Tin-plated Copper Alloys for Replacing Gold-plated Terminals

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Abstract

Plated copper alloys are used for automotive terminals. The terminal plating used in low-voltage circuits includes tin-plating and gold-plating. Tin is a general-purpose plating material that offers an excellent balance between cost and electrical reliability, while gold-plating is used in areas where electrical reliability is critical at low contact loads. Gold-plating, however, is subject to high manufacturing costs, and there is a need for tin-plating as a low-cost alternative. Therefore, attention has been focused on the fracture mechanism of the oxide film on a tin-plated surface, and by providing the surface with fine convex shapes of tin, low contact resistance has been obtained even under low contact loads. This paper introduces the performance of tin-plating for low contact pressure, which can partially replace gold-plating.

Introduction

The trends toward electrification and automation in vehicles entail an increase in the number of electrical components, and with this, the number of wires and terminals that connect these components.

Terminals must exhibit contact reliability to transmit electrical signals and power from the time the vehicle is manufactured until the end of its service life, which is why plated copper alloys are used for these components.

Tin and gold are the most common metals used for plating terminals in circuits with a voltage of 30 V or less and a current of 10 A or less (hereafter, low-voltage circuits).1), 2)

Tin-plating provides a good balance between cost and contact reliability and is used in a wide range of applications; however, it is inferior to gold-plating in terms of contact reliability. Gold-plating has good corrosion resistance, and although it is often used where contact reliability is critical,1), 2) it is very expensive, so there is a need for a low-cost alternative to reduce costs. As such, Kobe Steel developed a plating that is more economical than gold and has better contact reliability than tin-plating.

This paper introduces the performance of low-pressure-compatible tin-plating as an alternative to gold-plating.

1. Terminal plating and the required characteristics for terminal plating

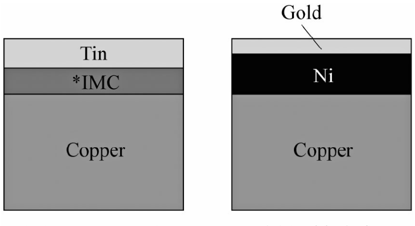
1.1 Plating composition and structure

A comparison of reflow tin-plating and gold-plating, which are commonly used for automotive terminals, assists with describing the properties required of contact plating that can replace gold-plating. **Fig. 1** shows the cross-sections of plated copper alloys. Reflow tin-plating is a plating process in which a tin film is formed on a copper alloy by electro-plating, followed by heating above the melting point of tin (hereafter, the reflow process). This process creates an intermetallic compound layer of tin and copper (hereafter, copper-tin IMC layer) between the copper alloy and the tin film, and the surface is covered with tin.

Gold-plating is implemented as a two-layer structure of gold plated on a nickel substrate. Since gold is soft and prone to wear, plating with a small amount of hard alloy, such as cobalt or nickel, is a common practice with gold-plating to impart wear resistance.1)

1.2 Contact reliability

Contact reliability is one of the most important characteristics in considering substitutions for gold-plating. To ensure contact reliability, it is necessary to maintain low electrical contact resistance in the terminal contacts (hereafter, contact resistance). Contact resistance is the electrical resistance between mating surfaces. It is the sum of the film resistance, which is the electrical resistance of the film itself, and the constriction resistance due to the convergence of electric current, as expressed by Equation (1).2), 3)



(a) Reflow tin-plating (b) Gold-plating

Fig. 1 Schematic images of cross section of plated copper alloys *IMC: Intermetallic compound layer of tin & copper

$$R = R_f + R_c \quad \cdots\cdots \quad (1)$$

Here, R is the contact resistance (mΩ), R_f is the film resistance (mΩ), and R_c is the constriction resistance (mΩ).

Equation (2) expresses film resistance and constriction resistance when like metals are in contact.

$$R_f = \frac{\rho_f d}{\pi a^2},\ R_c = \frac{\rho}{2a} \quad \cdots\cdots \quad (2)$$

Here, ρ_f is the film-specific resistance (Ωm), d is the film thickness (m), ρ is the metal-specific resistance (Ωm), and a is the radius of the contact surface (m).

