

Frequently asked questions #4

Is it possible to braze ceramics?

It is an established fact that the properties of ceramics in regard to both hardness and their excellent stability at elevated temperatures has meant that they are increasingly found as a vital constituent in a wide range of modern engineering applications. To enable their use for a particular job often means that they need to be joined either to themselves or to metals, and for practical reasons the direct welding of ceramics is nearly always impossible. (*However, in a few very special cases where either Silicon Carbide or Silicon Nitride is involved, laser-beam processes are available that allows the direct welding of ceramic to ceramic*). Thus to satisfy the need to use ceramics in engineering applications it was clear that alternative joining processes would have to be developed. As a result intensive research into joining methods for ceramics was undertaken.

One area of joining research was brazing, and in the initial years of the use of ceramics in industry, the chosen route was to use a technique that is now internationally known as the molybdenum-manganese metallising technique. With this procedure it is found that alumina, in conjunction with a sintering process, can be given a metallic coating. The parts to be coated are covered with a mixture of metal and oxide powders, placed in a furnace, and sintered at about 1500°C in wet hydrogen. (*Naturally, specific information relating to the dew-point of the atmosphere is known to the user but this is regarded as a 'process secret' and is therefore never disclosed to third parties!*). The coated parts are cooled, removed from the furnace, and then given a very thin electro-plated coating of nickel. The components are then re-sintered at about 950°C to consolidate the plated layer to the Mo-Mn metallised substrate. The components are cooled, and removed from the furnace.

This procedure provides a surface that can then be wet by a number of brazing filler materials, typically silver-copper eutectic, silver-copper-palladium, gold-nickel, and derivatives of these three alloy systems. Certainly, the Mo-Mn metallising system provides a viable process that allows alumina to be brazed to metals, but due to the complexity of the various stages it was apparent that something 'better' was called for and, as if almost by chance, an important development occurred.

As mentioned earlier, research into brazing as a method of ceramic joining was being actively pursued. One worker in the American aircraft industry noted that when he was brazing Mo-Mn metallised surfaces at around 1150°C with experimental brazing alloys containing a small addition of zirconium, the filler material not only wetted the metallised surface, but the 'small overflow' of filler material that flowed out onto the alumina appeared to have wet that too!

It was this 'discovery' that is widely believed to be the 'founding father' of 'active brazing' alloys. Their development made it possible to effect the direct brazing of ceramic to itself, other ceramics and cermets, and to a whole range of metals. Among the **ceramic** materials that are wet by 'activated' brazing alloys are:

| | | | |
|----------|-----------------|---------------|-------------------------|
| Alumina | Silicon Nitride | Boron Carbide | Boron Nitride(hex/cub.) |
| Sapphire | Silicon Carbide | Zirconia | Aluminium Nitride |
| Diamond | Glass | Pure Graphite | |

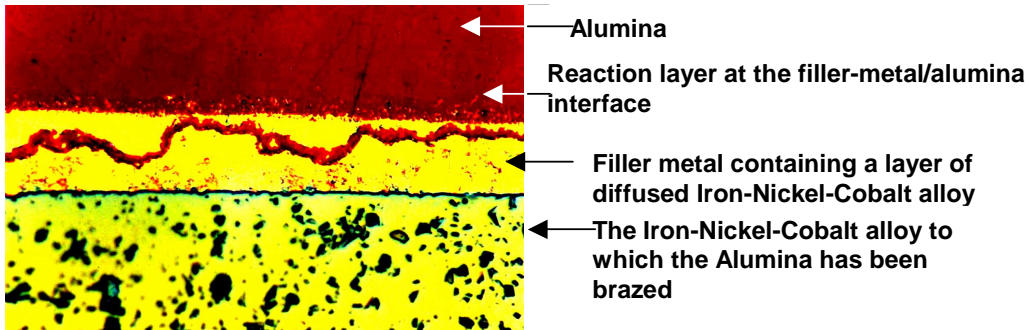
General properties of filler materials for the direct brazing of ceramics

Essentially, the filler materials that are to be used have been formulated to incorporate an 'activating' element. This is very often titanium, but hafnium, niobium and zirconium are also a possibility. During the brazing procedure, (which **must** be carried out under vacuum or pure, ultra dry, argon or hydrogen), the activating element reacts with the ceramic substrate to form a series of highly complex inter-metallic metallurgical phases these being subsequently wet by the molten filler material.

