Technical Trends in Copper Alloys and Plating for Automotive Terminals

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Copper alloys and tin-plated strips are widely used for automobile terminals. These terminals are being downsized, requiring their copper alloy materials to have higher strength and excellent stress relaxation resistance. The tin plating is now required to have high fretting corrosion resistance, in addition to a low friction coefficient and low contact resistance. This paper describes the technical trends in automobile terminals and the properties of newly developed copper alloys and tin plating, as well as future trends in technical development.

Introduction

Lately, in the field of automobiles, electric vehicles have been spreading rapidly, viewed from the environmental aspect, in addition to vehicles equipped with higher level self-driving technology and cars that can be connected to external communication networks. With such trends, the number of electronic components mounted in an automobile has increased remarkably, and the number of electrical wiring and connectors connecting them continues to increase. Along with this, electrical wiring has become finer, and the terminals that constitute connectors have become smaller. Also, their materials have been made thinner, and higher strength has been demanded.

In addition, the number of electronic components mounted in high-temperature environments such as engine rooms has increased, and there has been a demand for heat resistant copper alloys with excellent stress relaxation resistance.

In general, automotive terminals with surface treatment such as tin plating have difficulty in ensuring contact reliability, due to downsizing, and have a major issue in dealing with the slight sliding abrasion phenomenon caused by vibrations and impact.

Kobe Steel has been developing high-performance copper alloys and surface treatments to meet such technical demands for automotive terminal materials. This paper describes the copper alloys for automotive terminals, the technology required for surface treatment, and their development status, as well as future performance requirements.

1. Copper alloys for automotive terminals

Fig. 1 schematically shows the cross-sectional view of a typical automotive terminal and the characteristics required for its material. A terminal consists of a female terminal and a male tab. The most important function of a terminal is to maintain the contact pressure of the spring of the female terminal (hereinafter referred to as "contact pressure") and keep the contact resistance of the contact point stable and low.

For this reason, a high proof stress is required for the copper alloy so that the stress does not exceed the elastic limit even when the spring is greatly bent, so as to be suitable for and tolerant of a high load. In addition, sufficiently high electrical conductivity is required to allow the passage of an electric current. Furthermore, stress relaxation resistance is important in maintaining the contact pressure to press the male tab without losing the spring function even in high-temperature environments such as engine rooms. Moreover, in order to form a terminal of a box shape, the material must also have excellent bendability.

Fig. 2 shows the relationship between the proof

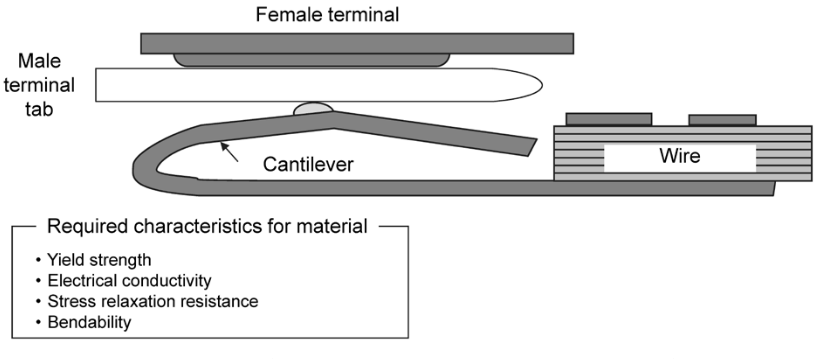


Fig. 1 Cross section of terminal and characteristics required for material

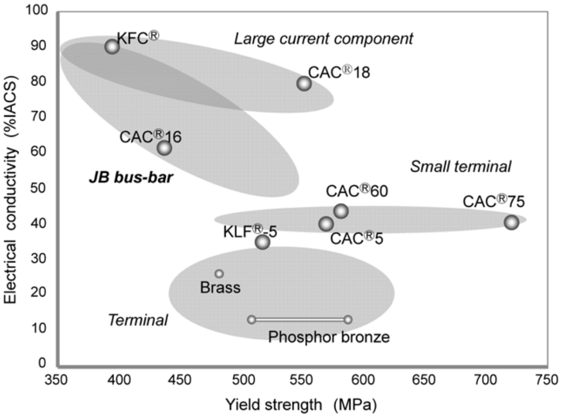


Fig. 2 Relationship between yield strength and electrical conductivity of copper alloys for terminals

stress[Note 1] and electrical conductivity of Kobe Steel's copper alloys for automotive terminals. In general, proof stress and electrical conductivity are in a trade-off relationship, and elements added to increase the strength (proof stress) of copper decrease its electrical conductivity. Broadly speaking, copper alloys with emphasis on conductivity are used for power system parts such as junction blocks (JBs) that carry large currents. On the other hand, copper alloys that emphasize strength are often used for small female terminals.