Per Equation (2), film resistance decreases as film-specific resistance decreases, and constriction resistance decreases as the radius of the contact surface increases (i.e., as the contact area gets larger).

Fig. 2 shows the relationship between contact load and contact resistance for reflow tin-plating and gold-plating. Contact resistance was calculated based on the voltage drop measured by the four-terminal method applied to a flat-sheet-shaped specimen and a probe comprising a gold wire bent into a U-shape. The probe was pressed against the specimen and the voltage drop was measured while the downward force was gradually increased from 0.5 to 5 N. Although it is possible to incorporate sliding of the probe in this test,4), 5) we did not do so, ensuring gradual destruction of the oxide film to confirm the effect of oxide film destruction on contact resistance. Fig. 2 shows that the contact resistance of reflow tin-plating decreases significantly as the contact load increases, and that the rate of the decrease in contact resistance declines starting at 2.0 N. Gold-plating exhibits a lower contact resistance than reflow tin-plating from 0.5 to 5 N, however.

Oxide films generally exhibit higher resistance than the metal they form on, so areas with an oxide film are insulative. As a result, the conductive contact area becomes smaller and contact resistance increases due to increased concentration resistance.2), 3)

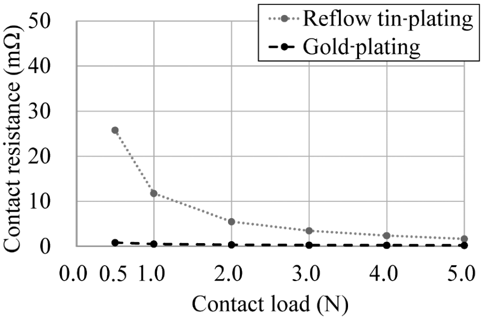


Fig. 2 Relationship between contact load and contact resistance of tin-plating and gold-plating

The surface of reflow tin-plating has a protective oxide film. In low-voltage circuits where dielectric breakdown is not a possibility, the oxide film cannot be mechanically destroyed by contact pressure alone, resulting in a higher contact resistance than with gold-plating. Gold-plating is only covered by a very thin oxide film of about a single molecule on the surface, in which case the tunneling effect ensures conduction.2), 6)

In reflow tin-plating, a thin, hard oxide film (Vickers hardness 16.5 GPa) forms on the soft tin (Vickers hardness 50 - 70 MPa).7) Here, the tin-plating deforms when a load is applied, but the oxide film cannot deform in tandem as the load increases and is broken. Thus, contact between the tin and gold is easily achieved.4) The destruction of the oxide film increases the contact area and decreases the concentration resistance, in turn decreasing contact resistance. Therefore, tin-plating is generally used where the contact load might be high and the oxide film can be sufficiently destroyed, whereas gold-plating is generally used in areas where contact reliability is critical and the contact load is low.2)

Tin-plating does not have the same contact reliability as gold-plating at low contact loads. Therefore, we developed tin-plating that can maintain contact reliability in low-voltage circuits even in terminals with low contact pressure. Here, low contact pressure is defined as the degree of load for which the contact resistance of tin-plating does not equal that of gold-plating.

2. Improving the contact reliability of tin-plating at low contact pressure

2.1 Mechanism of oxide film destruction in tin plating

As described above, tin-plating forms a highly resistive oxide film on the surface, the area covered by the oxide film becomes insulative, concentration resistance increases, and ultimately, contact resistance increases. Applying a contact load that can break the hard oxide film on the surface reduces contact resistance. Therefore, methods to reduce the contact resistance of tin-plating include suppressing the oxidation of tin and making the oxide film of the tin easier to destroy.

The oxidation of tin can be suppressed by using a precious metal that resists oxidation, such as gold or silver, or by incorporating an organic substance that inhibits oxidation. However, these methods are not ideal because they increase costs and resource consumption in the plating process. This led us to research effective methods for mechanically destroying the oxide film of tin even under low contact load.

