Fluxless soldering is required for joints in high-performance and aerospace electronics where no contamination is permissible from flux residues or cleaning agents.

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Successful soldering largely depends on the ability of the solder to wet and spread on component surfaces. A major barrier to wetting is presented by stable nonmetallic films and coatings, in particular oxides and carbon residues. Fluxes are chemical agents that remove these layers and thereby promote wetting by the molten filler. However, although the vast majority of commercial soldering operations involve fluxes, they are not appropriate for many high-performance electronics and photonics systems because residue contamination can diminish product function, performance, and life.

Unfortunately, it is normally not possible to make a fluxless soldered joint of the same quality as a fluxed joint because the flux removes surface oxides at the very instant when the solder is required to wet. In the absence of flux, the crux of a successful fluxless soldering process is to eliminate all surface contamination from the faying surfaces and to protect the surfaces from oxidation through the heating cycle.

However, this will likely still be insufficient to produce a good quality joint, and additional means are necessary to encourage wetting and spreading of molten filler metals. Generally, such methods involve non-oxidizable metallizations on the parent materials, minimizing the surface-area-to-volume ratio of the filler metal, applying mechanical means of enhancing solder flow, and sometimes, metallurgical modification of the contact angle. Because oxide films grow so rapidly on most base metals, in practice only gold or platinum can provide clean and solderable surfaces. Accordingly, for fluxless soldering, a gold coating is generally applied that must be of adequate thickness and sufficiently pore-free to ensure good solderability over its specified storage life (Fig. 1).

This article discusses the types of solders that are compatible with gold coatings, the preferred geometry of solder preforms, mechanically enhanced solder flow, and metallurgically enhanced solder flow.

Solderable component surfaces

It is important to bear in mind that the solderable shelf life provided by a gold coating is a function of the roughness of the underlying surface, the method of application of the coating, and its thickness. A 0.5 µm (20 µin.) thick gold layer deposited by sputtering can be relied on to maintain excellent solderability for several months, even where the coated surface is relatively rough.

On the other hand, the solderability of a gold layer of the same thickness, but applied by electroplating to a rough surface (Ra> 3 µm, or 120 µin.), may not offer adequate protection to an underlying base metal from atmospheric oxidation for more than a few days.

Gold-coated surfaces also impose constraints on the types of solders that can be applied. In particular, most tin-base solders, including lead-tin eutectic, are largely incompatible with thick gold metallizations. The problem stems from the high solubility of tin in gold, which results in the formation of AuSn4 and subsequent embrittlement of the joints if this phase becomes dominant. This restriction can be overcome only by applying high-quality gold coatings of minimum thickness to the joint surfaces, thus preventing the formation of AuSn4 as the primary phase.

Where thicker gold coatings are needed, fluxless...
soldering tends to be confined to high-gold and indium-base solders, which do not form catastrophic embrittling phases with gold. The necessity for a noble metal surface on the parent materials can be eliminated if the solder itself is applied as the barrier coating to previously cleaned component surfaces.

**Preform geometry**

The form in which solder is admitted into a joint gap can make a profound difference to the success of fluxed and especially fluxless soldering processes. Notwithstanding the condition of the faying surfaces, it is a general rule that the greater the solder volume in relation to its exposed surface area, then the more readily the process will work. This is simply because proportionally less oxide is present to impede wetting and spreading.

It is therefore perhaps not surprising that manufacturers of solder paste go to considerable lengths to ensure that the solder balls in the product are perfectly spherical and have exceptionally high surface smoothness (low Ra). For the same reason, the most common form of solder is round wire.

The most appropriate preform geometry for admitting solder into a joint gap depends on the shape of the components. Ideally, the solder preforms should be designed to have not only a high volume-to-surface-area ratio, but also an orientation that permits the advancing front of molten solder to sweep trapped gas out of the joint gap.

In some situations, it is necessary to make joints with very low aspect ratios; that is, thin in relation to the plan area. In this case, it is often not possible to achieve sufficient solder spread to reliably fill the joint completely. This scenario is commonly encountered in the microelectronics and photonics industries, where planar components must be joined with extremely narrow joint gaps because of the relatively poor thermal conductivity of most solder alloys.