Brass and phosphor bronze, which are general-purpose copper alloys with an electrical conductivity of less than 30% IACS, are used widely in accordance with the required performance.

1.1 Copper alloys for small automotive terminals

Table 1 shows the mechanical properties and conductivities of copper alloys for small automotive terminals. **Fig. 3** shows the stress relaxation characteristics of these copper alloys at 160℃.[1] In general, small terminals carry a small current, and copper alloys with a conductivity of 30-50% IACS are used, while copper alloys having low stress relaxation ratios are used in high temperature environments.

KLF® [Note 2]-5, which has long been used for small automotive terminals, is a copper alloy based on KFC® [Note 3] (Cu-0.1Fe-0.03P) and contains 2% tin in the solid solution for emphasizing strength. The new model alloy of this KLF-5 is CAC® [Note 4] 5. CAC 5 is a copper alloy containing a smaller amount of tin compared with that of KLF-5, and also contains nickel and phosphorus to exert the dislocation anchoring action of these solid solution elements. Its stress relaxation resistance has been improved to a level comparable to those of Cu-Ni-Si alloys.[2] This alloy is increasingly being used thanks to its simple manufacturing process and easy-to-process characteristics compared with Cu-Ni-Si alloys.

Table 1 Typical mechanical properties and electrical conductivity of copper alloys for small terminals

Alloy	Nominal composition (mass%)	Temper	0.2% Yield strength (MPa)	Elongation (%)	Electrical conductivity (%IACS)
KLF®5	Cu-0.1Fe-0.03P-2Sn	H	530	12	35
CAC®5	Cu-0.8Ni-0.07P-1.2Sn	EH/SP	570	12	40
CAC®60	Cu-1.8Ni-0.4Si-1.1Zn-0.1Sn-0.01Mg	H	580	16	44
CAC®75	Cu-2.5Ni-0.55Si-0.2Sn-1.0Zn	H	730	10	40

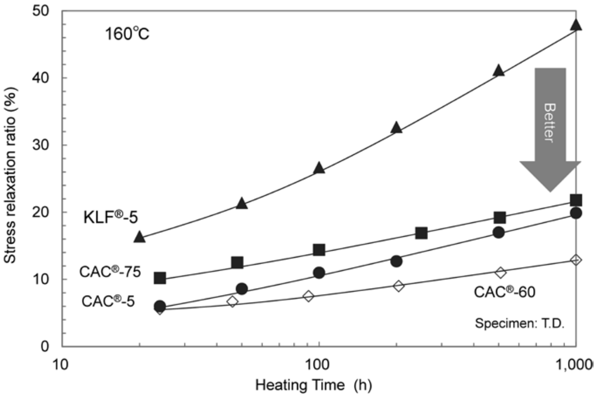


Fig. 3 Change of stress relaxation ratio at 160℃ heating (initial load: 0.2% yield strength×80%)

CAC60 and CAC75, on the other hand, are copper alloys that utilize the precipitation phenomenon of Ni and Si during aging to ensure strength, and each has both high conductivity and excellent stress relaxation resistance.

CAC60 is capable of W-bending with *R*/*t*=0.0 (the ratio of bending radius *R* to thickness *t*, called the "critical bending ratio") in both the good way (bending axis perpendicular to rolling direction) and bad way (bending axis parallel to rolling direction), and has an advantage of a high degree of freedom for designing terminals. One of the reasons for excellent bending workability is that the amount of Sn or Mg, element inhibiting bendability in Cu-Ni-Si alloys, is kept to the minimum amount necessary to improve stress-relaxation resistance. This made it possible to achieve both excellent bending workability and stress-relaxation resistance.[3]

CAC75 has further increased proof stress by the enhanced amount of Ni and Si compared with CAC60. It can be box-formed thanks to its W-bending of *R*/*t*=0.5 in both the good way and bad way.

