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Nanotechnology for Lead-Free PWB Final Finishes with Organic Metal

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ABSTRACT

The use of an Organic Metal finish_only a few nano-meters deposited onto copper pads of printed circuit boards provides effective protection against oxidation and preserves solderability. The Nano layer has a thickness of only 50 nm, and contains the Organic Metal (conductive polymer) and a small amount of silver. Being more then 90% (by volume), Organic Metal is the major component of the deposited layer; Ag is present equivalent to a thickness of 4 nm. This Organic Metal – Ag complex final finish performs as well as any of the established surface finishes with a significant reduction in energy and environmental impact.

1. INTRODUCTION

Although being an organic material, an Organic Metal (OM) is a special advanced form of a conductive polymer because it possesses metallic properties. It is synthesized and dispersed in the form of 10 nm size primary particles [1]. It has been published several years ago that the Organic Metal has a strong effect in the prevention of Cu oxidation [2]. The Organic Metal Technology has been in commercial use for almost 10 years in a process for finishing printed circuit boards, ensuring solderability after storage and thermal ageing. Here, the Organic Metal is used as the Cu surface preparation "predip" prior to an immersion Sn deposition [3]. This process has become well established and is widely used in the printed circuit board industry as one of the top quality alternative finishes which are required for successful lead-free electronics manufacturing. In this process the Organic Metal predip is applied as an approximate 80 nm thin adsorbed layer which leads to the selective formation of Cu(+1) and a passivation of Cu. It also takes part as a catalyst in providing electrons for the reduction of Sn (2+) which is subsequently deposited as Sn (0) onto the Cu.

Over the past 10 years it has been the object of Enthone's research to provide a solderable surface finish for PCBs which would mainly contain the Organic Nanometal. The first Organic Metal Universal Nanofinish was proposed to the market 4 years ago [4]. It was already suitable for lead free soldering (but not stable enough against discoloration). Now the new generation Nano finish with the Organic Metal – Ag complex performs as well as any other surface finish with regard to ageing resistance, discoloration and solderability.

2. PROCESS DESCRIPTION AND PERFORMANCE

2.1 Process Flow

The Process starts with a combination of a special acid cleaner and a specially adapted micro etch. A short pre-dip (conditioning 60 sec) prepares the boards for the active bath (OMN 35°C for 60 to 90 sec). A final rinse and a dryer complete the process.

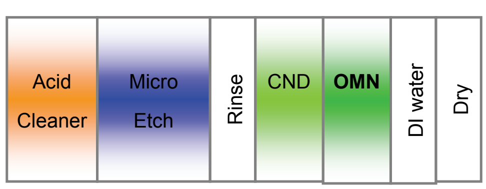

Figure 2.1.1: Process Scheme

2.2 Morphology investigation by SEM and GCM

Figure 2.2.1 shows a scanning electron microscopy (SEM) image of copper pad of a PCB after treatment with the Organic Metal / silver Nano size finish. It shows that the OM-Ag complex is exclusively located on the phase boundaries of the Cu crystallites. Most of the visible area is Cu-surface.

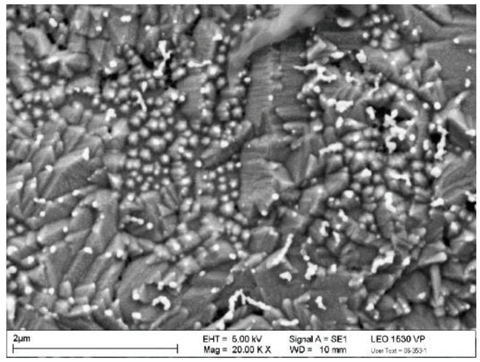

Figure 2.2.1: SEM image of a PCB after treatment with the Organic Metal / silver nano particle finish

2.3 Coulometric Investigation

The electrochemical investigation conducted by a galvanostatic Coulometric measurement (GCM) shows that the Organic Metal Universal Nanofinish has formed a new type of complex (Fig. 2.3.1). The potential at which this complex is oxidized is significantly different from Ag on Cu alone.

