Corrosion Resistance of Multilayered Sn/Ag3Sn Films Electroplated on Cu Alloys for Highly Reliable Automotive Connectors

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The corrosion resistance of multilayered Sn/Ag3Sn films with a 30–80 nm-thick Ag layer on refloved Sn layer (i.e., melting and resolidification of the electrodeposited Sn) on Cu alloy substrates was investigated by accelerated sulfidizing tests in (NH4)2Sx solutions and accelerated aging tests at 473 K, and compared to conventional Ag and refloved Sn films on Cu alloy. The multilayered Sn/Ag3Sn films exhibited stable electrical contact resistance even after immersion in a 0.2 mL/L (NH4)2Sx solution for 120 h. In contrast, the Ag films showed ever-increasing contact resistance with immersion time and eventually failed by losing their surface electric conductivity. Moreover, the multilayered Sn/Ag3Sn films showed low and stable electrical contact resistance equivalent to as-plated samples even after aging at 473 K for 3000 h, whereas the conventional Ag and refloved Sn films delivered unstable and ever-increasing contact resistances at 500 h. The excellent corrosion resistance of the multilayered Sn/Ag3Sn films can be mainly attributed to a thin SnO film on the intermetallic Ag3Sn layer, which is chemically stable in the presence of S2− ions, and the inclusion of Ag component in Cu6Sn5/Cu3Sn phases by inward diffusion, which enhances the oxidation resistance of the Cu-Sn alloy during aging at high temperature.

In the past, automotive connectors mounted in various electric control units (ECU) were used at temperatures up to 473 K, or Class II – III referring to the standards of United States National Council for Automotive Research (USCAR).1–3 Conventional coating materials on Cu alloy base materials, e.g., various tin-based films like refloved Sn (electrodeposited Sn that has been melted and resolidified), electroplated Sn and hot-dip Sn films, and the noble-metal-based coatings like Ag, Au-Co, Au-Ni, and Au/Pd/NS electroplating films, have been used in automobile applications to meet the demands at temperatures below 473 K.1 Recently, with the development of automatic electronic systems equipped on automobiles, the use of electronic and/or electric devices is continuously growing to meet various needs for security and convenience. Accordingly, more sensors and junction boxes connected to various electronic devices are increasingly mounted in engine compartments close to combustion chambers or near the exhaust systems. This requires that the materials for connectors and sensors withstand higher temperature of at least 453–473 K (USCAR-Class V) and a more corrosive environment than usual throughout the lifetime of vehicles. However, the conventional coating materials discussed above cannot meet the ever-increasing requirements for the harsher environment. Therefore, exploring new coatings with stable contact performance for automotive connectors is essential for higher functionality and higher reliability of electric control units.

Various Sn-based coating materials are mostly used for regular connectors because of the low cost, good soldering ability, and excellent ductility, yet the allowable temperature for stable electric contact resistance is usually up to 393 K.1 It is known that the failure of Sn-based coating materials as automotive connectors at high temperature, interpreting by the phenomenon of ever-increasing contact resistance with aging, can be attributed to the formation of insulating Cu oxide films on the surface by the fast Cu diffusion from the base materials.5 To solve this problem, a Ni underlayer electroplated beneath the Sn film has been adopted as a barrier layer to prevent the diffusion of Cu onto the surface.5 The Ni barrier layer, however, can only maintain stable contact resistance up to 423 K, above which Ni diffusion also occurred toward the surface and a more insulating Cu-Sn-Ni oxide film would form at high temperature. Recently, several works have been reported on applications of a multilayered Ni (1–3 µm)/Pd (0.3–1 µm)/Au (50–100 nm) coating on Cu for high reliable automotive connectors at high temperature.5–7 Despite of high cost, the high temperature automotive reliability of the noble metal coatings as special connectors was assessed to be equivalent to 423 K for 5000 h8 or 448 K for 500 h.8

Electrodeposited pure Ag films on Cu alloys are widely used in various electronic devices due to their excellent electric conductivity and good fretting performance. However, silver sulfide corrosion has been a big concern in various industrial applications, not only in the automotive industry, but also in vehicle exhaust fumes (exit/entrance ramps), rubber manufacturing, sewage/waste-water treatment plants, petroleum refineries, coal-generation power plants, large-scale farms, etc.9,10 In addition, other disadvantages of pure Ag films included dielectric migration and softening because of recrystallization of Ag at temperature above 373 K.11