[Note 1] In the case of copper alloys, which exhibit no clear yield points, the stress at which the material undergoes an amount of plastic strain equal to 0.2 percent is used as the proof stress.

[Note 2] KLF is a registered trademark of Kobe Steel.

[Note 3] KFC is a registered trademark of Kobe Steel.

[Note 4] CAC is a registered trademark of Kobe Steel.

Automotive terminals are expected to be further miniaturized in the future, and the materials will be made thinner. In order to ensure important spring reliability, it will be necessary to achieve a proof stress exceeding 1,000 MPa. In addition, the punch-ability and bending workability required for fine processing are also important, and there are high hurdles for material development. However, since the electric current applied is small, it is highly possible that a material with a brass level conductivity of less than 30% IACS could be used.

1.2 Copper alloys for power system parts

Table 2 shows the mechanical properties and electrical conductivity of copper alloys for power system parts. **Fig. 4** shows their stress relaxation characteristics at 180℃. KFC has a conductivity of 90% IACS and is widely used for medium-to-high current applications. This alloy, however, has a low stress relaxation resistance and is not suitable for a fitting-type terminal relying on spring connection.

CAC16, on the other hand, was developed by adding a small amount of Sn and Mg to KFC to impart stress relaxation resistance. This alloy is widely used in junction blocks with tuning-fork-type terminals. Its conductivity, however, is 60% IACS and is lower than that of KFC.

Hence, CAC18 was developed with a conductivity and stress relaxation resistance that represent an improvement over those of CAC16. CAC18 is a Cu-Cr-Ti alloy and ensures high strength and conductivity by the precipitation strengthening of Cr-based precipitates and solid solution strengthening of Ti. In a large-current circuit, the contact temperature may rise to approximately 180℃ due to instantaneous overcurrent. As shown in Fig. 4, CAC18 has a small change in the stress relaxation ratio even after 1,000 hours at 180℃. Stress relaxation is a phenomenon in which dislocations are moved by a thermal activation process, and excellent stress relaxation resistance is realized by suppressing the movement of the dislocations by adding a small amount of active metal element.4) CAC18 has a composition in the range of CDA18070, which has a proven record in the EU and US and is a global alloy available from multiple companies. With the backing of this experience, its market is expected to grow.

Table 2 Typical mechanical properties and electrical conductivity of copper alloys for power line

Alloy	Nominal composition (mass%)	Temper	0.2% yield strength (MPa)	Elongation (%)	Electrical conductivity (%IACS)
KFC®	Cu-0.1Fe-0.03P	H	390	7	90
CAC®16	Cu-0.1Fe-0.03P-0.4Zn-0.2Mg-0.2Sn	H	430	10	61
CAC®18	Cu-0.3Cr-0.05Ti-0.02Si	H	550	12	80

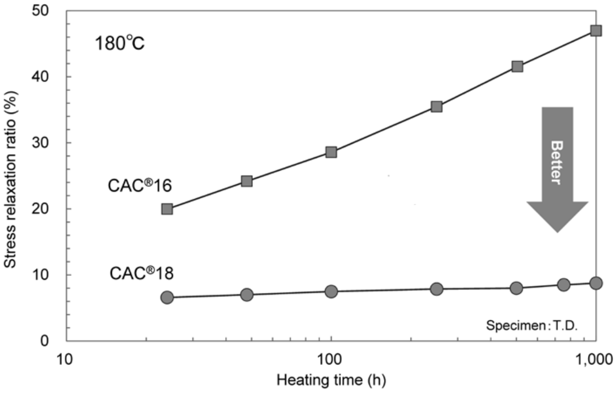


Fig. 4 Change of stress relaxation ratio at 180℃ heating (initial load: 0.2%yield strength×80%)

In the future, the market of electric vehicles will expand, requiring higher power density. Hence, it is anticipated that materials that can handle higher voltage and higher current will be needed, and a new material in a range of higher conductivity and strength must be found.

