Development of Cu-Sn Alloy Plating with Superior Excellent Sliding Characteristics and Corrosion Resistance

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ABSTRACT As a matter of consideration of plating materials for automobile terminals, we made a sample in which a Cu-Sn diffusion layer was exposed to the surface. We evaluated its anti-fretting characteristics, its corrosion resistance, its coefficient of friction, its solder wettability. As a result, when compared to the conventional plating materials with Sn on its surfaces, the material with the Cu-Sn diffusion layer (Cu-Sn alloy plating) showed much superior anti-fretting characteristics. Also, it met or exceeded its capabilities of coefficient of friction and corrosion resistance has sufficient performance for practical use. Its solder wettability was a little inferior to the conventional ones, though.

1. INTRODUCTION

In automobile terminals, electric currents are carried by connecting male and female terminals. In general, Sn-plating is on the surface of the terminals for corrosion prevention. Also, when female terminals nip male terminals, contact pressure of the contact points inside the female terminals is stable. The higher the contact pressure is, the more stable the current flow in male and female terminals is. However, in this case, the terminal insertion force which is generated when fitting connectors becomes stronger.

In recent years, connectors for automobiles are becoming more and more performing. Along with that, the number of terminals and their insertion force are increasing. The increasing workload of connector-fitting operators in automakers is becoming a problem. Therefore, the insertion force per terminal requires to be weaker. One of the possible countermeasures is designing low contact- pressure terminals.

However, it is known that when Sn-plating contact points slide at low contact pressure in a minute distance of about 20-30 μm continuously, the contact resistance rises rapidly. This phenomenon is called fretting [1]. The main factors affecting it are contact pressure, sliding distances, contact shapes, coating oil, kinds of plating and plating thickness [2), 3)].

We researched this phenomenon focusing on the thicknesses of Sn layers from the material research point of view. It was made clear that thinning Sn layers (0.25 μm) had a certain effect on reducing the amount of Sn-abrasion powder, which is the source of oxidative sediment, and restraining the rise of resistance during fretting [4].

In accordance with the result, we made a sample in which the Cu-Sn layer was deliberately exposed to the surface by thinning the Sn layer. We researched its anti-fretting characteristics, its corrosion resistance, its coefficient of friction and its solder wettability.

2. MATERIAL

In this research, a 0.25 mm thick Cu-Ni-Si alloy strip was selected as a substrate. It is frequently used as terminals for automobiles because it has a high strength, a high conductivity and a low stress-relaxation characteristic. Table 1 shows the chemical composition of the alloy.

Table 1 Chemical composition of the Cu-Ni-Si alloy substrate (mass%).

Ni	Si	Zn	Sn	Mg	Cu
2.0~2.8	0.45~0.6	0.4~0.55	0.1~0.25	0.05~0.2	Bal.

Using other kinds of copper alloys makes no difference in this research. The alloy strip was electroplated with Ni, Cu and nonglossy-Sn in this order. Then, it was reflow-processed. The thickness of each layer was adjusted by changing the current density. Figure 1 shows the section images of the samples. Table 2 shows the surface area rate of the plating samples and the thickness of each layer.

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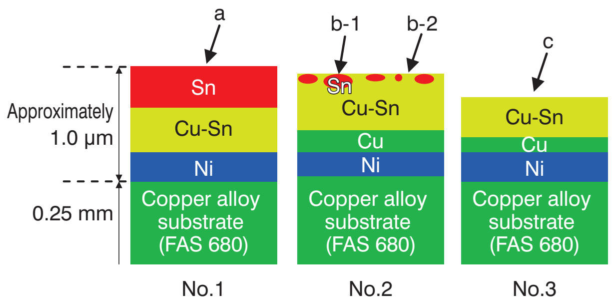

Figure 1 Section images of the plating samples.

Table 2 The surface area rate and the average thickness of the plating.