The present study reports a new solution to use a multilayered Sn/Ag3Sn film on a Cu alloy base material, which can be produced at lower cost than conventional pure Ag coatings. The multilayered Sn/Ag3Sn films demonstrated a high reliability of stable electric contact resistance at different aging temperatures, good fretting performance, and excellent resistance to the growth of Sn whiskers, thus being thought as a promising coating material for various electrical connectors and terminals.12–15 This paper focuses on evaluation of the corrosion resistance, i.e., sulfidizing resistance and oxidation resistance of the multilayered Sn/Ag3Sn films, compared to a commercial Ag film with 2 µm thickness and a conventional refloved Sn film with 1 µm thickness. The surface states and microstructures of the multilayered Sn/Ag3Sn films before and after accelerated corrosion tests were investigated by various analysis methods and the mechanism of improved corrosion resistance was discussed.

Experimental

Specimens.—The multilayered Sn/Ag3Sn specimens were prepared by consecutive electrodeposition of Sn and Ag films on Cu alloys. Briefly, a Sn film with 1 µm thickness was first electrodeposited on Cu alloys using a sulfuric bath, which mainly contained 0.25 M SnSO4 and 1.0 M H2SO4, followed by a heat-treatment at around 593 K to get a refloved Sn film (denoted as Sn-RF later). Here, the Sn-RF film meant that the electrodeposited Sn films was heated at a temperature above the melting point of metallic Sn, 505 K, to achieve a bright Sn film with smooth surface, better soldering ability, and more importantly, to inhibit the growth of Sn whiskers. After the
reflowed treatment, silver electroplating was performed on the Sn-RF specimen to achieve Ag films with 30–80 nm thickness using a cyanide bath, which mainly contained 0.1 M AgCN and 1.0 M KCN, followed by an alloying treatment below 373 K, to achieve a Sn-Ag alloy film on the Sn-RF film. Moreover, a commercial Ag film with 2 μm thickness and the Sn-RF film without Ag electroplating were used in various corrosion tests as reference samples.

**Corrosion evaluation methods.**— The corrosion resistance against sulfidization of the coating materials mentioned above was evaluated by immersing the specimens in 0.2 or 2 mL/L (NH₄)₂S solution (Japan Industrial Standard JIS-H 8621) at 298 K for 30 min – 120 h. The high temperature oxidation resistance or high temperature reliability for automotive connectors was assessed by aging in air at 473 K up to 3000 h, according to the Class-V standard of The United States Council for Automotive Research (USCAR).

The electrical contact resistance of the specimens before and after corrosion tests was measured by an electric contact simulator (Yamazaki, CRS-113-AU), in a 4 terminal method vs. Au wire, using a sliding mode with a distance of 0.5 mm, at low load from 0 to 0.49 N. A ‘dimple on flat’ sample style was adopted for contact pairs, which is similar to many real connectors with ‘male’ and ‘female’ contacts. Here, a sliding mode instead of a static mode was chosen to simulate the real movements of automotive connectors or terminals due to the vibration during driving and idling. A lower load (or small clapping force) of 0.49 N/pin compared to normal load of 5 N/pin was selected for a critical assessment for promising applications as mini-terminals.

**Characterizations.**— The morphologies of the surface and the cross-sections of the multilayered Sn/Ag, Sn films and reference specimens before and after various corrosion tests were observed in a commercial Ag film that are 200 nm – 2 μm across (Fig. 1c, 1f). From the cross-sectional image (Fig. 1e), the Ag-Sn alloy layer was composed of nano-grains 50–100 nm across (Fig. 1b), which are much smaller than the Ag grains and a unique Cu-Sn intermetallic compound layer in form of Cu₆Sn₅. Sn-RF specimen constitutes a smooth Sn film with uneven thickness and Ag films on Cu alloys substrates before corrosion testing. The Sn-RF specimen constitutes a smooth Sn film with uneven thickness and a Cu-Sn intermetallic compound layer in form of Cu₆Sn₅. The Cu₆Sn₅ was formed on Cu substrates due to the reflow treatment at high temperature above the Sn melting point (Fig. 1a, 1d). The multilayered Sn/Ag₃Sn specimen consists of an Ag-Sn alloy layer with thickness of 50 nm, and a Sn layer and a Cu₆Sn₅ layer similar to the Sn-RF specimen. It should be noted that the multilayered Sn/Ag₃Sn film is different from conventional Sn-Ag alloy electroplating and commercial Sn-Ag hot-dip coatings, in which the Ag component (the former) or the Ag₃Sn particles (the latter) are distributed within 0.1 eV. Moreover, the Sn-RF alloy layer was composed of nano-grains 50–100 nm across (Fig. 1b), which are much smaller than the Ag grains observed in a commercial Ag film that are 200 nm – 2 μm across (Fig. 1c, 1f). From the cross-sectional image (Fig. 1e), the Ag-Sn alloy layer in nano-grains on the Sn film agglomerated into

