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Effect of temperature on the fretting corrosion of tin plated copper alloy contacts

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Abstract

The effect of temperature on the fretting corrosion behaviour of tin plated copper alloy contacts in the temperature range of 25–185 °C, is addressed in this paper. The change in contact resistance with fretting cycles at various temperatures was determined. The contact zone after fretting corrosion test was analyzed using laser scanning microscope, X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray spectrometry (EDX), to assess the surface profile, phase content, morphology and compositional changes across the interface. The study reveals that temperature has a greater influence on the extent of fretting corrosion of tin plated copper alloy contacts. The softening of tin is responsible for the extended region of low contact resistance observed at 85 °C. The increase in thickness and the resistance of Cu–Sn intermetallic compounds (IMCs) is responsible for the decrease in surface roughness and the drastic increase in the contact resistance at higher temperatures. The study suggests that the tin plated copper alloy contact system should be considered as copper alloy/IMC/Sn/SnO_2 instead tin plated copper alloy. During fretting corrosion test at elevated temperatures, once the top surface layers are worn out, the contact interface is transformed from tin versus tin-to-tin-intermetallic versus tin-intermetallic. The study concludes that tin plated copper alloy contacts are not suitable for high temperature applications.

Keywords: Fretting corrosion; Tin plating; Electrical connector; Contact resistance; Intermetallic compound; XRD; SEM; EDX; Surface roughness

1. Introduction

Fretting, defined as the accelerated surface damage occurring at the interface of contacting materials subjected to small oscillatory movement, is a common problem encountered in many engineering application. The deleterious effect of fretting in electrical connections is considered to be of significant practical importance as it influences the reliability and system performance. A comprehensive review of fretting in electrical connections has been given by Antler [1]. Tin plated contacts have gained acceptance in many consumer applications as a low-cost alternative to gold. However, the susceptibility of tin plated contacts for fretting corrosion is considered to be a major limitation for its use in connectors. Fretting corrosion of tin plated connectors has been the subject of many papers [2–6]. The effect of contact force, wipe distance and fret amplitude has been considered as important variables. The extent of change in contact resistance as a function of process variables is determined and the increase in contact resistance has been attributed to oxide formation and accumulation of wear debris at the contact zone [2–6].

The requirements of connectors vary depending on the end use, whether they are put in to use in office equipment or in automobile car. In contrast to the connectors used in office equipment, the connectors used in automobiles encounter severe environmental conditions. The connectors used in automobiles have to protect against wear, changing temperature, road grit and vibrations as such conditions increase the rate of oxidation and fretting corrosion. Sealed connectors are used to prevent humidity and atmospheric corrosion of the connector contact interface. However, the ability of the connectors to withstand high temperatures becomes critical since the engine compartment that experienced ambient temperatures have slowly increased because of the more compact and low hood line design. Engine compartment electrical connectors designed to perform continuously at 125 °C are now required to perform at 150 °C. Electrical contact reliability at this higher temperature has to be investigated

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because many contact degradation modes such as fretting, oxidation, gas corrosion and alloy diffusion can become more severe and shorten the life of the contact. Though it is very difficult to simulate the exact conditions the automobile connectors encounter in real life, it is possible to study the effect of certain conditions and to correlate its influence on extent of fretting corrosion and in turn to predict the reliability of connectors.