The thinnest solder preforms that can be economically purchased are 15 µm (0.6 mil) thick. Handling these foils is almost an art form, and mechanically cleaning them is virtually impossible. The high surface-area-to-volume ratio of such preforms also runs counter to the need to minimize native oxides.

A growing number of companies are now offering a solution to this problem in the form of substrates on which the solder composition of choice has been pre-applied. The solder is usually deposited by electroplating only the required areas of the substrate. The solder thicknesses range from 2 to 50 µm (0.08 to 2 mil), and almost every common composition is available. Solder-coated substrates offer several distinct advantages:

- Piece-part inventory and number of suppliers are reduced by dispensing with preforms.
- Jigging is likely to be simpler.
- The thickness of the solder joint is lower because the solder layer can be substantially thinner than the minimum practicable thickness of approximately 25 µm (1 mil) required for a preform.
- Soldering behavior is improved by eliminating two joint surfaces with all the attendant problems, including oxide layers, from the joint gap.
- Solder spread is automatically confined to a precise area, and the responsibility of substrate wettability is also passed on to the substrate producer.

The quality of substrates prepared in this manner has improved substantially, and although cost is higher than traditional foil, they are now available to aerospace and telecommunications-qualified standards.

**Mechanically enhanced solder flow**

No matter what precautions are taken, during an industrial fluxless soldering process the solder will always be totally encased in a skin of oxide by the time the components and preform have been set in jigs, loaded into the protective atmosphere, and heated to the process temperature. If it is possible to extrude virgin metal through fissures or other defects in the solder skin, then the prospects are improved for achieving a sound joint. One method of doing this is to apply a compressive force to the joint gap.

The effectiveness of this approach is illustrated in Fig. 2, which shows how void levels decrease with higher applied loads. Clearly, the higher the compressive pressure, the more effective it is, with...
the optimal load in the region of 10 g/mm² (14 psi), or more. A loading such as this is relatively easy to achieve with weights or spring-loaded jigs for all but the largest components. Precautions need to be taken to ensure that the load is applied uniformly and parallel to the joint gap, and that the method of application does not impose a thermal sink that would give rise to adverse temperature gradients. Figure 3 shows exploitation of this approach in fluxless soldering of a GaAs semiconductor die to a gold thick-film metallized alumina substrate. The back of the semiconductor is metallized with gold, and the filler metal is a preform of Ag-96Sn solder, 15 µm (0.6 mil) thick. The process superheat was 30°C (54°F) above the melting point of the filler metal. X-radiography reveals the joint to be free of voids. The black circles are blind vias in the GaAs die, which are included for functional reasons.

Metallurgically enhanced solder flow

Occasional reports appear in the published literature about the significant difference that low concentrations of other metals can make in promoting wetting and spreading of molten solders. Virtually all fluxless aluminum brazes make use of the fact that ppm levels of bismuth and beryllium have a marked effect on the wetting and spreading characteristics of the Al-12Si eutectic alloy. (Further information on fluxless aluminum brazing is to be found in the companion volume, Principles of Brazing.)

The authors have investigated improving the fluidity of indium by minor additions of other elements with a view to enhancing indium filler metals in fluxless processes. Figure 4 shows the wetting angle as a function of heating time for pellets of indium solders of controlled weight and geometry wetted onto silver substrates at 200°C (392°F) in a vacuum of 1 mPa (1.5 to 10⁻⁷ psi). The measurements were taken from video stills of the substrate viewed edge-on, with the timeline beginning at the onset of observed melting. The added elements showed the following results:

- **Zinc** has an adverse effect, reducing wettability by raising the wetting angle.
- **Antimony** is initially neutral, but appears to impede any additional wetting.
- **Bismuth and gold** are beneficial additions that improve wettability, which requires an extended dwell at the soldering temperature to take effect.
- **Cerium**, the rare-earth metal, produces a marked and immediate reduction in contact angle. This could be a fruitful area for further research in developing new solder alloys.

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**Fig. 3** — Fluxless soldering of a GaAs monolithic microwave integrated circuit is achieved by application of a compressive load of 100 g/mm² (140 psi) during the heating cycle. Image courtesy BAE Systems.

**Fig. 4** — The effect of different doping additions on the fluxless wetting angle of indium on silver substrates is shown as a function of the amount of time following commencement of solder melting.