2. Tin plating for automotive terminals

2.1 Types of Kobe Steel tin plating

The cross-sectional structure of a tin-plated copper alloy mass-produced at Kobe Steel is schematically shown in **Fig. 5**.5) The term "reflow," as used in "reflowed tin plating," means remelting, and the term “reflowed tin plating” indicates that heat is applied after electrodeposition plating to remelt the electrodeposited tin. During remelting, a layer of intermetallic compound consisting of tin and copper is formed by the interdiffusion

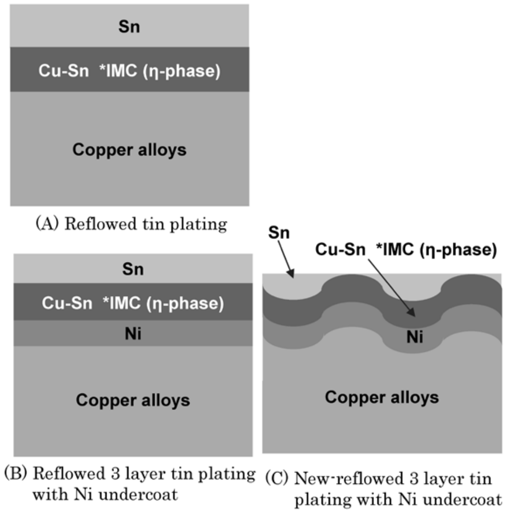


Fig. 5 Schematic image of cross-section of tin plated copper alloys
*IMC: intermetallic compound layer of Sn and Cu

between the Cu base material and tin layer (Fig. 5 (A)). The reflowed 3-layer tin plating with nickel undercoat consists of three layers: a nickel layer, an intermetallic compound layer of tin and copper, and a tin layer (Fig. 5 (B)). The new reflowed plating layer is deposited on an uneven surface of a copper alloy base, and consists of a nickel layer, an intermetallic compound layer of tin and copper, and a surface layer that is a mixture of tin and intermetallic compound layers (Fig. 5 (C)).

2.2 Friction coefficient

As automotive components become increasingly electrified and more sophisticated, an increasing number of circuits and connectors are being used per unit. In addition, as the number of electrodes per connector increases, a greater insertion force is required for fitting the connector.

The increasing insertion force deteriorates the workability of assembly and thus must be decreased. The insertion force of a terminal is determined by the friction coefficient of the material surface and the contact pressure of the terminal. In the case of friction between two tin-plated surfaces, adhesion friction becomes the main component, and the friction coefficient μ is expressed by Equation (1):[6)]

$$\mu = F/W = As/Ap = s/p \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

wherein F: friction force, W: load in the normal direction of the sheet, A: contact area, s: shear strength of the adhesion part, p: plastic flow pressure=material hardness.

Equation (1) indicates that the friction coefficient can be reduced by increasing the plastic flow pressure. The plastic flow pressure is the pressure that plastically deforms all the bulk close to the surface near the contact when the contact pressure is increased and corresponds to the hardness of the material. Therefore, one way of reducing the friction coefficient is to harden the plating, and another is to make the plating thin enough so that the hard base material exerts its effect, which increases the apparent hardness.

Fig. 6 is a schematic diagram of the friction coefficient measurement apparatus, and **Fig. 7** shows the friction coefficients of the tin-plated materials. The reflowed 3-layer tin plating with nickel undercoat has a thinner tin layer and is more easily affected by the hard base material, which increases the apparent hardness and reduces the friction coefficient. The new reflowed plating has a surface layer consisting of a mixture of tin and intermetallic compound layers. which makes adhesion less likely to occur. Such adhesion is more likely to occur in the friction between tin and tin, while the intermetallic compound of tin and copper suppresses the adhesion friction of tin. As a result, the friction coefficient is greatly reduced to about half that of reflowed tin plating.