The effect of temperature on fretting corrosion of tin plated copper alloy connectors has not been studied in detail. Lee et al. [3] have studied the fretting corrosion of tin plated contacts at elevated temperatures up to 110 °C. The results of their study convincingly prove that, at elevated temperatures, fretting corrosion of tin-plated contact materials was different from that at room temperature. Since tin plated contacts are continued to be used in engine compartments and sometimes they are closer to the engine, such as sensor connectors or environments where there is reduced air flow, the tin plated connectors are required to withstand a temperature of 150 °C [7]. Swingler et al. [8] have also reported that automobile connectors have to encounter several high temperature regimes namely, 85, 105, 125 and 155 °C. At higher temperatures, all contact degradation mechanisms may become more severe. This included higher wear because of metal softening with higher temperature, faster oxide formation, more intermetallic diffusion and other chemical reactions. Increased ambient temperature could cause significant thermal expansion and influence the contact interface movements. Variation in temperature could also influence the contact resistance of tin plated copper contacts since the rate of oxidation varies with temperature. Lee et al. [3] have reported that at elevated temperature, the rate of oxidation of tin will be increased and the hardness of tin gets decreased, both of which could influence the fretting corrosion of electrical contacts.

Intermetallic diffusion leading to the formation of intermetallic compound (IMC) is another important parameter of tin plated copper alloy connectors in determining their reliability. Though it is presumed that electro deposited tin plated copper alloy contacts are relatively free of IMC when plated, the formation of a very thin layer (25 micro inch) of Cu–Sn based IMC is possible after prolonged exposure. It has been reported that Cu/Sn thin film couple reacts and forms Cu_6Sn_5 IMC even at room temperature due to the high diffusivity of copper atoms into the tin lattice [9]. At elevated temperatures, diffusion of copper will be higher and enables the formation of Cu–Sn based IMC at a much higher rate. The formation of IMC will also increase the contact resistance. Elevated temperature also promotes the oxidation of tin plated copper alloy contacts and affects the contact resistance. Though both oxidation and formation of IMC could affect the contact resistance, the latter could cause a rapid increase in the contact resistance. It has been reported that the growth of Cu/Al IMC at the copper wire and aluminum interface can induce a mechanical failure and increase a potential contact resistance [10]. As IMC formation could drastically influence the contact resistance, a systematic study of the effect of temperature, covering a wide range of temperatures, on the fretting corrosion of tin plated contacts is highly warranted and hence forms the basis of this paper.

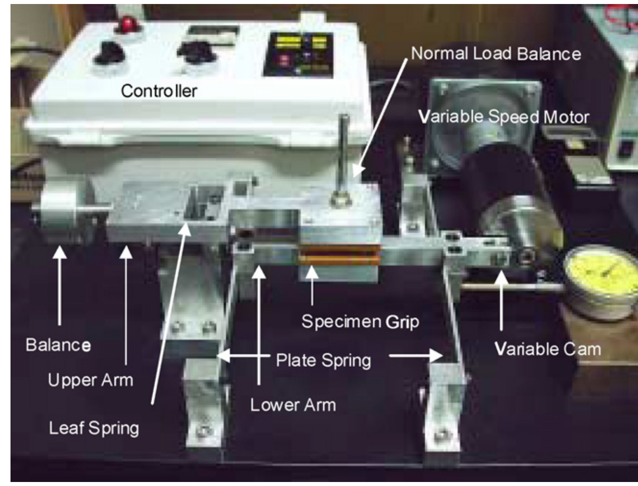

Fig. 1. The fretting apparatus used in the present study.

2. Experimental details

The fretting corrosion studies of tin plated copper alloy were conducted using the fretting apparatus shown in Fig. 1. The relative motion between the contacts was provided by a variable speed motor/precision stage assembly. The normal contact force was supplied by the weights placed on the balance arm. The contacts were flat verses 1.5 mm radius hemispherical rider (Fig. 2), both of them were made of copper alloy (Ni: 1.82%, Si: 0.75%; Zn: 0.01%; Sn: 0.37% and Cu: balance) and tin plated to a thickness of 3 μm, supplied by Korea Electric Terminal Company Ltd., Korea. The tin plated copper alloy rider and flat specimens were degreased using acetone in an ultrasonic cleaner, dried and carefully mounted in the fretting test assembly. The temperature of the rider and flat samples were kept constant using an electrically heated copper block, which is placed over the flat sample and controlled by a constant temperature device. The temperature of the tin plated copper alloy flat and rider was varied from 25 to 185 °C. Though tin plated connectors are expected to encounter a temperature in the range of 155 °C, a few experiments were also conducted at 185 °C, since for electrodeposited tin coatings 155 °C is reported to be the transition temperature at which the mechanism of diffusion changes from grain boundary diffusion to lattice diffusion [11].

