Technology for Improving Performance of Tin Plating for Automotive Terminals

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Abstract

Copper alloy, which has excellent electrical conductivity, is widely used for automotive terminals. Since copper alloys are oxidized in the atmosphere, and their oxide coating acts as electrical resistance, tin plating is applied to keep the contact resistance low. This paper explains the characteristics required for the tin plating of automobile terminals and introduces Kobe Steel's original tin-plated products with new reflow plating (high thermal resistance and low friction).

Introduction

Automobiles are equipped with electrical components that consist of, for example, control computers, sensors, and actuators, which are connected by wire harnesses. A wire harness is an assembly consisting of electrical wires and connectors, and the terminals built into each connector are one of the essential parts for transmitting power and signals. Recently, the electrification of automobiles is accelerating to realize "CASE," including automatic driving and electric driving. As a result, the number of onboard electronic devices has increased, and so has the number of electrical wires and terminals. These terminals are generally made of copper alloy, which has excellent electrical conductivity; however, copper alloys oxidize in the atmosphere, and the oxide film becomes electrical resistance. Hence, the common practice is applying a surface treatment such as tin plating to maintain the low contact electrical resistance (hereinafter referred to as "contact resistance") of each contact point, which is the connection part of the terminal.

This paper explains the characteristics required for the tin plating of automobile terminals and introduces Kobe Steel's original tin plating products, "new reflow plating (heat resistant specifications, low friction specifications)."

1. Characteristics required for terminal tin plating

The characteristics required for the tin plating of terminals are described, taking the tin plating used for the mass-production at Kobe Steel as an example. The cross-sections of copper alloy with reflow tin plating and new reflow plating in the plating/reflow process are illustrated in **Fig. 1**. Reflow tin plating is a type of plating performed by applying electric tin plating to a copper alloy and then heating and melting the plating above the melting point of tin (hereinafter referred to as "reflow treatment.") The reflow tin plating produces an intermetallic compound layer of tin and copper (hereafter referred to as copper-tin-based intermetallic compound) on top of the copper alloy and the surface covered with tin.

The new reflow plating consists of three layers of nickel, copper-tin-based intermetallic compound, and tin on the copper alloy. Fine asperities are given to the copper alloy surface in advance, and when plating is applied in the order of nickel, copper, and tin, the plating follows the asperities of the material. After that, the tin melts during the reflow treatment, the asperities formed after plating are smoothed, and the copper-tin-based intermetallic compound is exposed on the convex surface. As a result, fine copper-tin-based intermetallic compounds are dispersed on the tin-plated surface.

1.1 Contact reliability

Contact reliability is one of the most important characteristics required for terminals, and they are required to continue transmitting electrical signals and power from the moment of production until an automobile's end of life. To this end, the contact resistance of the terminal contact point must be kept low. Contact resistance is expressed by Equation (1) as the sum of film resistance, which is the electrical resistance of the film itself, and constriction

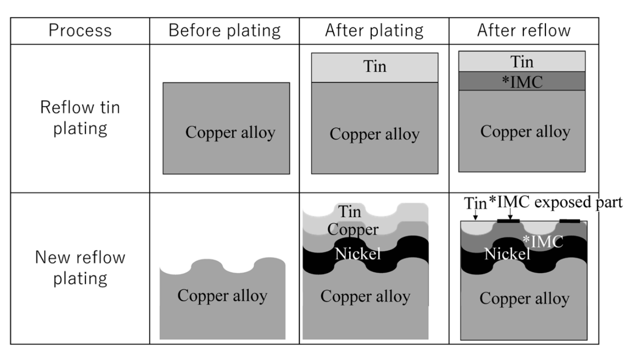


Fig. 1 Cross section structure of tin plated copper alloys in plating and reflow processes
*IMC: Intermetallic compound layer of tin & copper

resistance due to current concentration:[1), 2)]

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

wherein R is the contact resistance (Ω), R_f is the film resistance (Ω), and R_c is the constriction resistance (Ω).

The film resistance and constriction resistance when homogeneous metals make contact are expressed by Equation (2):

$$R_f = \rho_f d / \pi a^2,\ R_c = \rho / 2a \quad (2)$$

wherein ρ_f is the film-specific resistance (Ω·m), d is the film thickness (m), ρ is the metal-specific resistance (Ω·m), and a is the contact surface radius (m).

According to Equation (2), the film resistance decreases as the film thickness decreases and the contact area increases, and the constriction resistance decreases as the radius of the contact surface increases; that is, the contact area increases.