These include concentrating the contact load locally and increasing the contact load per unit area (surface pressure). To increase surface pressure, we developed a concept that involves creating fine convex shapes in the surface of the tin-plating.

2.2 Improving contact resistance by imparting convex shapes to the surface

To validate the concept, we developed a new tin-plating (hereafter, rough tin-plating) by creating fine convex shapes in the surface of reflow tin-plating. **Fig. 3** shows laser microscope images of the surface of the tin-plating and the arithmetical mean height Sa (ISO 25178). The reflow tin-plating is shown for comparison. The Sa of the rough tin-plating is higher than that of the reflow tin-plating, indicating a rougher surface. Sa is the arithmetical mean of the absolute values of the height from the mean plane of the surface. It extends the two-dimensional roughness parameter Ra into three dimensions.[8)]

Fig. 4 depicts the contact resistance test. It is common to plate male and female terminals with the same metal to preclude corrosion and thermal electromotive force due to contact between dissimilar metals.[9)] It is assumed that the tin-plating of the terminals will be in contact with each other. We placed the tip of the reflow tin-plating formed into a dome shape against the tin-plated sheet and measured the contact resistance.

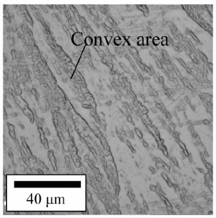
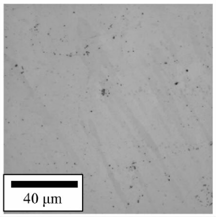
Sample	Rough tin-plating	Reflow tin-plating
Laser microscope images		
Surface roughness [Sa ; μm]	0.19	0.01

Fig. 3 Laser microscope images and surface roughness of tin-plating with different surface roughness

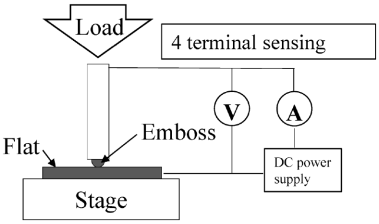


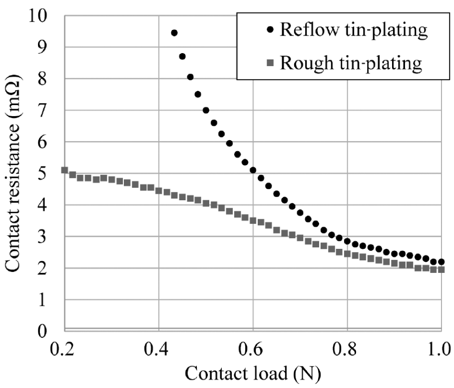
Fig. 4 Schematic image of contact resistance test

Fig. 5 shows the relationship between the contact load and contact resistance of the tin-plating. At a load of 0.2 to 0.8 N, the contact resistance of the rough tin-plating was less than that of the reflow tin-plating. At a load of 0.5 N, the contact resistance of the rough tin-plating was 4 mΩ, while that of the reflow tin-plating was 7 mΩ.

Fig. 6 shows the contact marks on the plated sample after applying a load of 0.5 N. The white circles indicate where deformation was observed by laser microscopy. We examined the cross-section near the center of the contact area, along the white dotted line. The reflow tin-plating has an overall convex shape in the contact area, whereas with the rough tin-plating, the apex of the convex tin area is lower than the surrounding area.