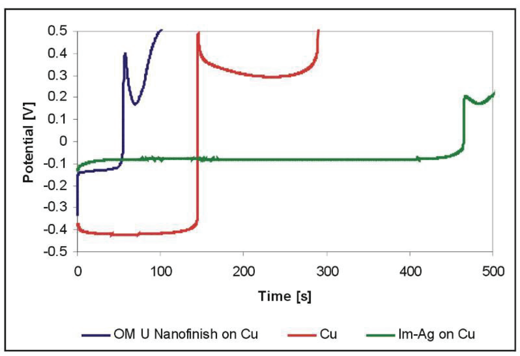

Figure 2.3.1: Potential-time-curves

The finish potentials on the copper surface in relation to the immersion time in the Organic Metal / silver nanoparticle bath are displayed in figure 2.3.2. The potentials indicate that the amount of free copper surface decreases slowly at the beginning of the process, having the highest coverage rate between 40 and 60 s immersion times. After 60 s the rest of the free copper surface is coated slowly, and after about 90 s there is no (electrochemically accessible) free copper detectable.

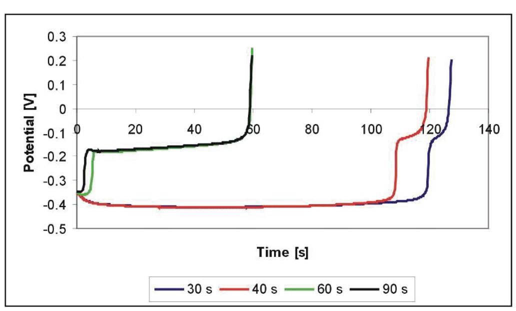

Figure 2.3.2: Potential-time curves for different immersion times

2.4 XPS investigations

XPS depth profiles [5] of copper and silver on the OrmeSTAR ULTRA finished copper surfaces show that the Ag is only detectable nominally to a depth of only 2 – 3 nm, before and after reflow. At the outermost surface the Ag:Cu ratio changes only slightly during the reflow process (becoming smaller), but from a depth of about 2 nm on no change in the ratio could be detected after the reflow process. Hence, no Ag:Cu migration needs to be worried about. The Ag:Cu seems to be immobilized in the complex with the OM.

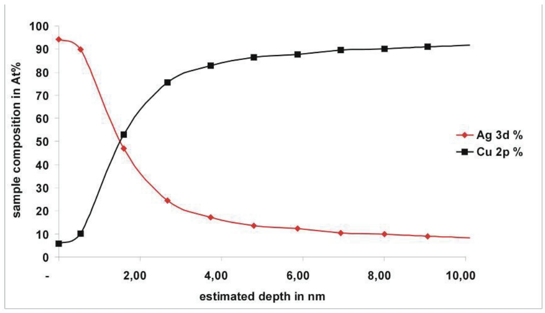

Figure 2.4.1: Distribution of silver and copper in the fresh sample (surface)

Even more interesting is the ratio of metallic to oxidized copper on the surface of the pad before and after reflow as shown in figure 2.4.2. This ratio did not change during the reflow process. This proves the exceptional capability of this new nanofinish in oxidation prevention of Cu.

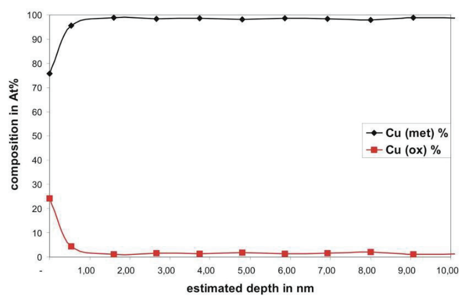

Figure 2.4.2: Ratio of metallic to oxidized copper in the fresh sample (surface)

2.5 Kelvin Potential

The surface potentials of copper, oxidized copper, silver on copper after immersion and Organic Metal / silver nanoparticle finish on copper after immersion were determined using a scanning Kelvin probe (SKP, UBM Messtechnik GmbH). The Kelvin potential is a very reliable indicator of the sensitivity of a surface towards oxidation. Figure 2.5.1 shows a copper surface treated with organic metal / silver nanoparticle finish in the fresh stage after finishing.