The tin plating applied to the copper alloy surface is covered with a thin oxide film. Oxide films have higher electrical resistance than metal and inhibit electricity transmission; hence, contact resistance generally increases when the oxide film is formed. However, in the case of tin plating, a thin hard oxide film (strength: 16.5 GPa)[3)] is formed on the soft tin (strength: 50-70 MPa).[3)] As a result, the oxide film cannot follow the deformation of the tin caused by sliding when the terminal is inserted and is broken, making it easy to obtain contact between the tins. Therefore, tin plating exhibits low contact resistance even when an oxide film is formed on its surface.

Tin plating is widely used for the contact points of terminals because it is a relatively inexpensive metal and provides stable contact reliability thanks to the breakage of the oxide film. However, in recent years, the miniaturization of the terminal has made it difficult for the oxide film to break, and the mounting environment, with factors such as heat and vibration, has become more severe, making it easier for tin plating to cause an increase in contact resistance. Hence, tin plating requires heat resistance to withstand high-temperature environments and fretting wear resistance to endure vibration and temperature changes.

1.2 Heat resistance

The primary heat source in an automobile is the heat-generating engine, and the engine room tends to be hotter than the car interior.[4)] The engine room reaches a maximum temperature of 120℃ under a scorching sun,[4)] and the accelerated life testing requires a heat resistance temperature of 150-160℃. In addition, due to the electrification of on-vehicle components, the number of terminals per connector is increasing, and the dense terminals make heat escape difficult. Therefore, the demand for heat resistance is becoming more stringent.

Fig. 2 illustrates the cross-section of a box terminal. Terminals include a box-shaped female terminal and a plate-shaped male terminal. The contact resistance is kept low by inserting the male terminal into the female terminal and applying a contact load with the spring of the female terminal. The miniaturization of terminals decreases the contact load of the spring holding down the contact point. Contact resistance depends on load, and the contact resistance tends to increase as the contact load decreases. This is because the contact area decreases as the contact load decreases,[5)] and the oxide film is less likely to be destroyed.

Gold plating, which has high electrical reliability, is generally used at locations of low contact load, where the oxide film is less likely to be destroyed, but gold plating is very expensive, and there is a need to reduce costs by applying tin plating. In addition, electrical reliability is highly required in high-temperature environments where oxide films easily grow. Hence, in areas where the contact load is low in a high-temperature environment, it is necessary to improve the contact reliability of tin plating.

Fig. 3 shows the contact resistance before heating and after holding at 160℃ for 1,000 h. The contact resistance was calculated on the basis of the voltage drop measured by the four-terminal method. A plate-shaped plating specimen and a gold wire bent into a U-shaped probe were used for the measurement. The probe was pressed against the specimen, and the voltage drop was measured at each load in the range of 1 to 5 N while gradually increasing the vertical load. The measurements were made while sliding in one direction at a speed of 1 mm/min. Before heating, all plating specimens maintained contact resistance below 1mΩ under the load of 1 to 5 N. This is considered to be because the tin oxide film had been destroyed by the sliding. After holding for 1,000 h, the contact resistance of the reflow tin plating increased significantly, exceeding 5 mΩ at load 3 N. On the other hand, with

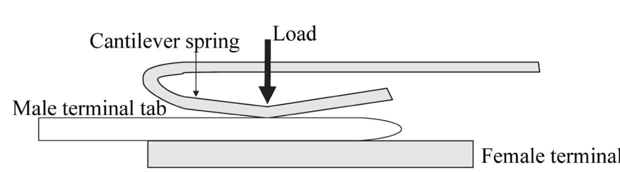


Fig. 2 Schematic image of cross section of terminal

the new reflow plating, the contact resistance was less than 1 mΩ at a load of 3 N and above, showing almost no increase, and maintaining 5 mΩ or less even at a load of 1 N.

Fig. 4 shows the results of cross-sectional SEM observation of tin plating after holding at 160℃ for 1,000 h and the construction of the oxide film in the surface layer. In the reflow tin plating, tin disappears, and a copper-tin-based intermetallic compound, Cu_3Sn (ε phase), is formed. It is considered that the exposure to a high-temperature environment has promoted the mutual diffusion of copper and tin in the material, forming a primary copper-tin-based intermetallic compound, Cu_6Sn_5 (η phase), depleting tin, and further diffusion has resulted in the formation of Cu_3Sn (ε phase).[6] In addition, a thick layer of Cu_2O is formed on the surface of the reflow tin plating. The specific electrical resistance of copper oxide (CuO: 10^6-$10^7 \Omega\cdot m$, Cu_2O: $10 \Omega\cdot m$)[7] is higher than that of tin oxide (SnO_2: $4 \times 10^{-4} \Omega\cdot m$)[7] and is considered to affect the contact resistance significantly. It is presumed that the formation of Cu_3Sn with a high copper content increased the thickness of the highly resistant copper oxide on the surface layer and the contact resistance. It is also presumed that the lower the load, the more difficult it is for oxide to be removed by sliding, which further increases the contact resistance.