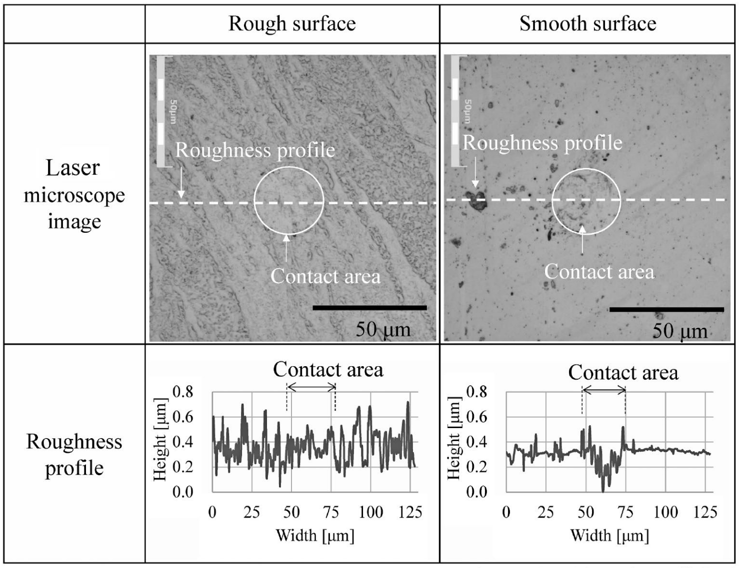
Fig. 7 shows the SEM images (backscattered electrons, BSE) near the center of the contact marks and outside the contact area of the plated sample. The white parts of the BSE images are tin, the gray parts tin oxide. Image processing was performed to make the tin white and the rest black. The entire surface outside the contact area of the rough tin-plating was covered with tin oxide, whereas tin and tin oxide were confirmed in the center of the contact area of the rough tin-plating and the reflow tin-plating. Additionally, the area ratio of tin was greater for the rough tin-plating. This means that the load partly destroyed the tin oxide film in the contact area, exposing tin on the surface. The contact marks show that the rough tin-plating had more dispersed islands of tin than the reflow tin-plating.

Fig. 8 depicts the contact areas. It is surmised based on the plating surfaces in Figs. 6 and 7 that with rough tin-plating, the load is concentrated in the convex area, destroying the tin oxide film on the surface and thereby reducing contact resistance.



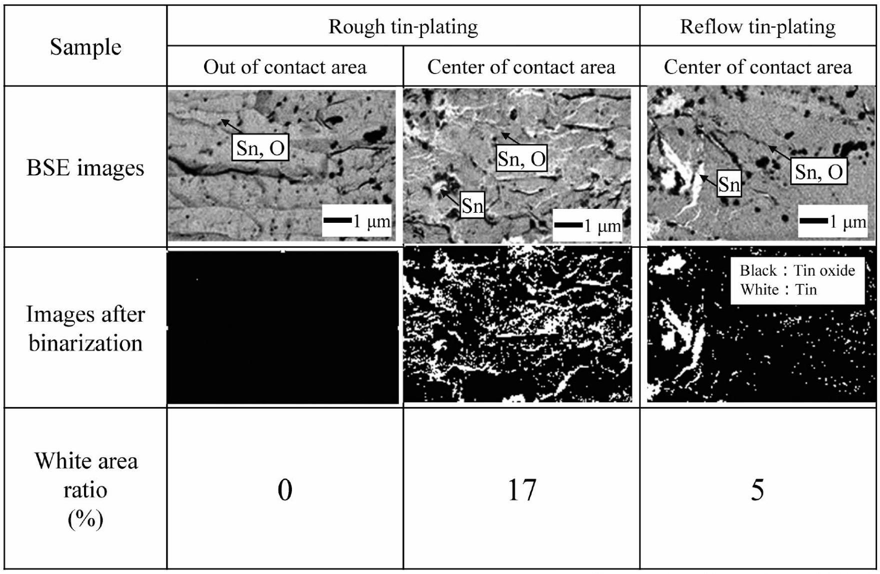
Source: adapted from reference[10)], Fig. 3

Fig. 5 Relationship between contact load and contact resistance of tin-plating with different surface roughness