The result is a vacuum tight joint that, dependent upon the composition of the chosen active brazing material, will withstand operating temperatures up to about 600°C. Fig 1 demonstrates the reality of brazing such materials!

Fig 1: Photomicrograph of a piece of Alumina that has been brazed to an Iron-Nickel-Cobalt alloy with titanium ‘activated’ Silver-Copper-Indium brazing filler material..Note particularly the presence of the *reaction layer* at the interface between the filler material and the ceramic. Photograph

Courtesy: Listemann AG, Liechtenstein.



There is a relatively wide range of ‘active’ brazing materials available. Originally, many of these materials were developed within the USA, and were only available there. Fortunately it is now possible to purchase them from a number of different sources in Europe. However, in this article we will only be commenting upon those materials that can be readily sourced in Europe. These are:

- 5 materials for the *direct brazing* of ceramics.
- 2 materials for the *direct soldering* of ceramics. (However, for the reasons given below the term ‘*solder*’ is questionable.)

N.B. It is very important to understand that the ‘activity’ which causes these materials to wet ceramics will only occur at temperatures above about 750°C depending upon the composition of the ceramic that is to be brazed. In general nitride- and carbide- can be more easily wet than the oxide-ceramic types. Thus in all cases the assemblies that are to be joined have to be heated to at least this temperature. As a result the description ‘Ceramic Solder’ is, in part, a misnomer. This is because these materials also have to be heated to at least the same temperature level as required for the active *brazing alloys*, however, because their *liquidus* temperatures are *below 450°C*, by International Convention the materials are described as ‘*Solders!*’ However, because there are a number of handling problems necessarily associated with their use, they are now tending to be seen as ‘curiosities’ rather than main-stream filler materials.

It is important to note that a certain minimum amount of the ‘activating’ element has to be present in the molten filler material in order that wetting of the ceramic substrate can occur. It is an established fact that during the wetting process much of the ‘activating’ element tends to migrate toward, and concentrate itself at, the molten filler material/ceramic interface. The effect of this phenomenon is that the *advancing front* of the molten filler material contains only a very small amount of the ‘activating’ element. This phenomenon very soon results in complete cessation of filler metal flow. This is due to the level of ‘activating’ ingredient in the material having fallen to a concentration that is insufficient to sustain the wetting action.

As a result the term ‘flow’ in relation to ‘active’ brazing alloys has a very different meaning when compared to what one normally expects when a conventional silver brazing alloy is wetting and flowing on a mild steel-to-mild steel joint. Indeed, joint penetration of 15-20 mm, (say about $\frac{3}{4}$ inch), would be considered a distinct possibility if a silver-bearing filler material which exhibits ‘good’ flow characteristics, for example the 56%Ag:Cu:Zn:Sn alloy conforming to EN1044 Type AG102, was being used. With an active brazing alloy being used to join

stainless steel to alumina for example, 'good' flow is considered to have occurred in those cases where the maximum flow has been of the order of 1.5 mm, (1/16th inch)!

This property of 'active' brazing alloys explains why most applications demand the use of a brazing alloy foil/wire or screen-printed paste that is 'sandwiched' between the parts to be joined. It is a well-understood fact that when the production of a sound and properly brazed joint is the sole objective, significant flow of a molten filler material is not necessarily a prerequisite for success! Thus it is clear that since 'active' brazing alloys do not exhibit good capillary flow, they are, in common with many of the nickel-base filler materials, best classified as **zero-flow** filler materials.