	Surface area rate (%)		Thickness (μm)			
No.	Sn	Cu-Sn	Sn	Cu-Sn	Cu	Ni
1	100	0	0.40	0.43	0	0.50
2	40	60	0.12	0.40	0.20	0.50
3	0	100	0	0.23	0.02	0.50

No.1 in figure 1 shows the section image of the sample in which the most surface layer was formed by a pure Sn layer. No.2 shows the one in which the Cu-Sn diffusion layer is partly exposed to the surface. No.3 shows the one in which the Cu-Sn diffusion layer is exposed all over to the surface. The term “surface area rate” in Table 2 shows the rate of the plated layers which are exposed to the most surface. The surface area rate was defined as the following:

First, the sections of the plated layers were exposed by FIB (Focused Ion Beam) process, then it was analyzed by AES (Atomic Emission Spectroscopy). Using AES, each layer in the plated sections was clearly sorted into the pure Sn layer, the Cu-Sn diffusion layer, the pure Cu layer, the Ni layer and the substrate by color mapping per element.

In No.2, the plated layers of the pure Sn layer and the Cu-Sn diffusion layer fluctuated in thickness. To be more precise, the Cu-Sn diffusion layer was uneven and the pure Sn layer was scattered.

Therefore, in this report, the surface area rate was defined as the exposed rate of each layer to the most surface. It was evaluated by measuring the lengths of the pure Sn layers (a and b-1 in Figure 1) and the Cu-Sn diffusion layers (b-2 and c in Figure 1) which are exposed to the most surface of the observation area (11.7 μm width) and dividing it by the overall lengths.

The average thicknesses were evaluated by measuring and averaging out randomly selected 5 points in the pure Sn layer, the Cu-Sn diffusion layer and the Ni layer.

3. TEST METHOD

3.1 Fretting test

Figure 2 shows the schematic view of the fretting tester.

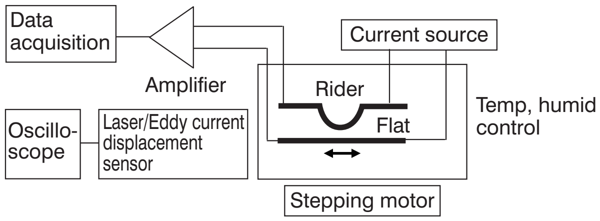

Figure 2 Schematic view of the fretting experiment tester.

A hemisphere shaped bulge of 1.0 mm radius was processed in the test specimen to simulate the contact point in a female terminal with a male terminal (dimple). It is called “the rider” (see Figure 2). Also, the strip-formed test specimen was cut flat to simulate the male tab of a male terminal. It is called “the flat” (see Figure 2). The test specimens of the rider and the flat were washed by ultrasonic in acetone solution for five minutes to eliminate contaminants like oil. Then, they were used as test specimens of the fretting test. In this report, the plating material of the rider side was standardized to No.1 in which the Sn layer was formed all over the surface. And on the flat side, the plating materials of No.1-3 were used. The contact load was set 3 N and the sliding distance was set 20 μm in the test.

3.2 Coefficient of friction measurement

The coefficients of friction were measured by a Bowden tester on the following conditions. [n=3]

Measurement condition: 300 g load; 0.5 R bulge reflow-Sn plating probe

Sliding condition: one sliding one way; 10 mm sliding distance, 100 mm/min sliding speed

3.3 Measurement of contact resistance before and after environmental tests

3.3.1 Conditions of environmental tests

Conditions of four types of environmental tests are the following:

- High temperature exposure test
  The test specimens were heated in a temperature-controlled bath on the following condition.
  Heating condition: 160°C×120h
- High temperature and humidity test
  A high temperature and humidity test was conducted in a pressure cooker on the following condition.
  High temperature and humidity condition: (105°C, 100%RH)×16h
- Mixed pollution gas test
  The specimens were exposed to mixed pollution gas in a mixed pollution gas tester on the following conditions.
  Exposure condition: (30°C, 70%RH)×48h
  Density of gas: H_2S 100 ppb, NO_2 200 ppb, Cl_2 20 ppb
- Salt spray test

The test specimens were exposed to salt water in a salt spray tester (compliant to JIS Z 2371) on the following condition.