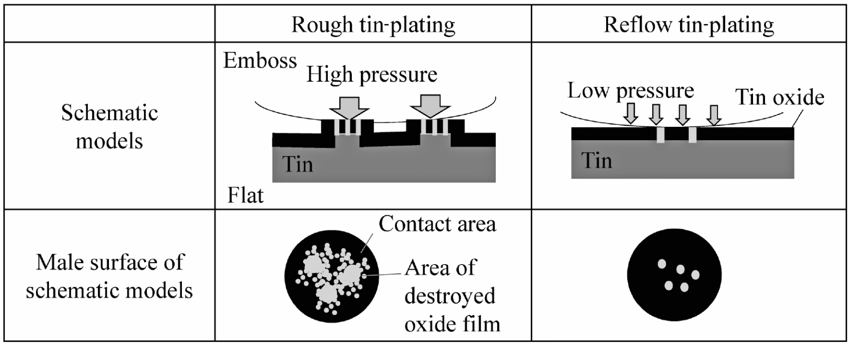
Source: adapted from reference[10], Fig. 4

Fig. 6 Laser microscope images of contact marks on the surface of test samples after applying 0.5 N load



Source: adapted from reference[10], Fig. 6

Fig. 7 SEM images of contact area and outside of contact area



Source: adapted from reference[10], Fig. 7

Fig. 8 Schematic models of contact area

3. Low-pressure-compatible tin-plating that combines heat resistance, fretting wear resistance, and ease of terminal insertion

Automotive terminals must maintain low contact resistance even when subjected to heat and vibration. Reflow tin-plating is susceptible to forming tin oxide under such parameters, potentially increasing contact resistance. Therefore, necessities in replacing gold-plating include heat resistance to withstand high-temperature environments and fretting wear resistance to withstand temperature changes and vibration.1), 2)

3.1 Heat resistance

A vehicle's engine compartment usually gets hotter than its interior11); accelerated life testing requires heat resistance temperatures of 150 -160℃.

Reflow tin-plating promotes mutual diffusion of the copper and tin in the material in a high-temperature environment, causing a copper-tin IMC layer to form.3) As such, the tin is depleted and a highly resistive copper oxide film forms on the surface, increasing resistance.3)~5)

An effective method of suppressing the diffusion of copper and tin and thereby improving heat resistance is to employ a three-layer structure in which there is a nickel layer under the copper-tin IMC layer of reflow tin-plating.3)~5)

3.2 Fretting wear resistance

Electrical contacts can become displaced due to thermal expansion and contraction caused by vibration during engine operation and vehicle travel, temperature changes in the environment, and heat generated by electricity.3)~5) This displacement abrades the plating, a phenomenon known as fretting wear. Soft tin is prone to fretting wear, potentially increasing contact resistance, so this phenomenon must be prevented. Exposing the copper-tin IMC layer on the surface improves fretting wear resistance.3)~5)

3.3 Coefficient of friction

Wire harnesses are connected manually during vehicle assembly. Therefore, efforts are underway to reduce the maximum insertion force for mating connectors to reduce physical stress on workers.3)~5) This means that the coefficient friction of the plating must be reduced, as this correlates to a connector's insertion force.3)~5) Running contrary to this objective is that reflow tin-plating is prone to wear because tin is soft. Specifically, wear of the tin could increase the coefficient of friction by presenting resistance during sliding.

Exposing the copper-tin IMC layer on the surface reduces the coefficient of friction.3)~5)

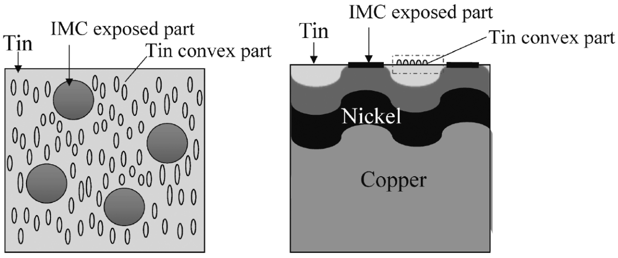
3.4 Low-pressure-compatible tin-plating

Fig. 9 depicts the surface and cross-section of low-pressure-compatible tin-plating, which comprises three layers to improve heat resistance: tin, copper-tin IMC, and nickel. The copper-tin IMC layer is partially exposed on the surface for fretting wear resistance and a low coefficient of friction. In addition, as described in Section 2, convex shapes were created in the topmost layer of the tin surface to improve contact reliability.