Fig. 2. The rider and flat samples used in the present study.

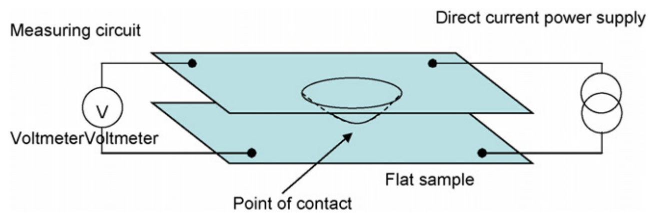

Fig. 3. The geometry of the rider and flat samples and the circuit used to measure the contact resistance.

Fretting motion was started after the system had reached thermal equilibrium at the desired temperature. Since the geometry of the flat and rider specimens are relatively small, they will be in thermal equilibrium within a few minutes after reaching the desired temperatures. A periodic relative displacement with amplitude of ±90 μm and a frequency of 10 Hz were applied between the rider and flat contacts loaded by a constant normal force of 0.5 N. The contact area is defined to be a point contact by "sphere plane" geometry. An electric current of 100 mA was applied by an electrical circuit. All the tests were performed in unlubricated conditions at 45 ± 1% RH. The contact resistance was continuously measured under dry circuit conditions as a function of fretting cycles for predetermined number of cycles (Fig. 3).

The change in contact resistance as a function of fretting cycle was recorded at all temperatures studied. The surface profile across the fretted zone was assessed using a Carl Zeiss laser scanning microscope (Model, LSM 5 PASCAL). After subjected to fretting corrosion testing, the samples were stored in air tight containers to prevent them from further oxidation and analyzed within 24 h. In order to correlate the extent of change in contact resistance and the surface roughness as a function of temperature, separate tin plated copper alloy contacts were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) to identify the phases present, the morphology and compositional changes across the interface.

3. Results and discussion

3.1. Change in contact resistance with fretting cycles as a junction of temperature

The change in contact resistance of tin plated copper alloy contact across the contact zone as a function of fretting cycles at 25 °C is shown in Fig. 4(a). There observed to be a hump in the initial stages followed by a low contact resistance region up to a few thousand cycles. Beyond that region there observed to be a rapid increase in contact resistance. The observed results correlate well with those of other researchers [2–6]. The initial hump is due to the presence of a thin film of tin oxide on the surface of the tin plated contact, which is removed in a very short span of time. The low contact resistance region observed up to a few thousand fretting cycles is due to the conducting nature of the soft tin plating. The subsequent region of gradual increase in contact resistance could be attributed to the formation of oxide film as well as accumulation of debris and corrosion products, further reducing the electrically conducting area. The rapid increase in contact resistance suggests that with increase in the number of fretting cycles, the current is conducted through an increasingly smaller area of contact.

The change in contact resistance of tin plated copper alloy contact across the contact zone as a function of fretting cycles at 85, 105, 125, 155 and 185 °C are shown in Fig. 4(b)–(f), respectively. A comparison of the change in contact resistance obtained at ambient (Fig. 4(a)) as well as elevated temperatures (Fig. 4(b)–(f)) make evident of the fact that irrespective of the temperature, the basic characteristics remains the same; an initial hump followed by a low contact resistance region and increase in contact resistance beyond certain fretting cycles. However, certain distinct and interesting features could also be observed. The extended region of low contact resistance observed at 85 and 105 °C and, the decrease in the number of fretting cycle where the contact resistance starts to increase at higher temperatures of the order of 125–185 °C assumes significance.

