES: PRACTICAL RELEVANCE

The practical relevance of the three main brazing processes evaluated for their potential to ameliorate the effects of filler/base metal interaction are considered.

5.4.1 Minimisation of Intermetallic Growth

From the foregoing conclusions, minimising the extent of intermetallic formation through strict control of brazing parameters is an obvious way to produce better joints in zirconium; in fact this was the approach used to braze Ti-318 to steel joints in the construction of the Space Shuttle main engine (30). In the current investigation, induction brazing was used to achieve this aim, although the same result could probably be achieved using resistance brazing, or, in thin sheet metal, infra-red brazing.

This was the most immediately practical approach investigated. Due to equipment limitations joints with vanishingly thin intermetallic layers could not be produced: this would have required more sophisticated temperature control. A solution could be to have a circuit in the induction heater which, after a certain pre-set time into the heating cycle, lowered the work-coil voltage to a lower, pre-determined level. This would provide increased flexibility without the need for closed-loop control.

The principal disadvantage of induction brazing is that it is not a versatile process and consequently not widely used (31). Whilst it may be very suitable for joining simple-geometry parts in a production environment, it would be of little use for, say, repair work on a nuclear reactor.

5.4.2 Reactive Brazing

The use of copper as a filler to inter-alloy completely with the zirconium is an example of reactive brazing, with the refinement of using induction heating to limit interalloying. Although the method produced the strongest joints, it too lacked versatility; it could not be used for brazing zirconium to steel. The fact that cracks did not form during cooling of these joints was fortuitous and there is no guarantee of the same solidification mode applying to similarly brazed joints in titanium and beryllium. Even so, the high quality products is produced could make it a useful technique in limited situations.

5.4.3 Diffusion Heat Treatment

Although attempts to diffusion weld zirconium butt joints by heat treating as-brazed joints were not in the end successful, there is no shortage of ideas which could be used to improve the process.

The reason why the process was much less effective for zirconium than titanium was due to the former metal's lower capacity to dissolve solute atoms; this is why a liquid phase formed in the centre of the reheated zirconium joints. However, the fact that fusion occurred around the periphery of these joints shows that the method was possible. One solution could be to pre-place filler rings in concentric grooves cut into joint-faces: as the filler melted the faces would come into contact and weld together, while the molten core would be allowed to react with the zirconium. Eventually it would solidify on reaching the β zirconium solidus line, and on cooling transform to the eutectoid constituent. A simpler solution could be to use a filler with greater diffusivity in zirconium, such as the Au-18Ni alloy used for titanium to steel joints. This process could be worth developing W Feduska (32) showed that Zircaloy-2 was readily joined using a fine capillary diffusion bonding technique, which could be adapted as a post brazing diffusion bonding process; the use of platinum as an interlayer material for bonding Zr-2½Nb to steel has also been reported (33). Microstructural control of a reactive braze can be obtained using the calculations used by R R Wells (34).

An approach not considered in this investigation is the use of barrier layers, extensively studied by the International Tin Research Institute as a soldering pre-treatment (35-37). The rationale is to employ a barrier metal which forms intermetallics with the base metal at a much lower rate than the filler metal would; this approach could be evaluated for use in reactive metal brazing.

It is considered, however, that for reasons of flexibility and versatility, the best avenue for future research is via filler alloy development. Underlining this conclusion is a recently-obtained paper by Lugscheider (38), which describes the use of a Ti-15Cu 15Ni filler for brazing titanium: joints with strengths approaching that of the base metal were obtained.

VI CONCLUSIONS

In relation to the aims stated on page 5 of this thesis, the following conclusions can be made:

1. The mechanical testing scheme and joint design succeeded in providing useful information at low cost on the strength of zirconium joints brazed with silver-copper eutectic filler metal. Joints were of a modified Izod type, unnotched, with a joint area of about 60mm^2; they were produced by vacuum and induction brazing. Rigid control of joint gaps was not attempted at this stage. Filler metal washers tailored to the precise shape of mating surfaces were used to guard against joint gap variation, giving a nominal gap of 75µm. An opportunity to measure the gaps of stainless steel joints brazed for different times was missed due to loss of specimens by AWRE. Work on brazing Be-Monel 400 joints (Ref 17) showed that, in fact, comparatively little joint gap variation occurred for different brazing conditions, with no consequent effect on joint strengths; this being cited by the authors as a justification for neglecting rigid joint gap control.

Due to the unnotched joint geometry used, joint strengths were found to be seriously affected where poor fillet-forming had occurred; furthermore the testing method did not provide direct information on defect tolerance. Notched joints would probably have been less susceptible to poor fillets and would have provided direct information on defect tolerance. In any future work it is recommended that both notched and unnotched joints are tested, the latter providing information on joint strength in the absence of a defect and the quality of the fillet.