Fig.10 shows the relationship between the contact load and contact resistance of the plating before and after annealing. We studied contact resistance under a test load of up to 2.0 N to confirm the effect of an oxide film on this parameter. The contact resistance of reflow tin-plating increased significantly after annealing, whereas that of gold-plating and of low-pressure-compatible tin-plating remained low.

Exposure to high temperature accelerates the formation of the copper-tin IMC layer in reflow tin-plating. This depletes the tin, leading to the formation of a highly resistive copper oxide film on the surface and thereby increasing contact resistance.3)~5) As explained in Section 2, it is surmised that the convex shapes in the tin reduce initial contact resistance in the low-pressure-compatible tin-plating. It is also surmised that the contact resistance of the gold-plating and the low-pressure-compatible tin-plating remained low because the underlying nickel layer suppressed the diffusion of copper into the plated surface.1), 3)

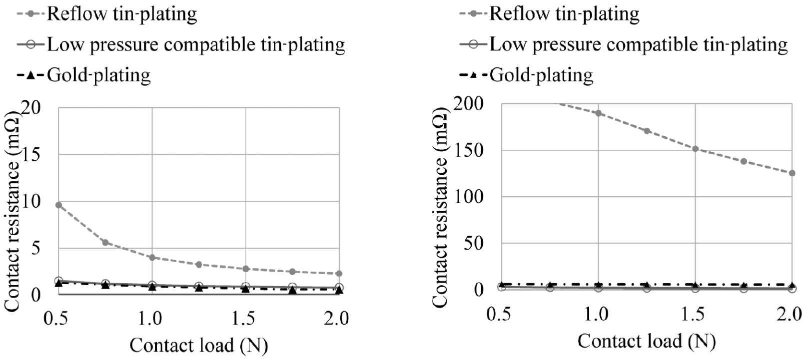
Fig.11 depicts the fretting wear test equipment and conditions. A sheet-shaped specimen (Flat) and a specimen with a hemispherical protrusion with a radius of curvature of 1 mm (Emboss) were brought



(a) surface image (b) Cross section image

Low pressure compatible tin-plating

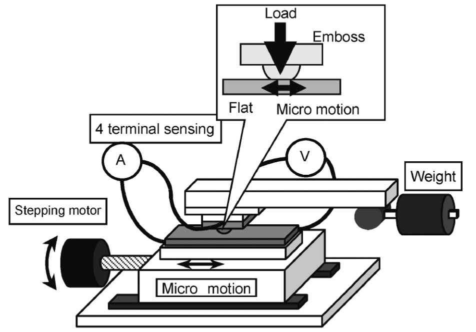
Fig. 9 Schematic models of low pressure compatible tin-plating



Initial

160℃×120 h.

Fig.10 Relationship between contact load and contact resistance before and after 160℃×120 h. annealing



※Yamasaki seiki CRS-B1050CHO

Conditions
Flat: Specimen, Emboss: Reflow tin-plating
Curvature radius: 1.0 mm, Current: 10 mA
Load: 1 N, Sliding distance: 50 μm, Sliding frequency: 1 Hz

Fig.11 Schematic image of fretting test system

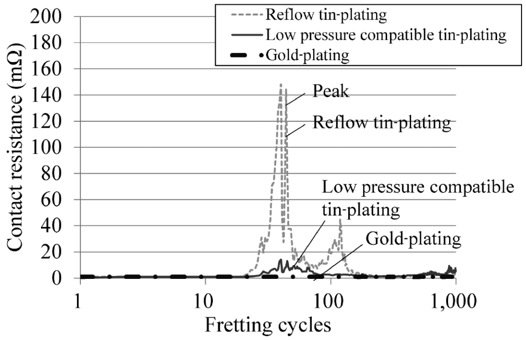


Fig.12 Changes of contact resistance of plating during fretting test

into contact, and a load of 1 N was applied. The sheet-shaped specimen was then slid repeatedly along a distance of 50 μm, and the contact resistance during sliding was measured by the four-terminal method.