In the case of the new reflow plating, Cu_6Sn_5 and a certain amount of tin is retained even after holding for 1,000 h. Unlike the reflow tin plating, no thick copper oxide is formed. Therefore, it is presumed that the oxide has been easily removed by sliding to maintain the low contact resistance. Tin and Cu_6Sn_5 are maintained because the underlying nickel plating suppresses the diffusion of copper from the base material, making it difficult for copper oxide to form.

It should be noted, however, that when tin plating is directly applied to the nickel plating, an intermetallic compound of nickel and tin is formed, reaching up to the plating surface due to mutual diffusion of nickel and tin in a high-temperature environment, resulting in the formation of nickel oxide with high resistivity (NiO: $4 \times 10^{11} \Omega\cdot m$)[7] on the surface. As a result, the contact resistance increases.[8] Therefore, it is necessary to form

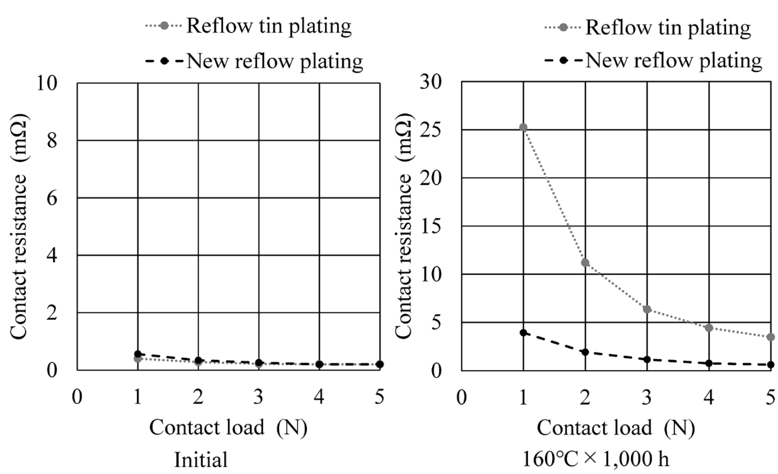


Fig. 3 Relationship between contact load and contact resistance before and after 160℃×1,000 h annealing

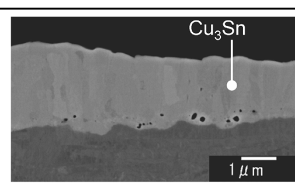
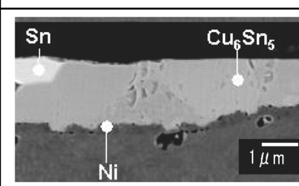
		Reflow tin plating	New reflow plating
SEM images of cross section			
Etching depth	0 nm	SnO_2,Cu_2O, CuO	SnO_2,Cu_2O, CuO
	5 nm	SnO_2,Cu_2O	SnO_2,Cu_2O
	15 nm	SnO_2,Cu_2O	SnO_2
	20 nm	SnO_2	-

Fig. 4 Cross sectional SEM images and composition of oxide films of tin plating after 160℃×1,000 h annealing

the 3-layer structure with a copper-tin-based intermetallic compound between the nickel and tin layers to suppress the diffusion.

The above facts show that it is essential to maintain tin and Cu_6Sn_5 to suppress the increase in contact resistance at high temperatures. To that end, it is effective to increase the thickness of the tin or use a 3-layer plating structure with a nickel layer, as in the case of the new reflow plating.[1)]

1.3 Fretting wear resistance

Fretting wear is a phenomenon in which slight rubbing occurring between the contact points of terminals causes wear of the plating at the contact points. Once fretting wear occurs, the contact resistance may increase as the wear debris of tin accumulates and oxidizes between the contact points. Fretting wear has been said to be attributable to contact point displacement caused by vibration during engine drive and automobile running, and thermal expansion and contraction due to, for example, temperature changes in the surrounding environment and heat generated by energization.[1), 6)] As the miniaturization of terminals progresses, the contact load at the contact points decreases, making the contact points more prone to displacement due to vibration and impact that hitherto have not been a problem, increasing the importance of fretting wear resistance.