An alternative procedure is to create an 'active' filler material in-situ in the joint. This is often achieved by mixing, say, silver-copper eutectic powder with titanium hydride powder. During vacuum brazing, at a temperature of about 700°C the titanium hydride decomposes to produce pure titanium and modest quantities of hydrogen, this latter being immediately pumped out of the furnace. The titanium metal that remains then alloys with the silver-copper eutectic powder, to produce an 'active' silver-copper eutectic alloy in-situ in the joint. It is perhaps interesting to note that this approach was often adopted when 'active' brazing filler materials were in their infancy, and when the foundry techniques in use at the time were not sophisticated enough to deal properly with the melting of titanium-bearing materials!

Indeed more than 45 years ago at least one UK producer of silver brazing alloys was supplying a titanium-cored silver-copper eutectic wire into the electronics industry where it was used in the manufacture of diamond- or sapphire-tipped 'needles' for playing the newly-developed high-fidelity records designed to rotate at a rate of 33 1/3 revolutions per minute! In this case when the silver-copper eutectic alloy melted it dissolved a proportion of the titanium core, thus generating an 'activated' filler material. This material brazed the 'jewel' that was to become the tip of the needle into its shank; from about 1963 to the late 1980's millions of such joints were made each year throughout the world.

In yet other situations titanium-base filler materials like those in the Titanium-Copper-Nickel system can be readily used for the joining of ceramics.

Table 1 lists the range of five 'active' brazing filler materials and two of the, so-called 'active' solders that will be discussed later in this Paper.

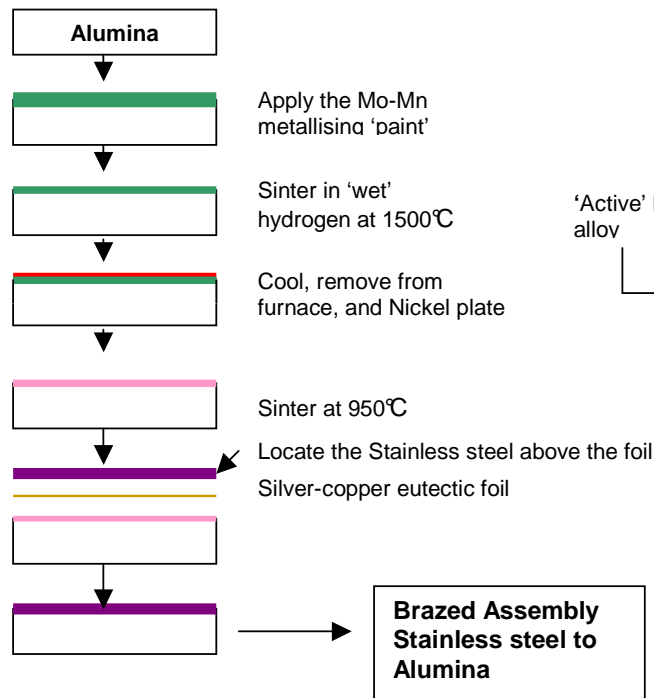
| 'Active' material type | Nominal Composition | Active Element | Approximate Melting Range °C | Brazing Temperature Range °C |
|------------------------|---------------------|----------------|------------------------------|------------------------------|
| Brazing | 72.5Ag/19.5Cu/5 In | Titanium 3% | 730 - 760 | 850 - 950 |
| Brazing | 96Ag | Titanium 4% | 970 | 1000-1050 |
| Brazing | 70.5Ag/26.5Cu | Titanium 3% | 780 - 805 | 850 - 950 |
| Brazing | 64Ag/34.2Cu | Titanium 1.8% | 780 - 810 | 850 - 950 |
| Brazing | 98.4Ag/1 In | Titanium 0.6% | 948 - 959 | 1000-1050 |
| 'Soldering' | 89.5Sn/10.5 Ag | Titanium | 220 - 275 | 850 - 950 |
| 'Soldering' | 96Pb/4 In | Titanium | 320 - 325 | 850 - 950 |