The effect of fretting corrosion behaviour of tin plated connectors at a temperature range of 25–110 °C was studied earlier by Lee et al. [3]. The extent of fretting corrosion of tin plated contacts increases with increase in temperature up to 80 °C due to the higher rate of oxidation of tin plating with increase in temperature. However, they have observed a reversal in fretting corrosion behaviour at 85 °C and attributed the behaviour due to the low softening temperature of tin and increase in contact force. Improvement in fretting performance due to softening of gold at higher temperatures of the order of 200 °C is reported by Aukland et al. [12]. Williamson [13] suggests that softening of a homogeneous contact interface, e.g., Cu–Cu or Ag–Ag, usually results in self-healing of the contact due to growth of the contact area. Hence the extended region of low contact resistance observed at 85 and 105 °C (Fig. 4(b) and (c)) could be ascribed to the softening of tin that enables better electrical contact. Under such conditions relatively less fresh metal is exposed for oxidation with each fretting cycle and hence the contact resistance remains low for extended number of fretting cycles. The increase in contact resistance observed at higher temperatures of the order of 125–185 °C could be due to several factors. The rate of oxidation will increase with increase in temperature. Enhanced wear due to cold welding and delamination of the tin plating at elevated temperatures could also considerably influence the contact resistance [3]. In order to get a better insight about the parameters influencing the contact resistance at various temperatures, the surface profile of the fretted zone was analyzed using laser scanning microscope.

3.2. Surface profile of the fretted zone at different temperatures

Fig. 5(a)–(f) shows the 3D view of the fretted zone of the tin plated copper alloy flat specimens subjected to fretting corrosion at 25, 85, 105, 125, 155 and 185 °C, respectively. The corresponding surface profile of the fretted zone is depicted in Fig. 6(a)–(f) and the roughness parameters calculated based on the surface profile is complied in Table 1. It is evident from Figs. 5 and 6 and Table 1 that the surface roughness is increased