**Results and Discussion**

**Microstructures of multilayered Sn/Ag₃Sn films on Cu alloys.**— Figure 1 exhibits the as-deposited multilayered Sn/Ag₃Sn, Sn-RF, and Ag films on Cu alloys substrates before corrosion testing. The Sn-RF specimen constitutes a smooth Sn film with uneven thickness and a unique Cu-Sn intermetallic compound layer in form of Cu₆Sn₅. The Cu₆Sn₅ was formed on Cu substrates due to the reflow treatment at high temperature above the Sn melting point (Fig. 1a, 1d). The multilayered Sn/Ag₃Sn specimen consists of an Ag-Sn alloy layer with thickness of 50 nm, and a Sn layer and a Cu₆Sn₅ layer similar to the Sn-RF specimen. It should be noted that the multilayered Sn/Ag₃Sn film is different from conventional Sn-Ag alloy electroplating and commercial Sn-Ag hot-dip coatings, in which the Ag component (the former) or the Ag₃Sn particles (the latter) are distributed within 0.1 eV. Moreover, the Sn-RF alloy layer was composed of nano-grains 50–100 nm across (Fig. 1b), which are much smaller than the Ag grains observed in a commercial Ag film that are 200 nm – 2 μm across (Fig. 1c, 1f). From the cross-sectional image (Fig. 1e), the Ag-Sn alloy layer in nano-grains on the Sn film agglomerated into

**Figure 1.** (a – c) Surface and (d – f) cross-sectional FE-SEM images of (a, d) reflowed Sn, (b, e) multilayered Sn/Ag₃Sn and (c, f) Ag films on Cu alloys.
Illustrates the influence of immersion time in a 0.2 mL/L (NH₄)₂Sₓ solution for 60 min. A small amount of sulfur was detected on the surface of the multilayered Sn/Ag₃Sn film (Fig. 4d). In contrast, a strong sulfur peak was detected on the pure Ag film (Fig. 4e). From the relative intensity and the corresponding sputtering time of sulfur profiles in regions shown in dashed line, it can be deduced that only a thin Ag₂S film formed on the top of the Ag₃Sn layer, but a thick Ag₂S film formed on the pure Ag film. This phenomenon can be explained by the chemical reactions between sulfur and silver in the (NH₄)₂Sₓ solution as discussed later. From the viewpoint of chemical kinetics, intermetallic compounds (i.e., Ag₃Sn) are generally more stable than pure metals (i.e., Ag). Therefore, the alloying treatment after Ag electroplating played an important role in enhancing the sulfidizing resistance of the multilayered Sn/Ag₃Sn film. For comparison, GDOES spectra for Sn-RF films before and after the sulfidizing test are also given in Fig. 4. A strong sulfur peak was detected for the specimens after 60-min immersion, which can be ascribed to the formation of the CuS from the element distribution (Fig. 4f). This indicated that, although a thin Sn oxide film existed on the surface of initial Sn-RF specimen, the sulfidizing corrosion progressed through the Sn top layer into the underlying Cu₆Sn₅ alloy layer (Fig. 4c).