Fig. 5 shows a schematic diagram of the fretting wear test, and **Fig. 6** shows the contact resistance behavior during the fretting wear test at loads of 3 N and 5 N for reflow tin plating. For the load of 3 N, a peak of contact resistance (first peak) is observed around 40 to 80 cycles, but this is different for the load of 5 N. In the fretting wear of tin plating, the wear debris of tin is generated by sliding, and, although some of the wear debris is discharged outside, the rest accumulates between the contact points. The accumulated wear debris of tin oxidizes, increasing the contact resistance.[1)] After that, when wear progresses as far as the copper-tin-based intermetallic compound, more wear debris is discharged than is generated, decreasing the wear debris accumulated at the contact points and decreasing the contact resistance (first peak). Further sliding causes wear to progress, exposing the copper alloy base material, and finally contact resistance increases due to the wear and oxidation of the base material.[1)] The first peak of contact resistance observed at the load of 3 N is considered to be caused by the small contact load weakening the force to discharge the wear debris to the outside, making it easy to accumulate. Thus, in the case of

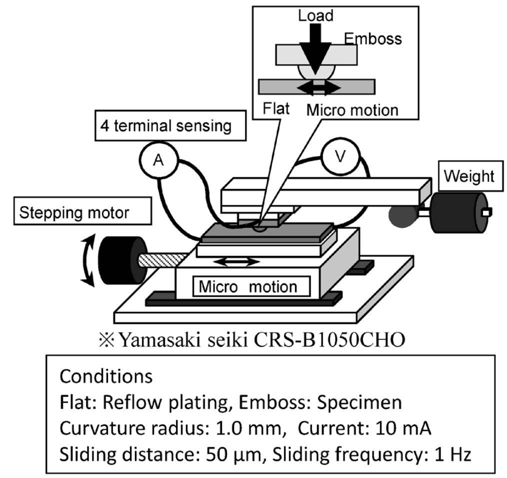


Fig. 5 Fretting test system

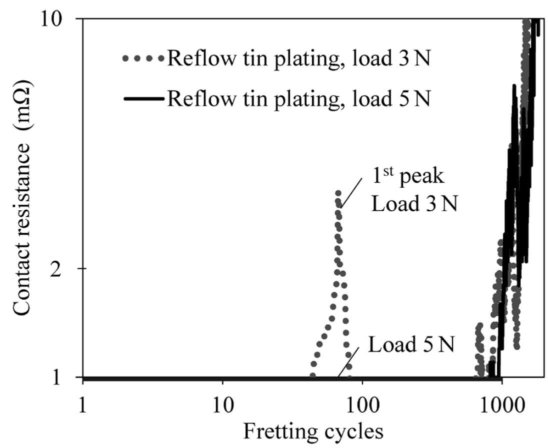


Fig. 6 Changes of contact resistance of reflow tin plating with different contact load

fretting wear, the lower the load, the easier it is for the wear debris to accumulate, which tends to increase the first peak value of the contact resistance. Therefore, plating is required to suppress the first peak of contact resistance at a low load. The first peak of contact resistance is due to the accumulation and oxidation of tin wear debris, and in order to lower the first peak of contact resistance, the generation and accumulation of wear debris must be suppressed. To this end, it is effective to reduce the thickness of tin plating, which is the source of wear debris, or to suppress tin wear.

Fig. 7 shows the relationship between the tin plating thickness of new reflow plating and reflow tin plating at the load of 3 N and the first peak contact resistance in fretting wear. Here, the tin plating thickness is the average thickness of the tin layer only, excluding the copper-tin-based intermetallic compound. For either type of plating, reducing the tin thickness lowers the first peak. The reason for this is considered to be the decrease in the amount of tin wear debris generated. When homogeneous metals are rubbed against each other,

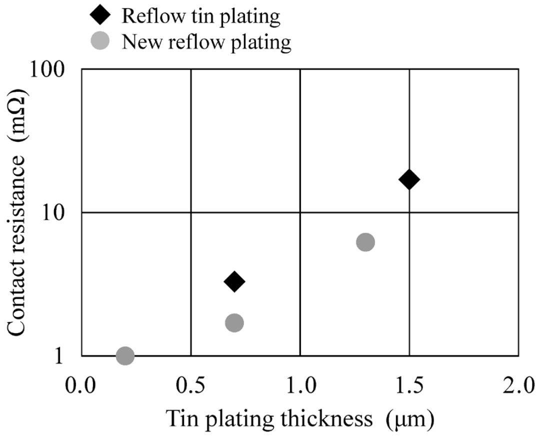


Fig. 7 Relationship between tin plating thickness and 1st peak of contact resistance

adhesion generally tends to occur, making the wear severe (adhesive wear).[9] Thus, the primary cause of wear between two layers of tin plating is regarded as adhesive wear. The new reflow plating exposes the copper-tin intermetallic compound on the surface to suppress the adhesive wear of tin. At around 0.7 μm tin thickness in Fig. 7, the new reflow plating has a lower first peak than the reflow tin plating. This is considered to be attributable to the effect, described above, of suppressing the adhesive wear of tin.