Exposure condition: 35°C×24h

Density of salt water: 5%NaCl

3.3.2 Measuring method of contact resistance

The voltage during a flow of a low current was measured by a contact resistance measuring machine. [n=10]

Measurement condition: 100 g load; 5 R bulge Ag probe

Conducting condition: 10 mA currency

3.4 Solder wettability

As measurement test specimens, samples of No.1-3 without heating and after heating (155°C×16h) were used. Their solder wetting time was measured by a solder checker. [n=2]

Kind of solder: Sn-3Ag-0.5Cu; 245°C

Flux: RMA type (Solbond RM615)

Steeping time: 10 mm/sec steeping speed, steeping time: 10 sec, steeping depth: 9.9 mm

4. RESULT AND REVIEW

4.1 Result of fretting test

Figure 3 shows the results of the fretting test. The initial contact resistance was nearly equal to 0.8 mΩ in No.1, 1.0 mΩ in No.2, 0.5 mΩ in No.3.

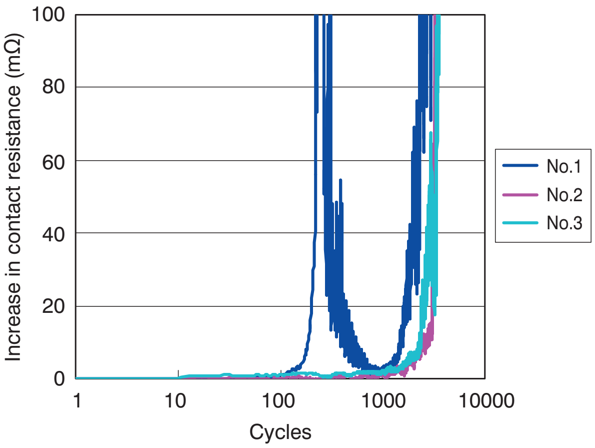

Figure 3 Profile of contact resistance on fretting test.

In the plating material of No.1 in which the pure Sn remained on the surface, the resistance increased up to about 100 mΩ after 100 times of sliding, then, it decreased to less or equal to 10 mΩ. The contact resistance stayed low after a certain period of time. When sliding exceed 1000 times, the resistance increased again.

Next, the resistance of the plating materials of No.2 and 3, in which formed the Cu-Sn alloy layers on the surfaces, stayed less or equal to 10 mΩ until sliding exceeded 1000 times, then, it increased as in No.1.

This result shows that plating materials, which form pure Sn on the most surfaces (such as No.1), are prone to the rapid increase of resistance because tin oxide is generated by abrasion. On the other hand, plating materials which don't form pure Sn on the most surfaces (such as No.3) or form little Sn (such as No.2) are not prone to generate tin oxide, the cause of the increase in resistance. Therefore, their anti-fretting characteristics are superior[5].

4.2 Measurement result of coefficient of friction

Figure 4 shows the measurement results of coefficient of friction.

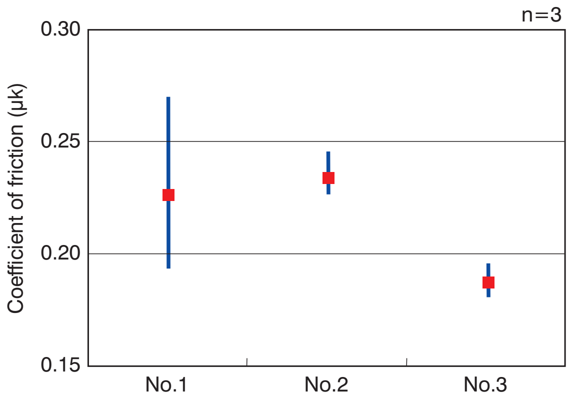

Figure 4 The coefficient of friction in the samples.

The results of No.1 and 2 are close. No.3 showed the lowest coefficient of friction. One likely reason is that the scraped amount in No.3 is small due to the hard Cu-Sn diffusion layer on the surface. Another likely reason is related to the contact with the Sn contact shoe. The contact between Sn and Cu-Sn is likely to be less prone to adhesion than the one between Sn and Sn.