In order to investigate the mechanism of sulfidizing resistance of the multilayered Sn/Ag₃Sn film, high-resolution XPS analysis was used to further determine the chemical states of the surface components for specimens before and after immersing in 0.2 mL/L (NH₄)₂Sₓ solution for 7 h and 95 h, as shown in Fig. 5. In good accordance with the GDOES analysis results, a strong S peak corresponding to Ag₂S was detected on the Ag film after immersion for 7 h, while a weak S peak with less than 1/5 intensity was measured on the multilayered Sn/Ag₃Sn film even after a prolonged immersion for 95 h. This confirms that the sulfidizing resistance of the multilayered Sn/Ag₃Sn film is apparently advantageous over the conventional Ag film. Moreover, it is noticeable that strong Sn and O peaks were present on both the initial multilayered Sn/Ag₃Sn specimen and the ones after sulfidizing tests. The binding energy values of the centers of Sn 3d₅/₂ peaks are 486.8, 487.1, and 487.3 eV for the specimens before immersion and after immersion for 7 and 95 h, respectively, which close to those of SnO₂ (E₀ = 486.0–486.8 eV) and SnO₂ (E₀ = 486.4–486.9 eV). This indicates that tin oxide films, probably in forms of SnO and/or SnO₂, existed on the surface of multilayered Sn/Ag₃Sn specimens irrespective of the sulfidizing test. The tin oxide films on multilayered Sn/Ag₃Sn specimens can be attributed to the oxidation of Ag₃Sn layer during the alloying treatment after Ag electroplating. It appears reasonable to hypothesize that it is the thin oxide films that protected the Ag₃Sn layer by isolating the Ag in Ag₃Sn layer from the corrosive S²⁻ ions in the test solution.

Moreover, with increasing immersion time from 7 to 95 h, the peak centers for Sn 3d₅/₂ shifted from 486.8 to 487.3 eV. This is owing an increase in the SnO₂ component of the tin oxide film, possibly through the following reactions:

\[ 2Ag₂Sn + 3S²⁻ + 5O₂ + 16H⁺ \rightarrow 3Ag₂S + 2SnO₂ + 8H₂O \]  \[ 2SnO + O₂ \rightarrow 2SnO₂ \]
Figure 4. GDOES spectra of (a, d) multilayered Sn/Ag₃Sn, (b, e) Ag, and (c, f) reflowed Sn films (a – c) before and (d – f) after immersing in a 2 mL/L (NH₄)₂Sₓ solution at 298 K for 1 h. The dashed lines indicate in (d – f) the thickness of the sulfides formed on surface of the specimens after the sulfidizing test.

The SnO₂ film, in turn, also protected the Ag₃Sn, thus hindered the sulfidizing reaction. In contrast, strong sulfur peaks were detected on the pure Ag film after being immersed for 7 h, indicating the formation of a large amount of Ag₂S simply by a chemical reaction between Ag and S²⁻ ions as below:

\[ 4\text{Ag} + 2\text{S}^{2-} + \text{O}_2 + 4\text{H}^+ \rightarrow 2\text{Ag}_2\text{S} + 2\text{H}_2\text{O} \]  

It should be noted here that a Sn oxide film also existed on the Sn-RF specimen due to the solidifying process of electrodeposited Sn, yet it did not provide enough protection from the corrosion of chemically active Sn and the underlying Cu₆Sn₅ in ammonia sulfide solution (Fig. 4f). Since it is difficult to differentiate SnO and SnO₂ by XPS analysis and peak fitting, cyclic voltammetry measurements were utilized to determine the chemical states of the tin oxide films on

Figure 5. High-resolution XPS spectra of (a) multilayered Sn/Ag₃Sn and (b) Ag films after immersing in a 0.2 mL/L (NH₄)₂Sₓ solution at 298 K for different times.
multilayered Sn/Ag$_3$Sn and Sn-RF specimens. Figure 6 illustrates the linear sweep voltammetric (LSV) curves for the as-plated Sn/Ag$_3$Sn and Sn-RF specimens. For comparison, LSV curves for specimens after aging at 433 K for 24 h were also given in Fig. 6 as a reference of stable SnO$_2$ films. It can be seen from Fig. 6a that the as-plated multilayered Sn/Ag$_3$Sn film presents one reduction peak at around −1.17 V (vs. Ag/AgCl), whereas the specimen after aging at 433 K gives a relative negative reduction peak at −1.40 V (vs. Ag/AgCl), which can be indexed to the reduction peaks for anhydrous SnO and SnO$_2$, respectively. This confirms that the tin oxide film on the as-plated Sn/Ag$_3$Sn film exists in form of anhydrous SnO, consistent with the XPS analysis (Fig. 5). In contrast, the as-plated Sn-RF film gives a main reduction peak at −1.02 V (vs. Ag/AgCl) and a weak peak at −1.35 V (vs. Ag/AgCl), which can be ascribed to hydrated Sn$_2$O$_3$(OH)$_2$ and SnO$_2$·$n$H$_2$O, respectively, according to Nakayama et al. Since tin hydroxides and hydrates are generally less stable than the corresponding oxides, it follows that the tin oxide films on Sn-RF specimens provided less protection in the sulfidizing tests than that on Sn/Ag$_3$Sn (Fig. 4). This proved that the chemical stability of intermetallic Ag$_3$Sn phase plays a critical role in the advantageous performance of corrosion resistance for the multilayered Sn/Ag$_3$Sn specimens over the Sn-RF and pure Ag films. In addition to the corrosion enhancement of Ag$_3$Sn alloy due to the inclusion of noble metal Ag component, the chemically stable anhydrous SnO film formed on the Ag$_3$Sn layer physically isolated the Ag from the corrosive circumstance. Therefore, the excellent sulfidizing resistance of the Sn/Ag$_3$Sn film can be mainly attributed to both the chemically stable Ag$_3$Sn alloy layer and the protective SnO film on it, which effectively hinders the chemical reaction between the Ag and the S and enhances the sulfidizing resistance of the Sn/Ag$_3$Sn film.