Table 1: A selection of 'active' filler materials that are frequently used for the direct joining of ceramics

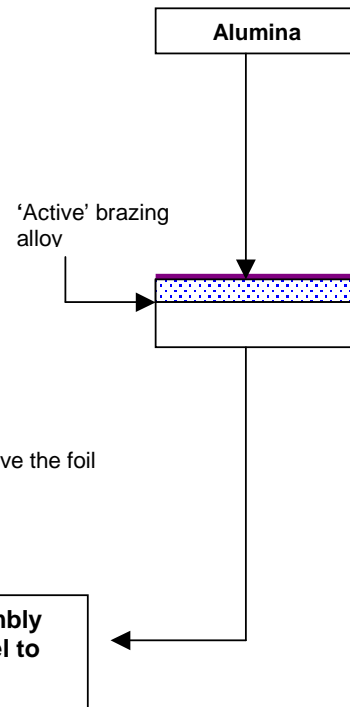
Filler material selection for specific applications

Before we move on to discuss this important aspect, it will be interesting to compare the metallising process with the use of an active brazing filler material. Clearly, the following sketches are **not** to scale

The Metallising Route



The 'active' metal brazing route



Which route do you think is the more convenient?

In 'best practice' joint design in regard to the positioning of the mating materials, the controlling factor are the respective coefficient of thermal expansion of the parts that are to be joined. This is important in all cases, and particularly in those situations where a sleeve joint has to be made.

When ceramics are to be brazed, particularly in those situations where the mating part is a metal, the respective differential thermal coefficient of thermal expansion between the mating parts is of paramount importance. As a general rule engineers tend to assume that the coefficient of thermal expansion of a metal will be several times that of a ceramic. This is not always true, however. For example ceramics such as silicon nitride and silicon carbide do, indeed, have very low coefficient of thermal expansion, and problems arising from stresses generated during the cooling stage can be expected in situations where such materials are brazed to stainless steels or copper both of which being metals that possess a high coefficient of thermal expansion. However titanium, titanium alloys and some special materials such as Invar and Kovar each have a coefficient of thermal expansion which is close to that of alumina, while expansion coefficients of molybdenum and tungsten are close to those of both silicon carbide and silicon nitride. This means that when choosing the 'active' filler material that will be used for a particular job it is vital to determine the differential coefficient of expansion that exists between the materials that are to be joined.

The **Fundamental Rule** is:

Choose a filler material that has ductility that is good enough to avoid stress failure during the cooling cycle together with a solidus temperature that is as low as possible in order to minimise ΔT where shrinkage can occur

The following paragraphs provide recommendations that will assist in the selection of the most appropriate material for a given application.

a. 72.5Ag: 19.5Cu: 5In:3Ti

This material has the lowest melting range of any of the five materials that form the range of 'active' *brazing alloys* shown in **Table: 1**. It exhibits good wetting and flow characteristics, has a high intrinsic strength, *but a relatively low level of ductility*. It is these two latter characteristics that demand further comment in the light of the 'Fundamental Rule' mentioned above

The fact of the high intrinsic strength bestows a seemingly obvious advantage to its use. However this advantage can only be realised when the parts that are joined by this material have coefficients of expansion that are broadly similar, for example Nilo K and alumina. If parts of widely differing coefficients of expansion are to be joined it is clear that that the amount of 'contraction induced stress' applied to the joint during the cooling stage of the process may lead to one or both of joint and/or component failure.

While the alloy possesses good strength, its ability to deform plastically, and so absorb contraction induced stress, is relatively limited.

b. 96Ag: 4Ti

This material has the highest melting point and the greatest titanium content of any of the materials in **Table 1**. This is both an advantage and, according to the application for which it is to be employed, a disadvantage!