1.4 Terminal insertability

In recent years, the number of terminals per connector has increased, and the connector insertion force has increased accordingly. Since the work of inserting connectors is done manually, there is a move to tighten the insertion force standard to reduce the burden on workers, and reducing the insertion force of the connector is considered to become even more critical in the future. Since the friction force of the tin plating affects the insertion force of the connector, a reduction in the coefficient of friction is required for the tin plating.

Friction force is expressed as the sum of a force component required to separate the adhered parts (adhesive friction), a force component due to a hard surface digging into a soft surface (friction due to digging), and a component based on the energy loss caused by the difference in deformation force when pushing and pulling the material (elastic hysteresis loss).[1] In general, the difference in hardness of two layers of tin plating has little effect on the friction between them, the friction caused by digging is slight, and the adhesive friction becomes dominant. Therefore, the coefficient of friction is given by Equation (3):[9]

$$\mu = F/W = As/Ap = s/p \cdots\cdots\cdots\cdots (3)$$

wherein F is the friction force (N), W is load (N) in the direction normal to the plate thickness, A is the contact area (m^2), s is the shear strength of adhered part (N/mm^2), p is the plastic flow pressure (N /mm^2) = hardness of the material (N/mm^2).

The plastic flow pressure is the pressure at which the entire interior close to the surface near the contact part undergoes plastic deformation when the contact load is increased and corresponds to the hardness of the material.[1] According to Equation (3), the coefficient of friction can be reduced by lowering the shear strength of the adhered part and/or increasing the plastic flow pressure.

Fig. 8 is a schematic diagram of the method for measuring the coefficient of friction. The coefficient of friction was measured following the Japan Copper and Brass Association technical standard JCBA T311:2002. A plate-shaped test piece (Flat) and a test piece with a hemispherical protrusion with a radius of curvature of 1.0 mm (Emboss) were brought into contact, and the coefficient of friction was calculated from the friction force when a load of 3 N was applied in the normal direction of the plate surface.

Fig. 9 shows the relationship between tin thickness and coefficient of friction for new reflow

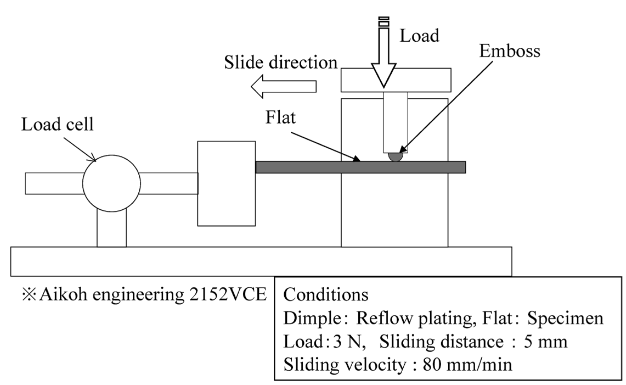


Fig. 8 Friction coefficient measurement system

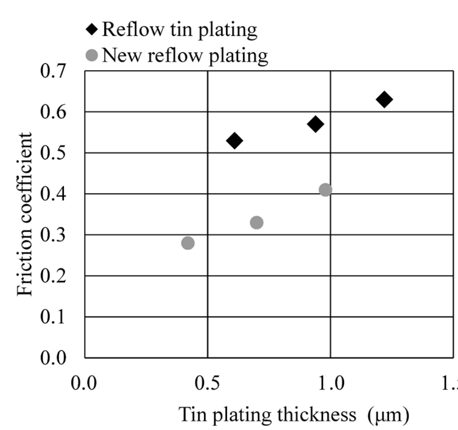


Fig. 9 Relationship between tin plating thickness and friction coefficient

plating and reflow tin plating. For both cases of plating, the thinner the tin layer, the lower the coefficient of friction becomes. Thinning the tin layer makes the plating more susceptible to the rigid base material, increasing the apparent hardness and decreasing the coefficient of friction by suppressing the adhesive wear of the tin. Also, the new reflow plating results in a coefficient of friction lower than that of the reflow tin plating. The new reflow plating has a copper-tin-based intermetallic compound exposed on the surface, and the hard copper-tin-based intermetallic compound increases the apparent plating hardness and suppresses the adhesive friction of the tin, which is considered to have reduced the coefficient of friction.