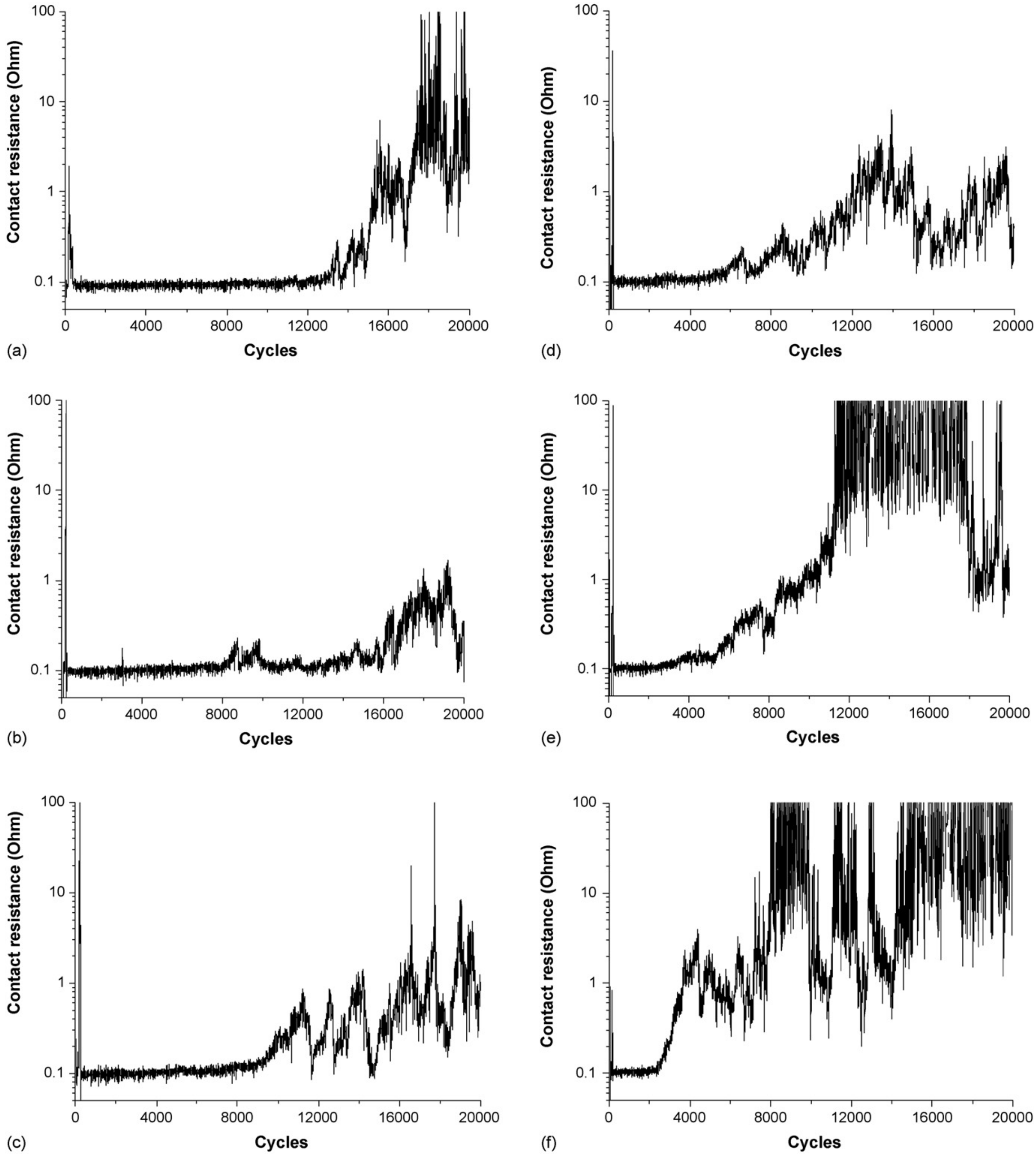

Fig. 4. Change in contact resistance of the tin plated copper alloy contact measured across the contact zone as a function of fretting cycles (a) 25 °C; (b) 85 °C; (c) 125 °C (d) 155 °C; and (e) 185 °C.

when the temperature is increased from 25 to 85 °C and started to decrease with further increase in temperature. The increase in roughness with the increase in temperature from 25 to 85 °C could be due to increased rate of oxidation. The decrease in roughness observed at 85 and 105 °C is due to the softening of tin at these temperatures. The extended region of low contact resistance (Fig. 4(b) and (c)) also supports this view. The increase in rate of oxidation when the temperature is increased from 25 to 80 °C and softening of tin in the temperature range of 85–100 °C has also been observed earlier by Lee et al. [3]. It is interesting to note the continuous decrease in roughness when the temperature is increased from 125 °C to 155 and