Due to the high titanium content, its wetting behaviour is superb, but for the same reason the material is *unsuitable* for use for the brazing of *Silicon Carbide*. This is because of the well-know phenomenon of the formation of extremely brittle intermetallic phases when silicon and titanium react with each other.

Because of the high silver content, the material present in the joint after brazing is, to all intents and purposes, 'pure silver' and as a result:

- Is extremely ductile
- Exhibits excellent oxidation resistance up to about 600°C
- Has a very low tensile strength, (which reduces even further as the temperature rises above 200°C!).

In consequence, for operating conditions above 200°C this material will only be suitable for use where vacuum-tight joints are required **and where the joints will *not* be required to sustain service loads**.

The range of brazing temperatures recommended for this material, 1000 – 1050°C. Unfortunately, at this temperature level there is the certainty that if vacuum brazing has been selected as the heating method the evaporation of the silver is likely to occur. This problem can be avoided by the introduction of a partial pressure of pure, dry *argon* into the furnace chamber to suppress the tendency for the volatilisation of silver during the final stages of the heating process.

c. 70.5Ag: 26.5Cu: 3Ti

This material is, essentially, 'activated' silver-copper eutectic. As a result it is the most 'universal' of the materials in the range under consideration. It possesses good wetting and flow characteristics, but has a lower post-braze ductility than the 96%Ag:Ti material and, perhaps, also that of the 64%Ag: Cu: Ti alloy mentioned below.

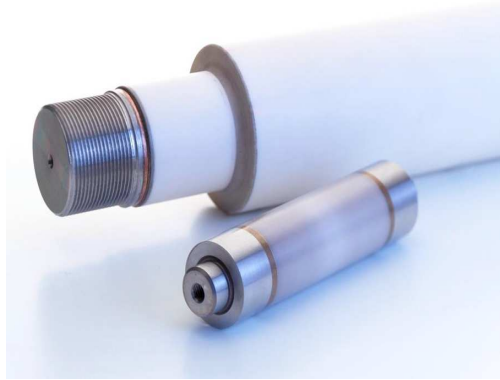
d. 64Ag: 34.2Cu: 1.8Ti

This material has the lowest titanium content of any of the range, and thus its ability to flow, and its wetting characteristics are not particularly good. However, due to the comparatively low titanium content the post-braze ductility of the material is relatively good.

e. 98.4Ag: 1In: 0.6Ti

This material has been specially developed for the brazing of *silicon nitride* and *diamond*.

It has no other uses, and should therefore only be employed when these materials are required to be brazed to themselves, to each other, or to other materials.



Here, **Fig 2** shows the technical viability of the brazing of stainless steel to alumina with titanium 'activated' silver brazing alloy. The joint also incorporates a copper interlayer to assist in the minimisation of stress-induced failure during the cooling stage of the vacuum brazing process

**Photograph Courtesy:
Listemann AG
Liechtenstein.**

The 'Active' solders

These materials have low mechanical strengths, and are therefore best suited for use as a seal where:

- Service stresses are low,
- Where the operating temperature of the joint is below 100° C, and
- Where the components that are to be joined have **widely different** coefficients of thermal expansion.

While heating to about 900°C is mandatory in order that the 'activity' provided by the presence of titanium will function, it is clear that these materials will not solidify until the assembly, and hence the joint, has cooled to about 300°C. Clearly, by the time that this temperature has been reached the majority of the contraction experienced by the components as they cool from brazing temperature will have taken place. Due to the excellent ductility of the 'active' soldering materials, the alloy will normally readily absorb the contraction that still has to occur without joint failure occurring. It is this feature that makes them so useful for use in those applications where wide differences in the coefficient of expansion are a characteristic of the materials that are to be joined. It should be noted, however, that a supply of such materials is not easy to find and it could be the case that they would need to be 'specially produced' and this would have a profound effect upon their cost!

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The author wishes to express his special thanks to Manfred Boretius of Listemann AG for the help and comments he provided while this Paper was being drafted. Without that help this document would not have been written.