2. Introduction to new reflow plating (heat resistant specifications, low friction specifications)

The following introduces a new reflow plating (heat resistant specifications) that has improved heat resistance by varying the tin thickness compared with the standard new reflow plating and a new reflow plating (low friction specification), especially with improved terminal insertability.

2.1 Developmental approach to tin plating for terminals

Fig.10 shows the positioning of tin plating for terminals with respect to terminal insertability and heat resistance. As mentioned above, increasing the tin thickness improves the heat resistance, but on the other hand, the terminal insertability and the fretting wear resistance characteristics decline. Therefore, it is difficult to achieve both by controlling the tin plating thickness alone. The new reflow plating simultaneously achieves various characteristics that were difficult to attain with conventional reflow tin plating by having a three-layered structure and finely dispersed copper-tin-based intermetallic compound on the surface of the tin plating, and it has been adopted for automobile terminals.

However, with the recent changes in automobiles, the characteristics required for tin plating used for automobile terminals are becoming more stringent. Kobe Steel has developed a new reflow plating with heat-resistant specifications and low friction specifications as new variations in response to the increasing demand for heat resistance and terminal insertability.

2.2 New reflow plating (heat resistant specifications)

For improved heat resistance, the new reflow plating (heat resistant specifications) has a greater thickness of tin than the standard new reflow plating.

Fig.11 shows the contact resistance at a vertical load of 1 to 5 N when held at 160℃ for 1,000 h and 5,000 h. The contact resistance after 5,000 h of reflow tin plating is higher than after 1,000 h. This is presumed to be due to the thick growth of copper

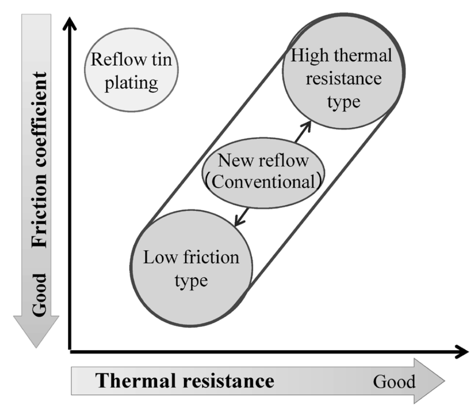


Fig.10 Positioning of friction coefficient and thermal resistance of tin plating for terminals

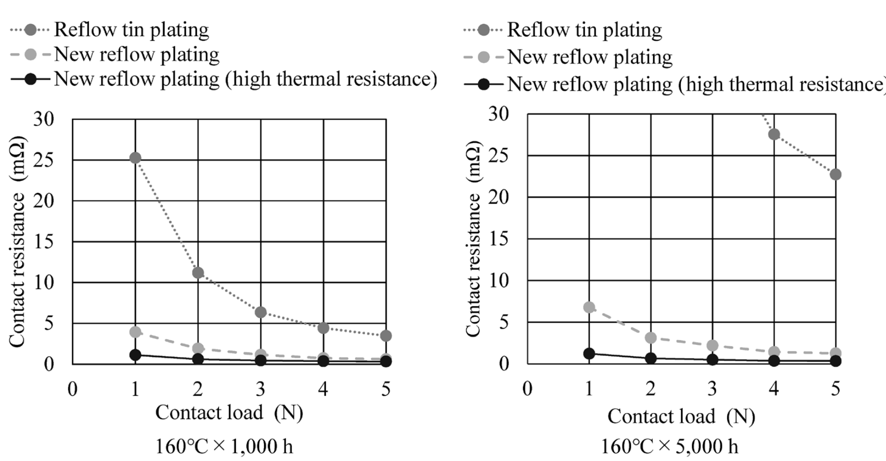


Fig.11 Relationship between contact load and contact resistance before and after 160℃×1,000 h and 5,000 h annealing

oxide. On the other hand, the new reflow plating (heat resistant specifications) maintains a contact resistance of 1 mΩ or less at load 1 N even after 5,000 hours and is more heat resistant than the new reflow plating. This is considered to be because thicker tin maintained the tin and Cu_6Sn_5 for a longer period than the new reflow plating did, suppressing the generation of copper oxide.

