Study on erosion resistance characteristics of Fe-MWCNT composite plating with respect to lead-free solder

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Abstract. Sn-3mass%Ag-0.5mass%Cu lead-free solder causes strong erosion of Fe plating, which is used in hand soldering. In order to improve the durability of the soldering iron tip, we tried Fe-MWCNT (Multi-walled Carbon Nanotube) composite plating on the tip. Microstructures and the erosion resistance of the Fe-MWCNT composite plating under heating were examined. On the basis of the SEM/EDS analysis, it was confirmed that there were MWCNTs in the Fe-MWCNT composite plating. Even when heated to 673 K, MWCNTs were found to be present in the plating film under a stable condition. It was shown that the performance of erosion resistance for lead-free solders under high temperature (673 K) is improved due to the MWCNT addition to the Fe plating.

1. Introduction
In recent years, the use of chemical substances for electronic materials devices has been reconsidered. Since 2006, the EU has enforced the RoHS directive, which is a set of strict regulations for using harmful chemical substances in electronic materials. The use of lead has been prohibited by RoHS. Therefore, we have to use lead-free solder when we mount electronic parts on printed circuit boards, and Sn-3mass%Ag-0.5mass%Cu lead-free solder (SAC305) is currently being used. One of the problems caused by using SAC305 is the erosion of the soldering machine. In the case of soldering with SAC305, a solder bath for flow soldering was damaged in a short amount of time. It is assumed that SAC305 has a high content of Sn and a high melting point of about 30 K compared with Sn-37mass%Pb (Sn37Pb), which has been used thus far. The erosion mechanism of the flow soldering machine by molten SAC305 solder was elucidated by previous research [1, 2]. In order to prevent erosion of the flow soldering machine, nitriding treatment is performed on the surface of the materials of the flow soldering machine. On the other hand, although a similar erosion phenomenon to that affecting the flow soldering machine has been also found in the hand soldering iron tip, a practical solution has not been suggested (Figures 1 and 2).
Different from the materials of the flow soldering machine, the hand soldering iron tip requires moderate wettability of SAC305 solder. Then, Fe plating is usually conducted on the surface of the tip. However, the Fe-plated soldering iron tip erodes faster by SAC305 solder. This is caused by increase in the Sn content, which reacts with Fe more than Sn37Pb solder. Moreover, the reaction between the Sn and Fe is also related to the temperature of the hand soldering iron tip: the hotter the tip, the faster the reaction. The temperature is a contributing factor to the reduced life of the hand soldering iron tip. In the case of the automatic soldering robot, the soldering iron tip was eroded by SAC305 solder more than twice as fast as when Sn37Pb was used. In addition to the difference in solder type, the hardness of solder is also affected by accumulative damage to the tip, because the hardness of SAC305 solder is higher than that of the Sn37Pb solder. Since a hard SAC305 solder wire touches the same point of the tip repeatedly in the soldering robot, physical damage by wear occurs easily.

Reducing erosion of the soldering iron tip should be done with a view toward reducing waste and being more friendly to the environment. To prevent erosion of the soldering iron tip, we focused on using multi-walled carbon nanotube (MWCNT) composite plating [3-5], which has high strength and high thermal conductivity. We coated the soldering iron tip with easily available MWCNTs, and tested the erosion resistance. It was reported that the Ni-MWCNT composite plating decreased the maximum erosion depth by approximately 50% compared to standard Ni plating [6]. In this study, we focus on MWCNT composite plating for the purpose of reducing erosion of the tip caused by SAC305. The microstructure, wettability, and erosion resistances properties of the MWCNT composite plating were evaluated.

2. Experimental
2.1. Preparation of Fe-MWCNT composite plating
Table 1 shows plating conditions of the Fe and Fe-MWCNT composite plating. A sample preparation was made by performing electrolytic Fe plating on the Cu surfaces. We used a commercial MWCNT called VGCF-H manufactured by Showa Denko Co. Ltd. An FeSO₄ solution that was adjusted to about pH 3 including MWCNT was used for the plating bath. Current density was set to 1.0 A/dm². When we adjusted the plating solution, sodium lauryl sulphate was used as a dispersant and to achieve an anti-pit effect. It was stirred continuously to disperse the MWCNT in the plating solution.
2.2. Characteristics of plating sample
The prepared Fe-MWCNT composite plating was evaluated using a scanning electron microscope (SEM), energy dispersive X-ray spectroscopy analysis (EDS), and electron back scattering diffraction pattern (EBSP) to investigate the microstructure of the composite plating and the effects of heating on the plating. SEM and EDS analyses were performed with acceleration voltages of 1 kV and 5 kV. EBSP analysis was performed using an acceleration voltage of 15 kV.