Figure 6. Linear sweep voltammetric curves of (a) multilayered Sn/Ag$_3$Sn and (b) Sn-RF films in a buffer solution of 0.5 M (NH$_4$)$_2$Cl and 0.5 M NH$_4$OH. Scan rate: 10 mV s$^{-1}$. Solid lines: as-plated specimens, dotted lines: after aging at 433 K for 24 h.

Oxidization resistance of multilayered Sn/Ag$_3$Sn films at high temperature. — Figure 7 illustrates the profiles of electric contact resistance versus applied load for the specimens before and after aging at 473 K (USCAR-Class V) for 500 and 2000 h, measured at 3–5 locations on the samples for reproducibility. The multilayered Sn/Ag$_3$Sn films showed excellent stable contact resistance at all load ranges even up to 2000 h, thus indicating the excellent high temperature reliability for automotive connectors. As for conventional Ag and Sn-RF films, vigorous oscillations in contact resistance at the lower load side occurred after aging for 500 h, implying that insulating oxide films formed in relatively short period at the high temperature.

Figure 7 summarizes the average values of contact resistance at load of 0.49 N for various specimens with the aging time at 473 K from multilayered Sn/Ag$_3$Sn and Sn-RF specimens.
Figure 8. Variation of electric contact resistance (load = 0.49 N) for multi-layered Sn/Ag$_3$Sn, Ag, and reflowed Sn films on Cu alloys before and after aging at 473 K for 120–3000 h.

Fig. 7. The initial contact resistance of the multilayered Sn/Ag$_3$Sn film was 1.36 mΩ, which was slightly higher than that of Sn-RF film in 0.95 mΩ and Ag film in 0.34 mΩ. This may be attributed to the existence of the insulating SnO film on hard Ag$_3$Sn alloy layer as described earlier in XPS analysis (Fig. 5) and LSV measurement (Fig. 6). It should be emphasized, however, that the multilayered Sn/Ag$_3$Sn films exhibited low and stable electrical contact resistances of around 1 mΩ even after aging for a prolonged period of 3000 h, equivalent to those of as-plated samples, which indicates an excellent electric conductive stability. In contrast, both the Sn-RF film and the conventional Ag film showed ever-increasing contact resistance with the progressing of aging. In particular, the contact resistance of the Ag film exceeded the measuring range of 20 mΩ after aging at 473 K for 2000 h, which indicates an insufficient stability at high temperature.

Figure 9 demonstrates the surface morphologies and the cross sections for Sn-RF, multilayered Sn/Ag$_3$Sn, and Ag films after aging at 473 K for 2000 h. The selected area EDX analysis results were also labeled in the Fig. 9. Please note that thick Cu oxide films formed on both Sn-RF and Ag films, whereas no apparent oxides were observed on the multilayered Sn/Ag$_3$Sn film, though the Ag$_3$Sn nano-grains agglomerated into micro-particles of 0.5–1 μm at prolonged high temperature. Through quantitative EDX analysis, the oxide films were determined to be CuO on the Sn-RF film and Cu$_2$O - CuO on the Ag film, respectively. It was found in a previous study that the crystalline structure of Ag$_3$Sn grains was unchanged even after aging at 473 K for 3000 h in air, indicating the excellent chemical stability under the high temperature. In addition, it was also confirmed that the underlying Cu-Sn alloy layers of Sn-RF and Sn/Ag$_3$Sn specimens had transformed completely from $\eta$-Cu$_6$Sn$_5$ to $\epsilon$-Cu$_3$Sn after aging at 473 K for 240 h because of the outward Cu diffusion from the base materials. This means that both Ag$_3$Sn and Cu$_3$Sn are stable crystalline phases at high temperature.