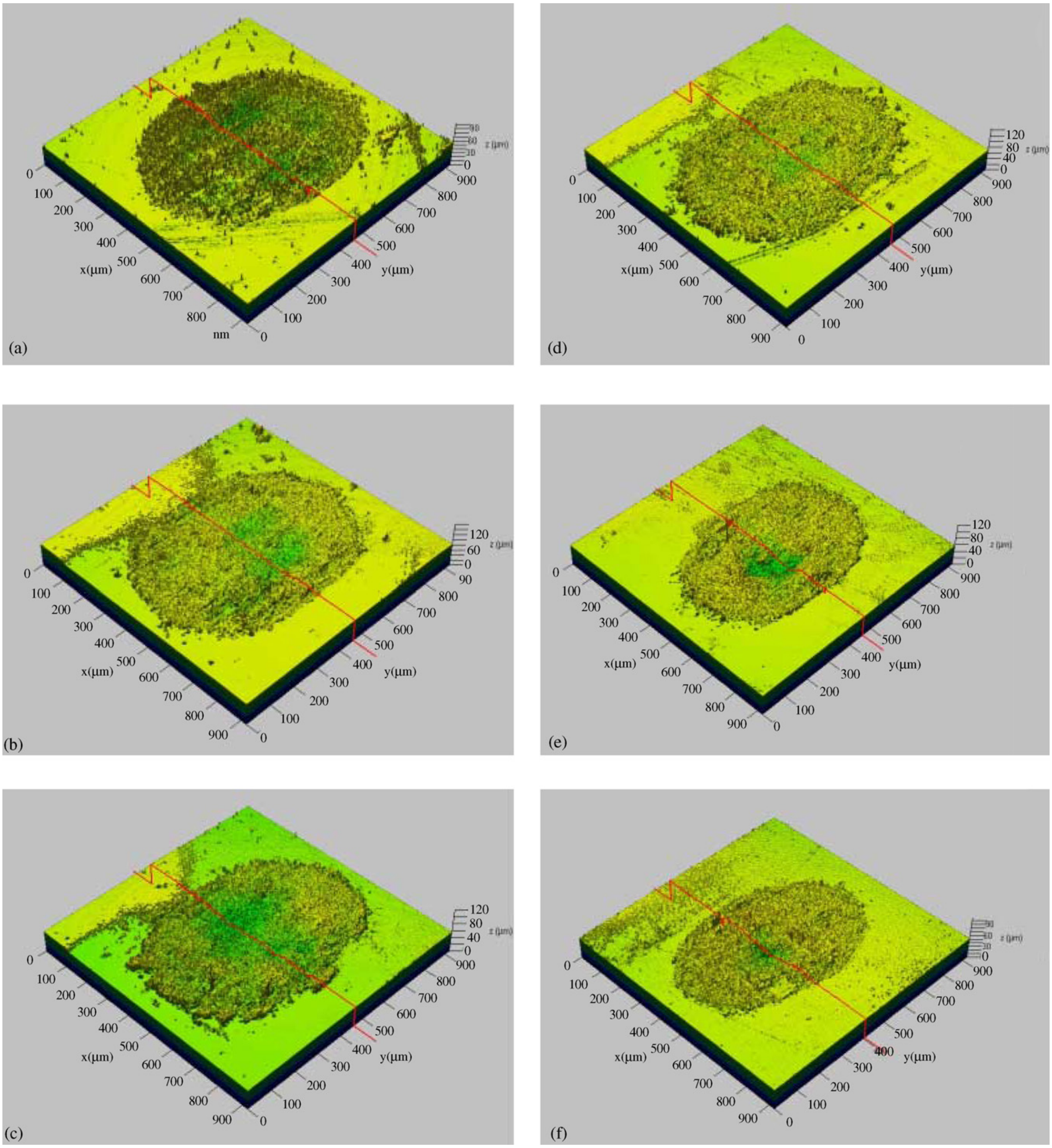

Fig. 5. 3D view of fretted zone after the tin plated copper alloy sample was run for 20,000 fretting cycles at various temperatures (a) 25 °C; (b) 85 °C; (c) 105 °C (d) 125 °C (e) 155 °C; and (f) 185 °C.

185 °C. As already mentioned, at higher temperatures, it is expected that the rate of oxidation will increase, the coated surface would experience enhanced wear due to cold welding and the tin coating might delaminate. All these factors could cause an increase in surface roughness. The decrease in surface roughness and the rapid rise in contact resistance observed at 155 and 185 °C indicate that some other factor is also responsible for this behaviour.