2.3. Solder wettability test of SAC305
The solder wettability test was carried out at temperatures of 523, 573, and 623 K, comparing SAC305 resin flux core solder wire with Fe-MWCNT composite plating to see if wettability changed or not, when composite MWCNT was used. The test method is shown in Figure 3. The prepared Fe plating and Fe-MWCNT composite plating samples included 1 g/L of MWCNT in the plating solution. Wettability properties were measured according to JIS-Z 3198-3. The surfaces of the samples were cleaned using 2-propanol and were dried well. 0.3 g of solder was placed on the plating samples and heated to the test temperature. After the solder melted, the temperature was held for 30 s. Thereafter, the plating samples were cooled to room temperature in order to allow crystallization, and the height of solder measured. The wetting rate was calculated from equations (1) and (2).

\[ S_r = \frac{D - H}{D} \times 100 \]  
(1)

\[ D = 1.2 \times V^{\frac{1}{3}} \]  
(2)

Table 1. Plating conditions.

|                      | Characteristic plating | Erosion test |
|----------------------|------------------------|--------------|
| **Base metal**       | Cu                     | Cu           |
| **Form of base**     | Flat plate             | Column       |
| **Plating metal**    | Fe (Electrolytic)      | Fe (Electrolytic) |
| **Composite material** | MWCNT (VGCF-H)         | MWCNT (VGCF-H) |
| **Addition agent**   | Sodium lauryl sulphate | Sodium lauryl sulphate |
| **Plating thickness**| 100 µm                 | 100 µm       |
| **Current density**  | 1.0 A/dm²              | 1.0 A/dm²   |
| **Amount of MWCNT in plating solution** | 1 g/L               | 0.5, 3 g/L |

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where $S_R$ is the wetting rate, $D$ is the diameter of the theoretical solder sphere, and $H$ is height of the measured solder. $V$ is the solder volume used in the test. In this test, $V$ was 39.7 mm³, as calculated by measuring the solder height after heating. The samples were heated on a hot plate.

![Figure 3. Wettability test method.](image)

2.4. Erosion test

To evaluate the erosion characteristic of the Fe and Fe-MWCNT composite plating, the erosion test shown in Figure 4 [7] was conducted using SAC305 at 673 K assuming the actual temperature of the soldering iron tip. Fe and Fe-MWCNT composite plating were coated on a Cu column ($\phi$ 5.4 mm) to a thickness of 100 µm. To investigate the effects of MWCNT composite, two different amounts of MWCNT were used in the plating solution 0.5 and 3 g/L. The soldering iron tip temperature was held at 673 K. The flux core solder wire ($\phi$ 1.0 mm) and the soldering iron tip came into contact horizontally every 3 seconds for a total of 3000 times. The total test time was 9000 seconds. Each time the solder wire comes into contact with the soldering iron tip, 5 mm of lead wire melts before the solder wire moves back, breaking the contact. After this test was completed, a cross sectional cut was made through the soldering iron tip, and the maximum erosion depth was measured. Chrome plating was performed on the surface, and the plating was used as a marker to measure the maximum erosion depth. Fe plating was performed as a reference for standard conditions.

![Figure 4. Erosion test method [7].](image)
3. Results and discussion

3.1. Microstructure analysis

Figure 5 shows the appearance of plating samples before and after heating. Before heating, the surface of the Fe plating was glossy, and the surface of the Fe-MWCNT composite plating was rough. After heating to 673 K, there was not much change in the Fe plating, but the color of the Fe-MWCNT composite plating was changed to deep blue. The Fe-MWCNT composite plating has an additional oxidation mechanism compared with the Fe plating. Figure 6 shows SEM images of the surfaces of the Fe and Fe-MWCNT composite plating. The appearance of needle-like MWCNT (White) in the Fe plating is obvious in the composite plating.

