Tears of Wine and Palladium-coated Copper Wire: The Marangoni Effect

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Mixing of palladium and copper within conventional palladium-coated copper wires is explained by the Marangoni effect. Proprietary dopants can counter this effect.

Tears of wine are the clear liquid rising and eventually falling inside of a glass filled with wine as shown in **FIGURE 1**. This is caused by water flowing away from evaporating alcohol because of differences in their surface tension. Water, with a higher surface tension, climbs up the glass wall by capillary action away from the alcohol-water mixture in wine. This is known as the Marangoni Effect named after physicist Carlo Giuseppe Matteo Marangoni who studied the reaction of oil on water in the 1860s. An illustration of this effect on mixed materials at the application of heat is shown in **FIGURE 2**.

Figure 1. Tears of wine flowing down inside a glass of wine blurring a lady's face behind it.

In thermosonic wire bonding, the most common method of interconnecting semiconductors, the Marangoni Effect is hypothesized to be the mechanism in the creation of the Free-Air Ball (FAB). The FAB is the spherical end of the wire molten by electric discharge that is then pressed and ultrasonically welded to the device to make the first bond of the interconnection.

FAB Formation

In the molten state of FABs made from conventional palladium-coated copper (PCC) wires, the palladium coating becomes mobile and flows from the high-temperature/low-surface tension in the bottom of the FAB caused by the electronic discharge of the Electronic Flame-Off (EFO) system towards the low-temperature/high-surface tension at the top region due to the thermal diffusion through the wire as shown in **FIGURE 3**. Consequently, the FAB surface of conventional PCC wire is only partially coated by palladium with the rest being copper. Copper, of course, is prone to oxidation and corrosion attack by halogens such as chlorine. Chlorinated substances are normally found in the environment and even in mold compounds used for semiconductor encapsulation.

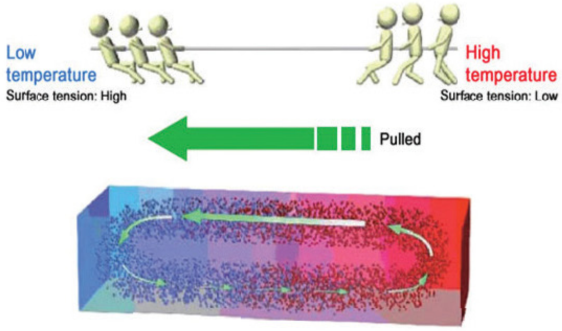


Figure 2. The Marangoni Effect explains the flow of component materials from high-temperature/low-surface tension towards low-temperature/high-surface tension in liquid phase.
Source : https://iss.jaxa.jp/kiboexp/theme/first/marangoni/haikei.html.

Optical inspection of conventional PCC wire FABs show reddish-brown coloration of exposed copper as shown in **FIGURE 4** (left). Electron Probe Micro-Analyzer (EPMA) of cross-sectioned FABs show circular pattern flow of palladium within (right). This is indicative of the Marangoni Effect where the high temperature difference

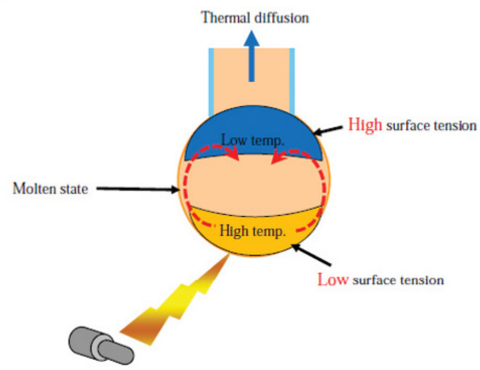


Figure 3. Palladium flow within a conventional palladium-coated copper wire during FAB formation.

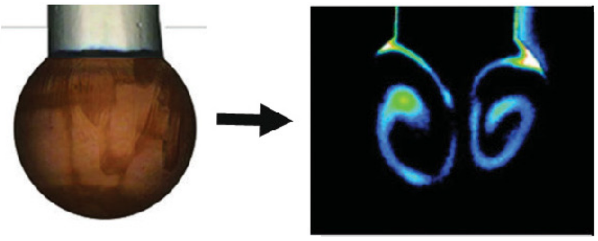


Figure 4. Optical image (left) and cross-section EPMA image (right) of FAB showing palladium flow (blue/green) in conventional palladium-coated copper wire.

between the bottom of the FAB and its relatively cooler top due to heat conduction through the wire above it causes inversely proportional surface tension difference. This difference is high enough to cause the original palladium coating to flow within the FAB and intermix with the original copper core as shown.