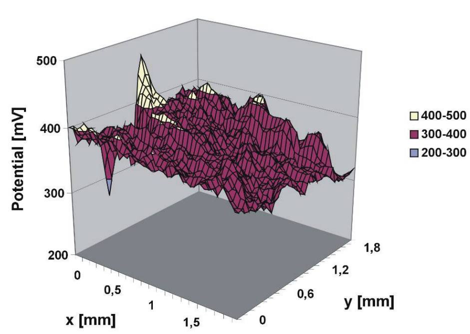

Figure 2.5.1: Copper surface treated with Organic Metal / silver nanoparticle finish

The Kelvin potentials of different treated and untreated copper surfaces are summarized in table 2.5.2.

Table 2.5.2 Kelvin potentials of different surfaces

Surface	**Kelvin potential [mV]**
Cu (pure, unoxidized)	70
Cu oxides	150 - 180
Cu treated with organic metal / silver nanoparticle finish (50 nm layer, containing nominally 4 nm Ag)	320 – 340
Cu treated with immersion silver (500 nm layer)	400

We can see that the new nanofinish composed from an organic metal-Ag nanoparticle size complex reaches almost the same potential as a pure Ag layer which contains over 100 times more silver!

2.6 Microvoids

For some immersion Ag surface processes micro voids may occur due to the galvanic displacement reaction. With the Nanofinish, no micro voids occur because the coating is nearly 100% additive. This deposit results in excellent solder joint strength with ball shear results similar to those found with OSP.

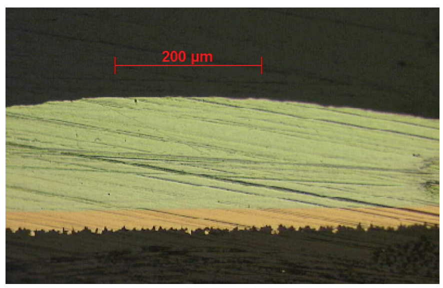

Figure 2.6.1

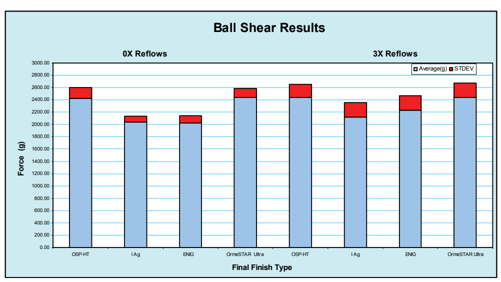

Figure 2.6.2

2.7 Solderability Testing

Wetting balance and wave solder testing were performed to determine solderability after multiply heat cycles. Using a mild rosin bearing flux with SAC 305 solder, test coupons were subjected to multiple reflow simulations with a peak temperature of 260°C. The Organic Metal surface finish performed in a manner similar to OSP-HT and Immersion Silver. Surprisingly, ENIG did not perform well in this testing. Due to the odd result on ENIG, this test was repeated with fresh samples from the same PWB vendor, a different vendor with the same bath, and a third vendor with a completely different system, all with the same results.

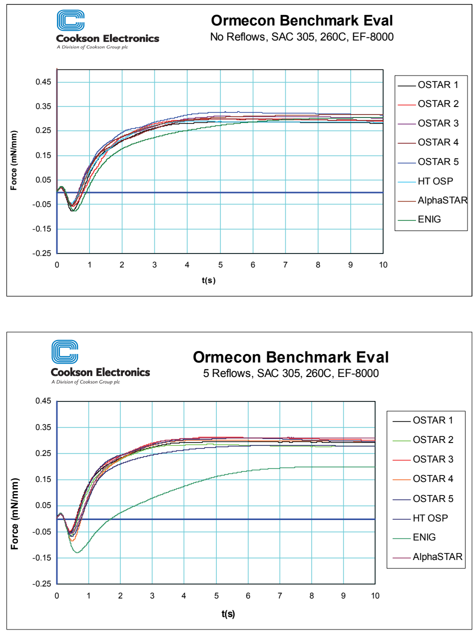

Figure 2.7.1

Wave solder testing was performed on a standard test vehicle with 1200 holes drilled at 10, 20 and 30 mils. The double sided test vehicle uses different pad sizes and shapes with two thicknesses at 0.063 and 0.093 inches.