![Figure 5](image)

**Figure 5.** Fe plating and Fe-MWCNT composite plating. Left: Non-heating. Right: After heating at 673 K for 1 h.

![Figure 6](image)

**Figure 6.** SEM images of plating sample surface.
Figure 7 shows a cross-sectional SEM image of the Fe-MWCNT composite plating after heating at 673 K for 1 h. The white area is Fe, and the black spots indicate MWCNT in the figure. The formation of a composite with MWCNT was confirmed not only on the plating surface but also in the plating film on the basis of the cross-sectional analysis. The results of EDS mapping analysis of the composite plating after heating at 673 K for 1 h are shown in Figure 8. The MWCNTs in the Fe plating did not change their size even after heating. The results showed that most of the MWCNTs remained in the composite plating even after it was heated to 673 K. Figure 9 shows the EBSP analysis results for the composite plating. Note that a trace amount of Fe$_3$C were precipitated at the grain boundaries of Fe. The MWCNT has a stable chemical structure, and therefore Fe$_3$C particles formed at grain boundaries due to heating. It has been reported that Fe$_3$C particles suppress the diffusion of Fe into SAC305 solder [8]. Therefore, we can improve the erosion resistance of the composite plating by the effective dispersion of Fe$_3$C particles.

**Figure 7.** Cross-sectional SEM images of Fe-MWCNT composite plating after heating at 673 K for 1 h.

**Figure 8.** EDS mapping of Fe-MWCNT composite plating after heating at 673 K for 1 h.
3.2. Solder wettability test of SAC305

Figure 10 shows the results of the solder wettability test. It was found that Fe plating has good wetting properties at all temperatures. Fe-MWCNT composite plating showed negative trends in the temperature range investigated compared to Fe plating. This means MWCNT affects the wetting properties of the solder spread. Figure 11 shows the results of the cross-sectional analysis using SEM/EDS after the wettability test. It was found that Fe-Sn compounds formed at the interface between solder and plating in both platings. The Fe-MWCNT composite plating had a worse wetting rate than the Fe plating. The worst result was at 523 K; however, SAC305 was not repelled and it has 50% wetting rate, which means that the Fe-MWCNT composite plating does not repel SAC305 solder and solder wets the surface of the plating. Moreover, Fe-Sn compounds formed at the wetting interface in the same manner as the Fe plating. Thus, Fe-MWCNT composite plating is expected to be applicable to the soldering iron tip.

**Figure 9.** EBSP mapping of Fe-MWCNT composite plating after heating at 673 K for 1 h.
Figure 10. Temperature dependence on wetting rate for Fe plating and Fe-MWCNT composite plating.

Figure 11. Results of SEM/EDS mapping analysis after the wettability test.
3.3. Erosion test of SAC305

Erosion test results are shown in Figure 12. The maximum erosion depth decreased approximately 23% in the Fe-MWCNT composite plating compared to the standard Fe plating. The effect of the MWCNT concentration in the plating solution on the maximum erosion depth is negligible. It seems that the amount of MWCNT in the plating solution does not affect the amount of MWCNT taken into the plating. It is assumed that the improvement of erosion resistance is due to the mitigation of physical damage by the action of MWCNT as a solid lubricant [9], because MWCNT has strong heat resistance and excellent abrasion characteristics. In addition, traces of Fe₃C that formed at the grain boundaries could suppress the diffusion of Fe into the SAC305. The inhibition effect would be one of the factors that improve erosion resistance.

4. Conclusions

The Fe-MWCNT composite plating was performed using an electrolytic sulphate plating bath. MWCNTs form a composite not only on the Fe plating surface but also in the plating film. In the Fe-MWCNT composite plating, MWCNTs were stable in Fe plating under heating conditions at 673 K. It is expected that MWCNT has excellent high-temperature wear properties when MWCNT contacts molten solder. A trace amount of Fe₃C was observed at the Fe grain boundaries in the composite plating by EBSP measurement. Fe₃C has the effect of inhibiting the diffusion of Fe into SAC305. This is expected to improve erosion resistance by increasing the number of Fe₃C particles. Although the Fe-MWCNT composite plating decreases the wettability of SAC305, SAC305 is not repelled on the surface of the composite plating and it has 50% wetting rate. Thus, SAC305 can be applied to the soldering iron tip. It was shown that the Fe-MWCNT composite plating was effective in reducing erosion of the plating layer by SAC305 compared to the standard Fe plating. This could be due to the reduction in physical damage because of the excellent high-temperature wear characteristics of MWCNT and the prevention of the diffusion of Fe into the SAC305 by the generation of Fe₃C.
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