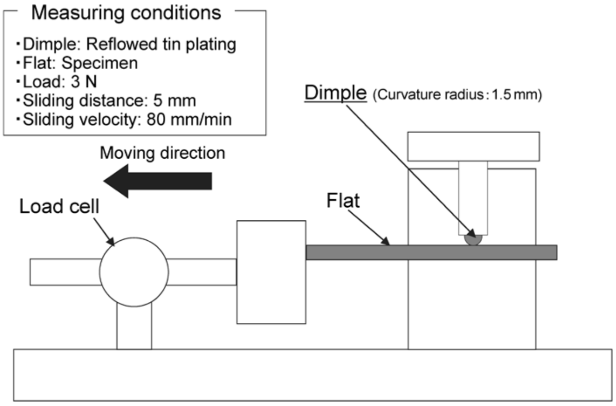


Fig. 6 Schematic diagram of apparatus for measuring friction coefficient

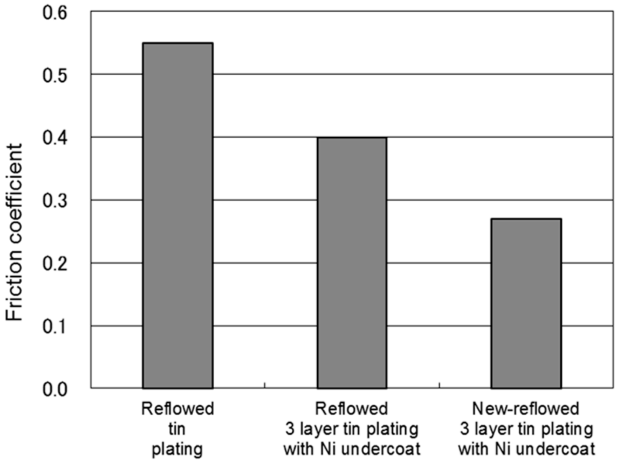


Fig. 7 Comparison of friction coefficients

2.3 Contact resistance characteristics

In order to secure space inside a vehicle, many electrical components that require low contact resistance at temperatures as high as 150 to 160℃ are being installed in the engine room. **Fig. 8** shows the change in contact resistance at the holding temperature of 160℃. **Fig. 9** shows the cross-sectional observation results after heating at 160℃ for 120 hours. The electrical resistivity of the base metal, plating layer, and oxide film are shown in **Table 3**.[7)-9)]

As mentioned earlier, the reflowed tin plating layer consists of two layers: a tin layer on the surface and a Cu_6Sn_5 layer (η phase) of copper and tin below it. The cross-sectional observation after 120 hours of heating shows that the tin layer has disappeared, and a Cu_3Sn layer (ε phase) has been

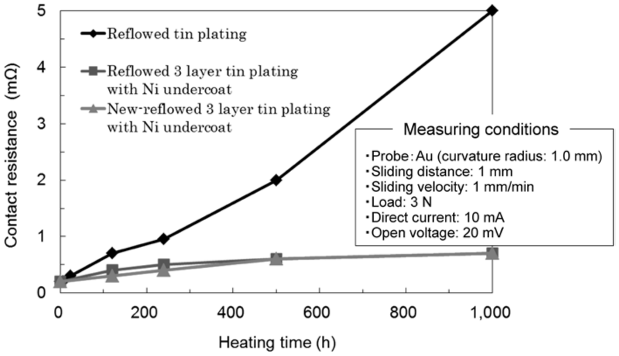
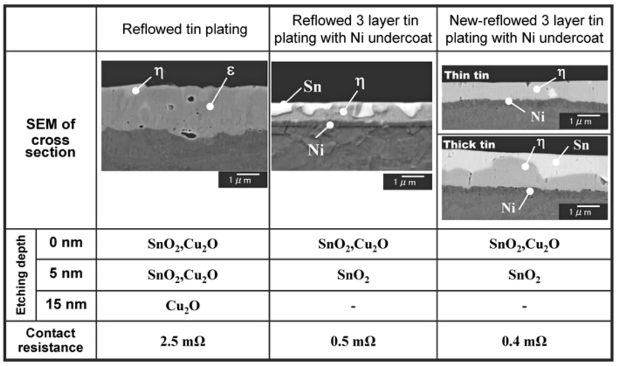


Fig. 8 Change of contact resistance during heating at 160℃



		Reflowed tin plating	Reflowed 3 layer tin plating with Ni undercoat	New-reflowed 3 layer tin plating with Ni undercoat
SEM of cross section				
Etching depth	0 nm	SnO_2,Cu_2O	SnO_2,Cu_2O	SnO_2,Cu_2O
	5 nm	SnO_2,Cu_2O	SnO_2	SnO_2
	15 nm	Cu_2O	-	-
Contact resistance		2.5 mΩ	0.5 mΩ	0.4 mΩ

Fig. 9 SEM of cross section after 160℃×120 h, and relationship between composition of oxide film and contact resistance

Table 3 Electrical resistivity

	Ω・m		Ω・m
Cu	1.7×10^{-8}	Cu_2O	10^6～10^7
Sn	12.6×10^{-8}	CuO	1~10
Cu_6Sn_5	12.5×10^{-8}	SnO_2	4×10^{-4}
Cu_3Sn	20.5×10^{-8}	NiO	10^{11}

formed, while a slight amount of the Cu_6Sn_5 layer (η phase) remains. This is because the copper of the base material has diffused while being held at a high temperature, and the tin layer has generated a Cu_6Sn_5 layer (η phase), while the diffusion further progressed to generate a copper-rich Cu_3Sn layer (ε phase).