Fortunately, there are elements that can counteract the Marangoni effect during FAB formation in thermosonic wire bonding. One such element "A" was identified by Tanaka engineers and is doped into the wire during fabrication. Dopant "A" reduces the temperature difference and thus the surface tension in the molten FAB low enough to prevent the flow of palladium and thus remain on the surface and resolidify in-situ thereby maintaining its covering function on the copper core as illustrated in **FIGURE 5**.

Optical inspection of High-Reliability PCC wire FABs show silvery coloration of palladium as shown in **FIGURE 6** (left). EPMA of cross-sectioned FABs show palladium (blue/green) coverage on its full surface (right). This proves that the temperature and surface tension within the FAB is relatively stable (no significant difference as to cause the Marangoni effect) and thus prevent diffusion and circulation of the palladium coating into the copper core. Thus, similar to the wire above it, the FAB is also protected against oxidation and corrosion attack by chlorinated substances common in the environment. Therefore, proprietary doping allows for the manufacture of High-Reliability PCC wires.

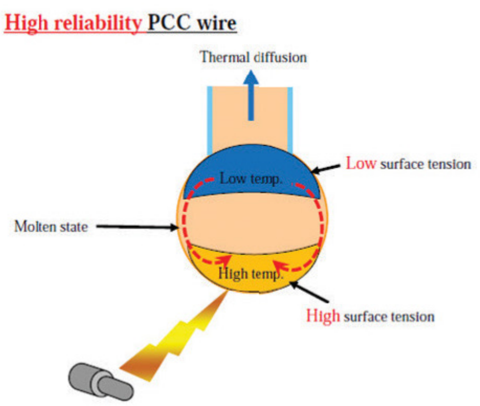


Figure 5. Palladium flow is minimal and its coverage is maintained in High-Reliability PCC wire.

FAB parameters: Current and time

Besides proprietary doping of High-Reliability PCC wires, the palladium covering of the FAB is also affected by EFO parameters because these directly affect the temperature difference within it. As mentioned earlier, typically the bottom region of the FAB is hotter due to direct exposure to the EFO discharge whereas the top region is cooled through the wire above it.

In the EPMA analyses shown in **FIGURE 7** (top), engineers at Tanaka have determined that the lower the EFO current, the more consistent is the palladium coverage of the FAB, this is likely due to the proportional lower temperatures generated during electronic discharge. Note that palladium coverage is complete until, at a high current of 85 mA, it starts to disappear at the bottom region presumably where the EFO discharge occurred.

Care should be taken, however, not to set the EFO current too low as to prevent the creation of a spherical FAB with the required diameter. Increasing the EFO time can compensate for this by producing the needed thermal energy to create the FAB. Further, Tanaka engineers have also determined that EFO current should be proportional to the wire diameter as shown in Figure 7 (bottom).

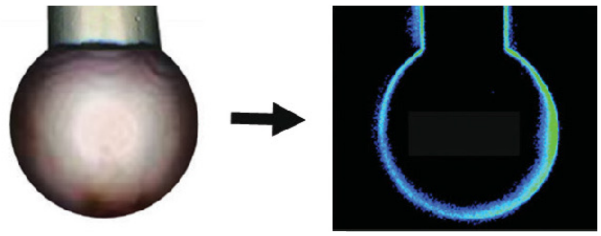
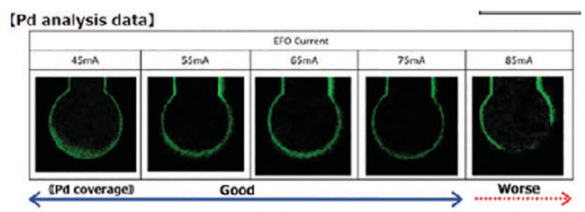


Figure 6. Optical image (left) and cross-section EPMA image (right) of FAB showing palladium coating (blue/green) of High-Reliability PCC wire.



➢ **Recommend parameter for each wire diameters**

Wire diameter	0.7mil	0.8mil	1.0mil	1.2mil
EFO Current [mA]	50-70	55-75	70-90	75-95

Figure 7. EPMA images of palladium coating of FABs made using various EFO current settings (top). Bottom table lists recommend settings for common wire diameters.

Conclusions

- The mixing of palladium and copper within the FAB of conventional PCC wires is explained by the Marangoni effect.
- Proprietary dopants can counter the Marangoni effect in High-Reliability PCC wires.
- EFO parameters should be optimized to ensure that high temperatures are not generated. SD

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