Fig.12 shows the change in the contact resistance of the plating during a fretting wear test at a load of 1 N. The peak in contact resistance occurred at around 10 to 100 cycles for tin-plating, and this peak was lower for low-pressure-compatible tin-plating. Gold-plating exhibited no peak and maintained low resistance.

Soft tin particles are created when tin-plating undergoes fretting wear. Although some of the wear particles are discharged from the system, the remainder accumulate between the contacts. Oxidation of the accumulated tin wear particles increases contact resistance.4), 5) As wear progresses to the copper-tin IMC layer, tin depletes and more wear particles are discharged than generated, reducing the amount of wear particles accumulating at the contacts and decreasing contact resistance. Therefore, it is important to suppress the wear of tin to reduce peak contact resistance. The low-pressure-compatible tin-plating suppresses the wear of tin by exposing the copper-tin IMC layer at the surface, reducing peak contact resistance.3)

Gold-plating is believed to suppress a peak in contact resistance because it is hard, reducing wear particles, and because its wear particles are resistant to oxidation.12)

Fig.13 depicts the equipment and conditions for testing the coefficient of friction, which was measured in accordance with the Japan Copper and Brass Association technical standard JCBA T311:2002. A sheet-shaped specimen (Flat) and a specimen with a hemispherical protrusion with a radius of curvature of 1 mm (Emboss) were brought into contact, and a load of 1 N was applied normally to the surface of the sheet. The coefficient of friction was calculated based on the frictional force when the sheet-shaped specimen was slid while a load was applied.

Fig.14 shows the coefficients of kinetic friction of the different types of plating. The coefficient of kinetic friction of the low-pressure-compatible tin-plating is no greater than that of reflow tin-plating or gold-plating. Friction between two tin surfaces is regarded as adhesive wear of tin; increasing apparent hardness reduces the coefficient of friction.3)~5) It is thought that the copper-tin IMC layer, being harder than tin, on the surface helps suppress the wear of tin.3)~5)

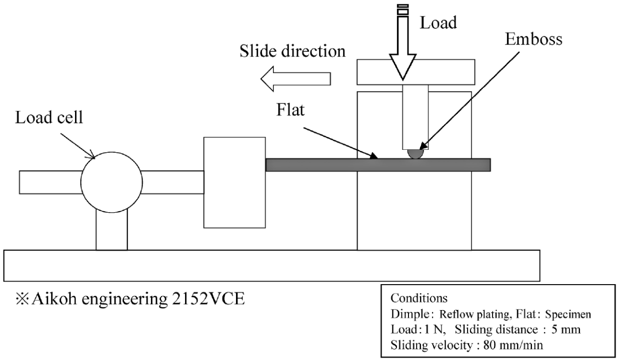


Fig.13 Schematic image of measuring apparatus of friction coefficient

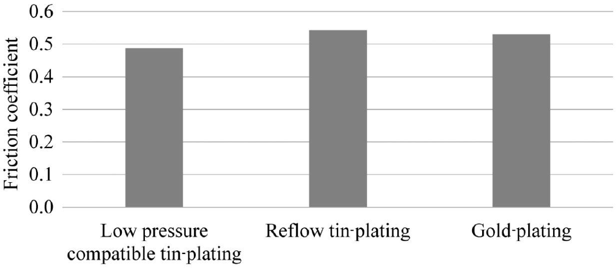


Fig.14 Friction coefficient of plating

Conclusions

To improve upon conventional reflow tin-plating, we have developed low-pressure-compatible tin-plating with superior heat resistance, fretting wear resistance, and contact reliability under low contact load. Since the fretting wear resistance of this plating is not as high as that of gold-plating, it has particularly strong potential as a substitute for high-cost gold-plating in applications where fretting wear resistance is not a concern. Mass production of this newly developed plating is the next stage in our endeavor since laboratory trials revealed strong performance characteristics.

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