Qualitative analysis detected Cu_2O at the surface and at a depth of 15 nm. Since the electrical resistivity of Cu_2O is so great, it is considered to increase the contact resistance. On the other hand, the electrical resistivity of tin oxide, SnO_2, is much lower than that of Cu_2O and has little effect on contact resistance.

The reflowed 3-layer plating and new reflowed plating, both with a Ni undercoat, exhibit only a small increase in contact resistance after the heating. In these, the nickel undercoat acts as a barrier against the diffusion of copper into the tin layer, preventing the copper-rich Cu_3Sn layer (ε phase) from forming and causing the tin layer and the Cu_6Sn_5 layer (η phase) to remain. Observations were conducted on thin and thick portions in the new reflowed plating, and neither one showed any Cu_3Sn layer (ε phase). In any type of the plating, Cu_2O exists only at the outermost surface as a very thin film, not extending in the depth direction, and is considered to have kept the low contact resistance.[10)]

2.4 Fretting corrosion characteristics

Fretting corrosion is a phenomenon in which an electrical contact, being worn due to sliding caused by vibration or thermal cycling, generates abrasion particles, which are oxidized, increasing the contact resistance.

As the terminals are downsized, the need for reduced insertion force has increased due to the decreasing contact pressure and increasing number of contacts, raising the susceptibility to fretting corrosion. As a result, the contacts have become more prone to shift due to vibration and impact, as well as to thermal expansion and contraction caused by the heat generated during energization. These problems, which hitherto have caused no trouble, have made fretting corrosion an increasingly important issue.

Fig.10 schematically shows the fretting corrosion test. **Fig.11** shows the change in contact resistance with sliding cycles. Once fretting corrosion occurs, wear particles are generated by sliding. Some part of the wear particles is discharged outside; however, most of what remains is deposited on the contact surface. These wear particles accumulate and oxidize, increasing the contact resistance (the 1st peak in Fig.11). Subsequently, once the intermetallic compound layer is worn out, the discharge amount becomes greater than the amount of wear particles generated, decreasing the amount of the wear particles deposited on the contact and reducing the contact resistance. Further sliding increases wear and exposes the copper alloy base material, which ultimately increases the contact resistance due to the wear and oxidation of the base material.[11)]

As shown in Fig.11, the 1st peak height decreases in the order of reflowed tin plating, reflowed 3-layer tin plating with nickel undercoat, and new reflowed plating. The 1st peak is attributable to the deposition and oxidation of the wear particles of tin, and to prevent the contact resistance from increasing, the generation and deposition of wear particles should be suppressed. To that end, it is necessary to suppress the wear of the tin plating, or to increase the contact pressure to promote discharge.

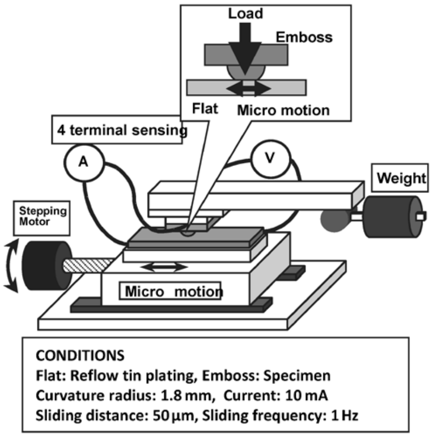


Fig.10 Schematic diagram of fretting corrosion test

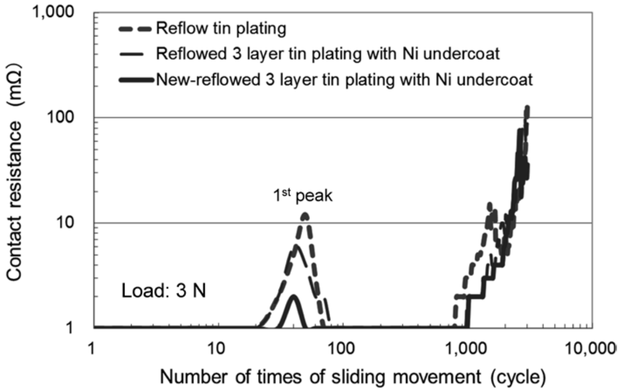


Fig.11 Relationship between contact resistance and number of times of sliding movement at 3 N of load