Fig.12 shows the relationship between the square root of the tin plating holding time at 160℃ and the thickness of the copper-tin-based intermetallic compound. The linear approximation of the plots has been extrapolated to obtain the growth rate of the copper-tin-based intermetallic compound. As mentioned above, increasing the tin thickness effectively improves the heat resistance. Therefore, the change in the time required for the tin to disappear when the tin thickness is increased from 1 μm to 1.5 μm has been calculated from the linear approximation of the growth rate of the copper-tin-based intermetallic compound. As a result, it was found that the reflow tin plating increases the disappearance time of tin by approximately 40 hours, whereas the new reflow plating significantly lengthens it to approximately 2,900 hours. Therefore, increasing the tin thickness of the new reflow plating is more effective in improving the heat resistance.

Fig.13 shows the coefficient of friction for the reflow tin plating and new reflow plating (heat resistant specifications). As mentioned above, the coefficient of friction increases as the tin plating thickness increases. The new reflow plating (heat resistant specifications) shows a coefficient of friction similar to that of the reflow tin plating, despite the thicker tin. The new reflow plating has the advantage of a coefficient of friction lower than that of the reflow tin plating. Hence, the new reflow plating (heat resistant specifications) has set the tin thicker than in the new reflow plating by determining the extent to which the coefficient of friction is equivalent to that of the reflow tin plating.

The new reflow plating (heat resistant specifications) is suitable for applications requiring improved heat resistance and maintenance of terminal insertability in high-temperature environments.

2.3 New reflow plating (Low friction specifications)

The new reflow plating (low friction specifications) has reduced tin thickness in comparison with the standard new reflow plating for improved terminal insertability.

Fig.14 shows the coefficient of friction of tin plating. The bar graph represents the average value of ten measurements, and the error bar indicates the maximum and minimum values. The new reflow plating (low friction specifications) exhibits a lower coefficient of friction than the standard new reflow plating and is more consistent with less variability.

Fig.15 shows the behavior of the friction force of tin plating. Several small peaks are observed with the reflow tin plating and new reflow plating, but few peaks are observed with new reflow plating (low friction specifications). As mentioned above, tin plating results mainly in adhesive friction. Adhesive friction is a phenomenon of repeated sticking and