In support of the mechanical testing programme, 66 butt joints were produced for various purposes, principally mechanical testing. A larger programme had been desired, but was constrained by restricted access to brazing facilities and machining capacity.

2. A clearer picture of the formation of intermetallic compounds in brazed Zr/Ag-Cu joints has emerged from a study of about 200 lap joints produced by vacuum and induction brazing, 50 of these being examined by optical microscopy, X-ray diffraction and electron optical/analytical techniques. Numerous wetting tests were also undertaken. Normal wetting conditions were encountered from the filler melting point up to about 850-860°C, producing joints characterised by an interfacial diffusion layer; this itself consisted of a thin layer, next to the zirconium, of Cu_4Zr with some $AgZr_2$, and a thick layer next to the filler of $AgZr_2$, $CuZr_2$ and free Cu. The zirconium exhibited a greater affinity for the copper component of the Ag-28Cu filler, with the result that the filler composition went off-eutectic into the mushy zone, with increased compound formation; this produced flow problems, especially with small joint gaps.

The protective interface layer was found to be stable at brazing temperatures of up to 850-860°C, when excessive dissolution by the filler prevented it from forming. As a result a transition to "overheat" conditions was observed in which deep erosion of the zirconium occurred, together with bulk isothermal compound precipitation, preventing adequate flow. Microstructures were highly alloyed, chaotic, and with many shrinkage cracks. The main silver-zirconium compound was AgZr.

At about 880-900°C a further transition in brazing conditions was encountered: very rapid base metal dissolution occurred, the liquid become very fluid, and the contact angle reduced to zero (spreading), due to an absence of isothermal solidification. Induction brazed joints displayed a cracked, platey microstructure containing the compound AgZr, rather than $AgZr_2$.

Mechanical testing and electron optical examination have shown conclusively the effect of intermetallic compound formation on joint soundness, in both quantitative and qualitative terms. Zirconium joints, induction brazed using Ag-28Cu filler, were found to have mediocre fracture energies: in the region of 2-3J, virtually all of this being due to crack initiation. Fracture occurred preferentially along the compound layer/base metal interface, due to a line of voids at this locality. These voids, which resulted from vacancy coalescence during the compound layer growth process, lowered the initiation energy and hence the overall fracture energy. Since they could be expected to grow in size with the compound layer, this deduction provides a firm explanation for the deterioration in mechanical properties with intermetallic layer thickness observed in brazing (Ref 17), as discussed on page 37.

In contrast, joints brazed using a pure copper filler exhibited higher fracture energies: up to 9.5J. In these joints compounds were formed by a straightforward eutectic solidification process, with no voids or defects of any kind.

3. To improve joint strengths, three main approaches were considered. Compared to vacuum brazing, induction brazing was found to produce joints with greatly reduced amounts of intermetallic phases; and although this process was not conclusively demonstrated to give stronger joints, it would seem possible, especially in the light of the foregoing conclusions.

The second technique considered was reactive brazing, using a pure copper filler, giving toughnesses higher than all other joints brazed. It is not known how suitable this technique would be for more complicated joint geometries, but for simpler ones at least it offers promise. Although joints were not ductile, this drawback can to a great extent be designed out.

The final approach investigated was that of diffusion brazing. Joints were produced in zirconium and, for comparison, titanium and titanium to stainless steel. Titanium was the easier to diffusion braze due to its large solubility for many elements. Copper and silver copper performed well as diffusion fillers; gold-nickel (Au-18Ni) was exceptionally good. Zirconium could be diffusion brazed using Ag-28Cu and pure copper, but only unreliably; diffusion of these elements into the zirconium could not be detected by EDS. The situation could probably be improved by specialised joint-face machining, or by using Au-18Ni as a filler. Success could give a versatile and reliable joining process.

In addition to the above, the following conclusions were also reached:

4. In the induction brazing of zirconium and stainless steel using Ag-28Cu filler, wetting and joint filling were promoted by a high heat-up rate: a lower one produced a state of non-wetting which persisted for the time observed. This was thought to be due to the thermodynamics and kinetics of the formation of a reaction layer at its very earliest stages of growth. A rapid increase in temperature gave rise to a high reaction rate and a large transient free energy change, which is associated with a strong wetting force.

5. Stainless steel joints brazed with Ag-28Cu demonstrated fracture energies of 2.3-3.1J. The weakness of these joints was attributed to the filler wetting and leaving in situ the oxide layer, forming a weak bond with it.

VII FURTHER WORK

It is considered that two avenues of further work would be worthwhile, namely:-

1. Wetting behaviour. The link deduced between wetting and heat-up rate during induction brazing was an entirely unexpected feature, deserving further investigation, for practical and theoretical reasons. A number of questions require answers. Is the hypothesis advanced to explain it correct, or is there a simpler explanation? Is the phenomenon restricted to Ag-28Cu? Does it occur during furnace brazing? Brazing technologists consulted had no experience of it, and were unable to offer an explanation (31).