Moreover, it can be seen from the cross-sectional images that some conspicuous Kirkendall voids formed at the film/Cu substrate interfaces for both the Sn-RF and Ag films. This can be attributed to the reactive diffusion between Cu base materials and the Sn or Ag films at high temperature, of which the outward Cu diffusion occurred preferentially to the inward Sn or Ag diffusion, thus leading to the formation of thick Cu oxide films. In contrast, only small Kirkendall voids can be observed at the Cu$_3$Sn/Cu interface for the multilayered Sn/Ag$_3$Sn specimen, which may be ascribed to the volume reduction of phase transformation from $\eta$-Cu$_6$Sn$_5$ ($\rho = 8.31$ g cm$^{-3}$) to $\epsilon$-Cu$_3$Sn ($\rho = 11.3$ g cm$^{-3}$) during aging. Noticeably, the Ag$_3$Sn grains were retained on the top of the coating film, irrespectively of the disappearance of Sn layer and the progress of Sn-Cu alloying with the outward Cu diffusion at prolonged high temperature. More importantly, some tiny particles, containing Ag component from EDX analysis, were observed at the Cu$_3$Sn/Cu interface. This reveals that the Ag component also diffused inward across the Cu-Sn alloy layer and ultimately accumulated at the film/substrate interface with aging. The Ag component that accumulated at the interface could also hinder the outward Cu diffusion locally, thus decreasing the formation of Kirkendall voids at the Cu$_3$Sn/Cu interface and improving the adhesion between the film and the base materials and the stability of electric contact resistance as well.

Element diffusion behaviors in multilayered Sn/Ag$_3$Sn films at high temperature.— In order to confirm the diffusion phenomenon of Cu...
and Ag during aging at high temperature circumstance, various specimens after aging at 473 K for 120, 500, and 2000 h were investigated by GDOES analysis, as shown in Fig. 10. After aging for 120 h, a small peak of oxygen corresponding to Sn oxide film was detected for the Sn/Ag$_3$Sn specimen (Fig. 10a), whereas a broad oxygen peak corresponding to Sn and Cu oxides was measured on the surface of Sn-RF specimen (Fig. 10g). This indicates that the oxide film formed on the multilayered Sn/Ag$_3$Sn specimen is thinner than that on the Sn-RF specimen, or in other words, the former exhibited higher oxidization resistance than the latter. As for the conventional Ag film, Cu and O elements were detected within the Ag film region (Fig. 10d). This revealed that outward Cu diffusion from the base material and inward O diffusion occurred concurrently with aging at high temperature, thus leading to the intrinsic oxidation of Cu inside the Ag film. With the progress of aging from 500 h to 2000 h (Fig. 10b-10c), the oxide film on the surface of Sn/Ag$_3$Sn specimen became thicker, yet only Sn rather than Cu oxide formed even after aging for prolonged 2000 h, consistent to the FE-SEM observation as shown in Fig. 9. In contrast, both the conventional Ag and Sn-RF specimens exhibited apparent Cu diffusion toward the film surface with aging (Fig. 10e-10f and Fig. 10h-10i), and finally producing thick Cu oxide films on the surface. According to the sputtering times and the profiles of oxygen element, it is calculated that the oxide films on Ag and Sn-RF specimens after aging at 473 K for 2000 h are approximately 50 and 10 times thicker than that on Sn/Ag$_3$Sn one, respectively. This clearly elucidates the advantageous oxidation resistance of the Sn/Ag$_3$Sn film over the conventional Ag and Sn-RF films. Moreover, it should be noticed that a small Ag peak appeared at the Sn-Cu/Cu substrate interface and its intensity increased gradually with aging time (Fig. 10b-10c). This indicates that Ag diffusion inward occurred simultaneously with aging at high temperature, which agrees with the result of the FE-SEM observation (Fig. 9c). It is known that the specific resistivity of Cu oxides, $10^6$–$10^7$ $\Omega\cdot$m, is significantly higher than that of Sn oxides, $4 \times 10^{-4}$ $\Omega\cdot$m. Therefore, the excellent stability of electric resistance for the multilayered Sn/Ag$_3$Sn films can be predominantly attributed to the effective inhibition of the formation of insulating Cu oxides on the film surface, which in turn, can be ascribed to the inward Ag diffusion which countered the outward Cu diffusion from the Cu base materials.