The reflowed 3-layer tin plating with nickel undercoat is thinner than the reflowed tin plating and is more resistant to being ground. As a result, it generates a smaller amount of wear particles and exhibits a lower peak value. On the other hand, the new reflowed plating has a tin layer and a hard intermetallic compound layer mixed on the surface, making the plating less likely to be abraded. Furthermore, the combination of different materials (tin layer and intermetallic compound) makes adhesion of the contact points unlikely to occur. This is considered to be responsible for the smaller amount of wear particles generated and lower peak value.

It is anticipated that terminals will be further downsized and have more electrodes, decreasing the contact pressure from 3 N to 2 N or to 1 N, requiring a fretting corrosion resistance at the lower contact pressure. In general, tin plating becomes difficult to use as the contact pressure drops. Gold plating may be used; however, gold plating is expensive and is not widely applicable to automotive terminals.

Figs.12 and **13** show the fretting corrosion characteristics for the contact pressures of 2 N and 1 N, respectively. In the case of reflowed tin plating, the 1st peak increases remarkably when the contact pressure is reduced to less than 3 N, and exceeds 100 mΩ at 1 N. The new reflowed plating, on the other hand, exhibits a peak that is less than 10 mΩ at 2 N and slightly higher than 10 mΩ at 1 N. These peaks are lower than the ones for reflowed plating. This is considered to be greatly attributable to the fact that, as described above, this plating is more resistant to abrasion and adhesion of the contacts is less likely to occur.

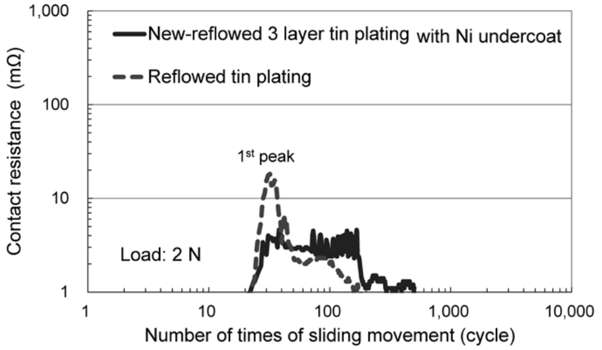


Fig.12 Relationship between contact resistance and number of times of sliding movement at 2 N of load

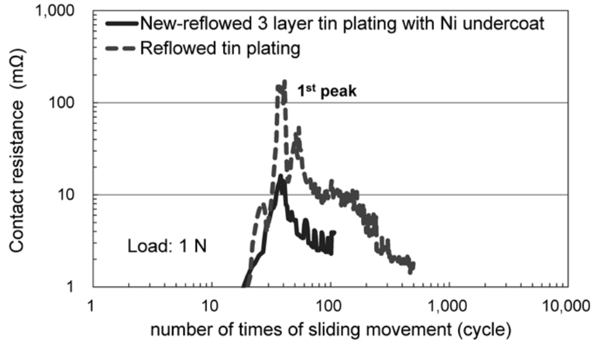


Fig.13 Relationship between contact resistance and number of times of sliding movement at 1 N of load

Kobe Steel will continue to develop tin plating that can ensure contact reliability even at a low contact pressure by further improving the plating.

Conclusions

Automobiles will continue to undergo functional upgrading and to be provided with more advanced electrical equipment. A greater number of cars will be electrically powered. Meanwhile, copper alloys for automotive terminals have a number of challenges to address: e.g., to increase strength and improve stress-relaxation resistance and conductivity, while ensuring the electrical reliability of contacts. Kobe Steel will strive to develop materials while considering more urgent needs for the future and aiming for higher performance and reliability. The company also intends to strengthen its proposal ability not only for material technology, but also for the best matching in combination with surface processing technology.

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