4.3 Measurement results of contact resistance before and after environmental tests

Figure 5 shows the measurement results of the increase in contact resistance (average value of n=10) after the environmental tests. The initial contact resistance was nearly equal to 1.4 mΩ in No.1, 1.2 mΩ in No.2, 1.8 mΩ in No.3.

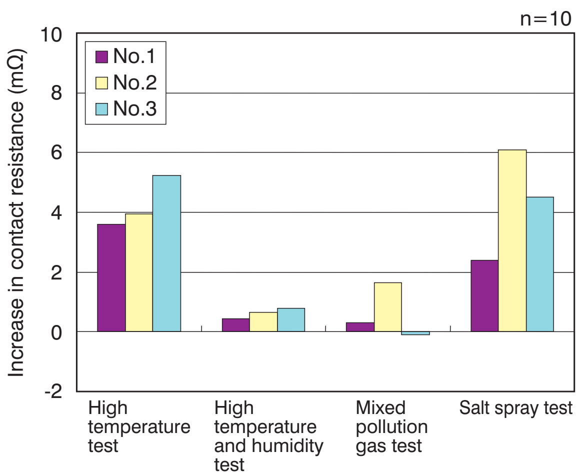

Figure 5 Contact resistance after the environmental tests.

If contact pressure exceeds 10 mΩ after the environmental tests, it means that the three samples have some defects as electric contacts. However, the increase in contact resistance didn't exceed 10 mΩ in all of them. Also, no wide gap was observed among them. Therefore, the plating material in which the Cu-Sn diffusion layer is exposed to the most surface has sufficient corrosion resistance for practical use.

4.4 Evaluation result of solder wettability

Figure 6 shows the evaluation results of solder wettability.

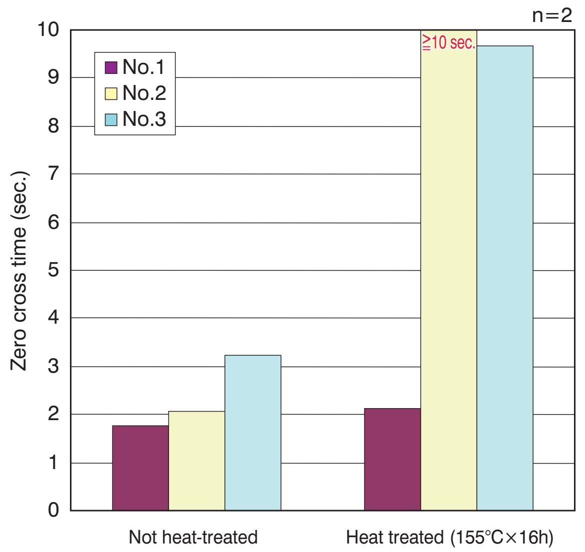

Figure 6 Wetting time of Sn-3Ag-0.5Cu solder.

As test specimens, non-heat-treated one and heat-treated (155°C×16h) one were used. The purpose of using the latter one is to simulate an oxidized state of the surface to some extent. The results are: In No.1, the zero-crossing time of both non-heat-treated and heat-treated ones were approximately two seconds. However, in the heat-treated one of No.2, it was 10 seconds or longer, and in the heat-treated one of No.3, it was a little less than 10 seconds. It means solder wettability deteriorated in No.2 and 3. The likely reason is that stable Cu-Sn composite oxide [6], which is difficult to eliminate with flux, was formed on the surface of the Cu-Sn diffusion layers.

5. CONCLUSION

Compared with the conventional plating materials with Sn on the surfaces, the material with a Cu-Sn alloy plating showed superior anti-fretting characteristics. Also, it showed the equivalent or better capabilities of friction of coefficient and the sufficient corrosion resistance for practical use. Its solder wettability was a little inferior to the conventional ones, though.

Therefore, the materials with the Cu-Sn diffusion layer are promising as plating materials for automobile terminals.

This article involves the contents [5] reported in the 50th Japan Copper and Brass Research Association.

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