Figure 11 shows a TEM image for the cross section of the Sn/Ag$_3$Sn film after aging at 473 K for 500 h. The Ag$_3$Sn grains that agglomerated during aging existed as single crystals from the selected area X-ray diffraction pattern. Noticeably, the Cu$_3$Sn grains in vicinity to the Ag$_3$Sn gains on the surface were much larger than those inside the film, and exhibited a different texture compared to the normal Cu$_3$Sn grains inside the film, inferring a different crystalline structure with different chemical components.

Table I lists the chemical compositions at different areas corresponding to the numbers in Fig. 11, which were measured by EDX analysis. A small amount of Ag was detected in the Cu$_3$Sn grain close to the Ag$_3$Sn grain (No.3). This reveals that Ag included in the Cu$_3$Sn

| Spot No. | Ag | Sn | Cu | O | Notes           |
|----------|----|----|----|----|-----------------|
| 1        | 58.2 | 18.9 | 2.4 | 10.5 | SnO$_2$ + Ag$_3$Sn (Cu) |
| 2        | 85.2 | 13.5 | 1.3 | -   | Ag$_3$Sn (Cu)    |
| 3        | 2.2  | 25.8 | 72.0 | -   | Cu$_3$Sn (Ag)    |
| 4        | -    | 11.3 | 11.6 | 53.6 | CuO + SnO$_2$    |
| 5        | -    | 27.1 | 72.9 | -   | Cu$_3$Sn        |

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Figure 11 shows a TEM image for the cross section of the Sn/Ag$_3$Sn film after aging at 473 K for 500 h. The Ag$_3$Sn grains that agglomerated during aging existed as single crystals from the selected area X-ray diffraction pattern. Noticeably, the Cu$_3$Sn grains in vicinity to the Ag$_3$Sn gains on the surface were much larger than those inside the film, and exhibited a different texture compared to the normal Cu$_3$Sn grains inside the film, inferring a different crystalline structure with different chemical components.

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Figure 11 shows a TEM image for the cross section of the Sn/Ag$_3$Sn film after aging at 473 K for 500 h. The Ag$_3$Sn grains that agglomerated during aging existed as single crystals from the selected area X-ray diffraction pattern. Noticeably, the Cu$_3$Sn grains in vicinity to the Ag$_3$Sn gains on the surface were much larger than those inside the film, and exhibited a different texture compared to the normal Cu$_3$Sn grains inside the film, inferring a different crystalline structure with different chemical components.

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![Figure 10. GDOES Spectra for (a-c) multilayered Sn/Ag$_3$Sn, (d-f) Ag, and (g-i) reflowed Sn films after aging at 473 K for 120, 500, and 2000 h, respectively.](image-url)
Figure 11. Cross-sectional TEM image and the corresponding diffraction pattern of multilayered Sn/Ag3Sn film after aging at 473 K for 500 h.

Figure 12. Schematic drawing of the element diffusion behaviors of (a) multi-layered Sn/Ag3Sn, (b) Ag, and (c) reflowed Sn films on Cu alloys under high temperature circumstance.