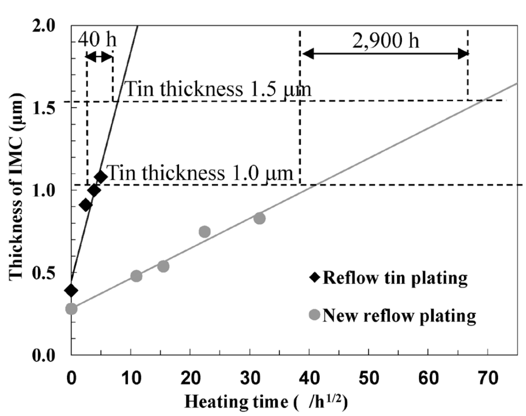


Fig.12 Growth of intermetallic compound layer at 160℃

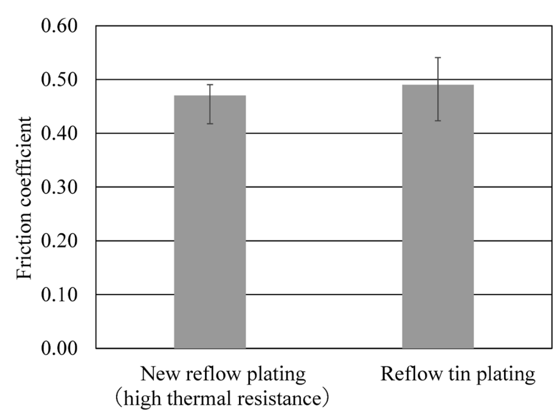


Fig.13 Friction coefficient of tin plating

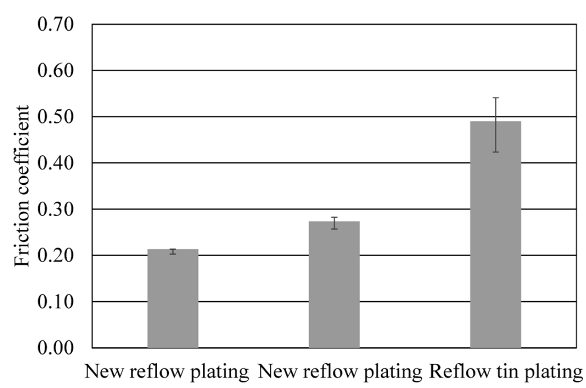


Fig.14 Friction coefficient of tin plating

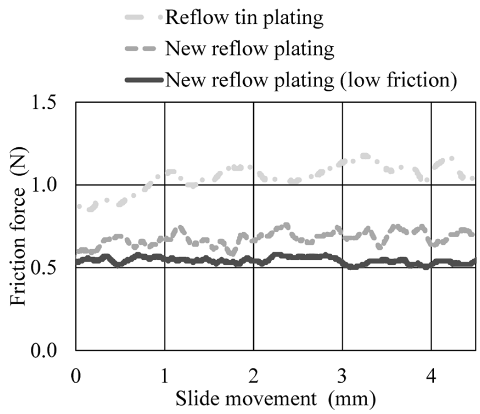


Fig.15 Change of friction force of tin plating

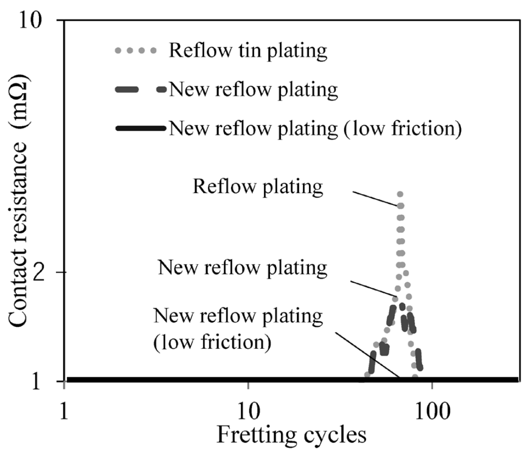


Fig.16 Changes of contact resistance of reflow plating

breaking,[9] and it is presumed that the small peaks of friction force have been caused by the repetition of the adhesive friction of tin. The new reflow plating (low friction specifications) achieves even lower friction and variability suppression by reducing the tin thickness and suppressing the adhesive friction of tin.

Fig.16 shows the contact resistance behavior during the fretting wear test of tin plating. The new reflow plating (low friction specifications) reduces the first peak even more than the new reflow plating by reducing the tin thickness.

Fig.17 shows the contact resistance of tin plating after holding at 160℃ for 1,000 h. The new reflow plating (low friction specifications) has slightly higher contact resistance at load 1 N than the new reflow plating but is more heat resistant than the reflow tin plating. This is because the three-layered structure suppresses the diffusion of copper.

The new reflow plating (low friction specifications) is suitable for applications with exceptionally high insertion force specifications and where fretting wear resistance is required.

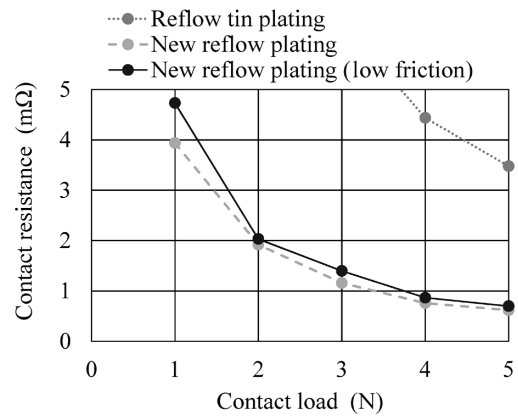


Fig.17 Relationship between contact load and contact resistance before and after 160℃×1,000 h annealing

Conclusions

The new reflow plating is a type of plating with improved heat resistance, fretting wear resistance, and terminal insertability compared with the conventional reflow tin plating and its use in tin plating for automobile terminals is spreading. Kobe Steel has added heat resistant specifications and low friction specifications as new variations of the new reflow plating. Utilizing these, the company will strive to propose tin plating suitable for the usage environment.

References

1) M. Tsuru et al. R&D Kobe Steel Engineering Reports. 2012, Vol.62, No.2, pp.59-62.
2) Latest Connector Technology '99 Editorial Committee. Latest Connector Technology '99. First edition. Japan Advanced Technology Co., Ltd., 1999, pp.1-3.
3) T. Tamai et al. IEICE Technical Report. EMD2008-2, pp.7-12.
4) S. Izumi. ESPEC Test Navi Report. 1997, No.9, pp.5-11.
5) S. Sawada. SEI TECHNICAL REVIEW. 2010, Vol.177, pp.36-42.
6) H. Sakamoto. R&D Kobe Steel Engineering Reports. 2019, Vol.69, No.1, pp.19-24.
7) G. V. Samsonov. The Oxide Handbook.-Physicochemical Properties-. 2nd Revised and Enlarged Edition, Japan-Soviet Press, 1979, p.209.
8) T. Hara et al. R&D Kobe Steel Engineering Reports. 2004, Vol.54, No.1, pp.9-12.
9) Y. Yamamoto et al. TRIBOLOGY. 2nd edition, Ohmsha Ltd., 2010, pp.41-42, pp.193-194.