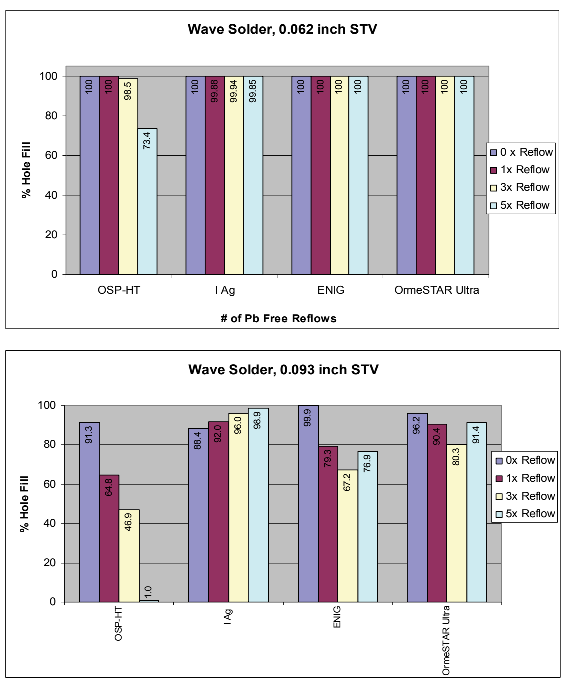

Figure 2.7.2

The wave soldering results show the Organic Metal surface finish solders as well as or better then immersion silver or ENIG.

The Nanofinish does not show any discoloration during reflow. The excellent solderability of the surface was also confirmed in reflow tests. Figure 2.7.3 shows a printed circuit board before treatment, directly after the surface finish with OrmeSTAR Ultra and the surface after treatment and reflow conditioning..

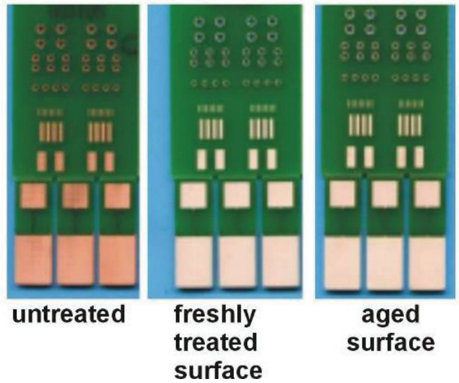

Figure 2.7.3: No discoloration after reflow

Figure 2.7.4 shows a test panel after three lead free reflow steps. First practical tests in PCB manufacturing and in assembly facilities have confirmed these results.

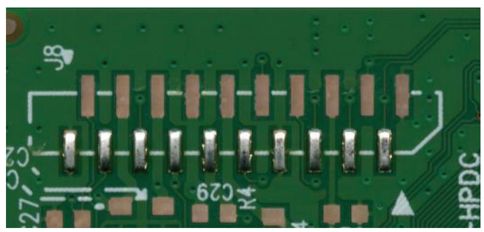

Figure 2.7.4: Excellent wetting after 3 lead free reflow steps

The very good solderability results have been confirmed by an external evaluation of Nanofinish is given in figure 2.8.1

2.8 Solder joints

An external study [6] shows that the lead-free-Sn solder joints (BGA pads) with the Nanofinish are of superior quality without defects compared to those solder joints made on the ENIG surfaces. Signs of wetting failure were not apparent and the Nanofinish solder joints are expected to be more long-term reliable.

Figure 2.8.1: Perfect solder joint

The ENIG surface showed an increase in P between the ternary phases and the NiP phase, which can lead to cleavage fractures. Critical phase formation was found in all NiP / Au samples. The external analysis concluded that “according to the actual results for lead free tin soldering all PCBs finished with the Nanofinish surface are distinctly superior to PCBs with NiP/Au surfaces, with regard to solderability and in view of forming reliable solder joints. “

3. Summary

The Organic Metal based Nanofinish is the first described example of a nanoparticulate complex between an Organic Metal and Ag. Although it does not form a closed nanolayer, it completely and effectively protects the Cu and prevents it from being oxidized even after four lead free reflow steps. Its aging resistance and wetting (soldering) performance is excellent and equal to or better than other well-established metallic finishes. This finish should be considered by anyone currently struggling with the cost and soldering inconsistencies of ENIG or attempting to use OSP on demanding multilayer PCBs.

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Additonal internal studies performed by Enthone SAMPL labs.