2. The methods of producing tougher joints examined worked to a degree, but all lacked flexibility. In any future work a better approach could be to concentrate on the filler metal composition. Studies could include reaction kinetics, mode of intermetallic formation, presence of flaws, joint strengths; filler metal compositions would be varied.

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APPENDIX

Further details and numbers of the tests undertaken are given to substantiate the claims made in this thesis.

LIST

A1 Wetting tests in vacuum brazing (VB), (4.1.1).
A2 Wetting tests in RF induction brazing (RFB), (4.2.2).
A3 Lap joint metallography (4.1.2, 4.2.3).
A4 Mechanical testing (4.5.1, 4.5.2).
A5 Electron optical and analytical work (4.3, 4.6.1, 4.6.4).

A1 WETTING TESTS - VACUUM BRAZING

Temperature (C)	Time (mins)	Contact Angle*	Characterisation
800	15	18°	Normal wetting
800	15	16°	" "
815	15	18°	" "
830	15		Visible compound formation
840	10		" " "
850	10		" " "
860	10		Gross over-reaction & erosion
860	10		" " "
870	10		" " "
880	5	0°	Rapid Dissolution
900	1	0°	" "
900	1	0°	" "

* Contact angle was measured where possible. At slightly elevated brazing temperatures (815-830°C) and above, compound formation at the drop periphery made measurement unreliable. Around 880-900°C a condition of spreading was encountered (0° contact angle). Broadly, contact angle measurement was not found a fruitful line of work in this study, partly due to the interalloying characteristics of the brazing system, and partly to the nature of the brazing processes used. Wetting tests could not, in general, be carried out by VB concomitantly with joint brazing due to the very extended times required to effect melting of the former. This became a serious constraint on work in this area.

A2 WETTING TESTS - INDUCTION BRAZING

Nos Brazed	Brazing Time (s)	Estimated Temperature (°C)	Contact Angle
20	10	800-820	14-20
30	10-100	800-820	180°*
10	10	860-880	None measureable
10	5	880-900	0°

* The condition of non-wetting described in Section 3.2.4, attributed to the heat-up rate.

A3 LAP JOINT METALLOGRAPHY

i. Vacuum Brazing

No of Tests	Temp (°C)	Time (mins)	Intermetallic Thickness (µm)	Microstructure	Failure Site
4	800	15		Normal	(1)
2	780	3	9.0	"	(1)
2	780	5	10.5	"	(1)
2	780	7	12.0	"	(1)
2	780	9	13.5	"	(1)
2	780	21	16.0	"	(1)
2	820	10			(1)
2	830	10			(1)
2	840	10			(1)
2	850	10			(1)
1	860	10		Overheated	(2)
1	870	10		"	(2)

ii. Induction Brazing

No of Tests	Temp (°C)	Time (mins)	Intermetallic Thickness (µm)	Microstructure	Failure Site
20	800-820	10	1-2	Normal	(1)
10*	"	10		"	(1)
2	"	2		"	(3)
10	860-880	10		Overheated	(2)
5	880-900	5		"Platey"	(2)

Failure site: (1) Predominantly through base metal/intermetallic layer interface.
(2) Along cracks in joint; through interface.
(3) Through filler (under-brased joint).

* Non wetted joints.

A4 MECHANICAL TESTING

All mechanical testing results are recorded in the Results Section. Load-time curves of all joints subjected to impact testing were recorded, but only one representative curve for each type of joint is presented (Figure 36, p104). A more extensive programme had been desired, but was constrained by limited access to vacuum brazing facilities, and by specimen production.

A5 ANALYTICAL WORK

No of Joints Examined	Type	Process	Analytical Tools	Defects Observed
4	Normal	VB	SEM;EDS;TEM;XRD	(1)
2	Overheated	VB	SEM;EDS;XRD	(2)
1	"	RFB	SEM	(2)(3)
2	High Temp	RFB	SEM;XRD;EDS	(3)
2	Cu Brazed	RFB	SEM;EDS;TEM	None

Defects: (1) Interface voids, transverse microcracks in intermetallic phases.
(2) Shrinkage cracks between intermetallic phases.
(3) Transverse fissues across joints.

XRD work on the first three types of (AgCu brazed) joint was undertaken at City of London Polytechnic and independently by AWRE. Comprehensive EPMA results were obtained but lost by AWRE.

TITLE THE FORMATION OF BRITTLE PHASES IN BRAZED ZIRCONIUM JOINTS

AUTHOR Julian Charles Bassett

INSTITUTION and DATE City of London Polytechnic CNAA 1991

CAMERA 8