Mechanism of oxidation resistance of multilayered Sn/Ag3Sn films under high temperature.—Figure 12 illustrates the scheme of the element diffusion models of multilayered Sn/Ag3Sn film during aging at high temperature, compared to the conventional Ag and the Sn-RF on Cu alloys. It is known that Cu from the substrate materials diffuses easily via electroplating films toward the film surface due to the highly diffusive nature at high temperature. In case of multilayered Sn/Ag3Sn film, elemental Ag diffuses simultaneously inward toward the film/substrate interface because of its strong migration nature with aging time. The inward Ag diffusion may be predominant to the outward Cu diffusion, thus leading to the accumulation of Ag nanoparticles at the film/substrate interface (Fig. 9e and Fig. 10b-10c). This, in turn, constituted a discontinuous barrier layer and hindered the outward Cu diffusion at prolonged aging time to some extent (Fig. 10). More importantly, Ag component also included in the intermetallic Cu3Sn phase in form of solid solution with aging (Fig. 11 and Table I), thus enhanced the chemical stability or oxidation resistance of the Cu3Sn phase at high temperature. Generally, it is known that, for Sn-based coatings on Cu substrates, the Cu component that diffused from the substrates during aging was trapped by Sn to form Cu-Sn alloys in forms of intermetallic Cu6Sn5 and Cu3Sn phases, thus retarding the formation of Cu oxides on the film surface compared to the Ag films on Cu materials (Fig. 10). However, as the Sn layer disappeared and totally transformed into the Cu3Sn phase with aging at high temperature, insulating Cu oxide films then formed rapidly on the Cu3Sn layer, assisted by the continuous supply of Cu that diffused from the base materials. Therefore, the stable electric conductivity of multilayered Sn/Ag film at high temperature can be mainly attributed to the chemically stable Ag3Sn particles and the Ag-included Cu6Sn5/Cu3Sn phase on the film surface (Fig. 12a). The Ag3Sn particles provided electric conductive sites irrespective of the oxidation of the surrounding Cu-Sn alloy regions (Fig. 11), and the inclusion of Ag component in Cu6Sn5/Cu3Sn phases enhanced the oxidizing resistance of the Cu-Sn alloy matrix, thus effectively inhibiting the formation of insulating Cu oxides on the surface and leading to the excellent stability of contact resistance at prolonged high temperature (Fig. 8).
with highly intrinsic diffusion coefficient via the Ag and Cu-Sn alloy layers (see Fig. 9, 10, and 12b-12c), thus leading to the ever-increasing electric contact resistances at high temperature (see Fig. 8).

Conclusions

The corrosion resistance of multilayered Sn/Ag3Sn films with 50 nm Ag thickness on Cu alloy materials was investigated through an accelerated sulfidizing test in a (NH4)2Sx solution according to a JIS standard and an accelerated aging test at 473 K up to 3000 h referring to a USCARD standard, compared to a commercial pure Ag film and a conventional Sn-RF film on Cu alloy materials.

The multilayered Sn/Ag3Sn films went through the accelerated sulfidizing test successfully, with unchanged appearance and stable electrical contact resistance, even after being immersed in a 0.2 mL/L (NH4)2Sx solution for 120 h. In contrast, the conventional Ag film failed the sulfidizing test, losing its metallic gloss turning a dark blue and delivering an ever-increasing contact resistance with prolonged immersing period. The excellent sulfidizing resistance and durability of the multilayered Sn/Ag3Sn film can be mainly attributed to the chemically stable AgSn alloy and the overlying anhydrous SnO film. The Ag3Sn alloy provides better corrosion resistance against S2− ions than pure Ag, and the chemically stable anhydrous SnO film protects the underlying Ag3Sn layer by isolating the Ag from the corrosive S2− ions. This hindered the chemical reaction between the Ag and the S and eventually improved the sulfidizing resistance of multilayered Sn/Ag3Sn film.

Moreover, the multilayered Sn/Ag3Sn films exhibited low and stable electrical contact resistances of around 1 mΩ even after aging at 473 K for 3000 h, equivalent to those of as-plated samples, indicating excellent oxidation resistance and reliably conductive stability at high temperature. In contrast, both the conventional Ag and Sn-RF films showed ever-increasing electrical contact resistance at 500 h, which can be ascribed to the formation of highly insulating Cu oxide films on the surface and of the generation of conspicuous Kirkendall voids at the film/Cu substrate interfaces due to the intrinsic outward Cu diffusion at high temperature. The excellent oxidizing resistance of the multilayered Sn/Ag3Sn film at high temperature can be mainly attributed the chemically stable AgSn grains and the Ag-included Cu3Sn phase on the film surface. The Ag3Sn grains provided conductive electrically paths irrespective of the oxidation of the surrounding Cu-Sn alloy regions, and Ag inclusion in Cu-Sn alloy enhanced the oxidation resistance of the Cu-Sn alloy matrix. Consequently, this effectively inhibited the formation of highly insulating Cu oxides on the surface at high temperature, thus leading to the excellent stability of contact resistance for highly reliable electric connectors at various harsh environments.

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