An important feature in tin plated copper alloys is the formation of Cu–Sn based IMCs at the interface. The Cu–Sn based IMCs are much harder than the soft tin matrix and the resistance of IMCs is very high. It has reported that the bulk Knoop hardness of pure tin and the Cu–Sn IMC are 8 and 350 kg/mm^2, respectively [14]. Shao and Zhang [15] have studied the electrical contact behaviour of Cu–Sn IMC formed on tin plated phosphor bronze substrates and suggested the use of lubricant

Table 1
Roughness parameters calculated based on the surface profiles of the fretted zone of tin plated copper alloy contacts subjected to fretting for 20,000 cycles at various temperatures

Roughness parameter	25 °C	85 °C	105 °C	125 °C	155 °C	185 °C
Arithmetic mean deviation, R_a (μm)	1.71	2.77	2.46	2.16	1.96	1.81
Highest peak, R_p (μm)	28.69	48.91	64.50	31.87	31.34	33.64
Lowest valley, R_v (μm)	23.68	40.00	37.00	38.45	35.93	29.74
Absolute peak to valley, R_t (μm)	52.37	88.90	101.50	70.32	67.27	63.38
Average peak to valley, R_z (μm)	24.56	31.98	22.61	27.47	21.96	19.22
Maximum peak to valley, R_{max} (μm)	52.37	88.90	90.54	57.70	59.73	63.32

to prevent the rapid increase in contact resistance. Liao and Wei [9] have observed a non-linear increase in the resistivity of Cu–Sn bimetallic thin film upon annealing due to the formation of highly resistive Cu–Sn based IMCs. Braunvoic [16] showed that the very hard Al–Cu IMC easily broke under pressure and caused severe contact problems. Hence it could be presumed that the formation of Cu–Sn based IMCs at elevated temperatures at the copper alloy-tin coating interface will have a drastic influence on the contact resistance. Moreover, the hardness of the IMC could be responsible for the observed decrease in roughness at 155 and 185 °C. In order to ascertain the formation of IMCs at the interface and to correlate the change in contact resistance and the surface roughness as a function of fretting cycles at different temperatures, separate tin plated copper alloy samples were characterized using XRD, SEM and EDX measurement, both in as-received condition as well as after annealing at different temperatures.

3.3. Characterization of tin plated copper alloy contacts using XRD, SEM and EDX

The XRD pattern of tin plated copper alloy contact in as-received condition is shown in Fig. 7(a). The XRD pattern exhibits the presence of characteristic peaks of the electrodeposited tin coating, which has a tetragonal structure ((β-Sn) (lattice parameter: $a = 5.831$ Å and $c = 3.182$ Å) and the peaks pertaining to the base metal. The peak for (101) plane is the most intense one, followed by the peaks for (200) and (211) planes, in accordance with the JCPDS standard 4–0673 [17], suggesting that the (β-Sn in the coating is in the preferred orientation of (101) plane. Fig. 7(a) also exhibits the presence of five distinct peaks at 30, 43.2, 60, 62.7 and 79.1° 2θ, which could not be accounted for either the tin coating or the base metal. These peaks indeed are pertaining to the Cu_6Sn_5 IMC according to JCPDS standard 2-0713 [18]. It is surprising to observe the formation of IMC on tin plated copper alloy contact in as-received condition. However, it has been reported that the Cu/Sn thin film couple reacts and forms Cu_6Sn_5 IMC at room temperature due to the high diffusivity of copper atoms into tin lattice [19]. In his review on Cu/Sn interfacial reactions in thin film and bulk, Tu [20] confirmed that copper reacts with tin at room temperature to form the Cu_6Sn_5 IMC. The formation of Cu_6Sn_5 IMC in as-deposited Cu–Sn films is also confirmed by Bandyopadhyay and Sen [21]. Braunovic [22] suggested the formation of Cu_6Sn_5 IMC in tin plated copper laminate owing to the high diffusivity of copper in tin. Beattie and Dahn [23,24] have suggested that deposition of binary Cu–Sn alloys from a single bath by pulsed electrodeposition does not result in compositionally modulated superlattice structure due to the interdiffusion of copper-rich and tin-rich layers. According to them though copper and tin layers of different composition were deposited, complete interdifusion of the tin and copper occurs within the film [23,24]. The results of these studies [19–24] advocate that interdiffusion of copper and tin is possible even in room temperature and the solid-state reaction between copper and tin might lead to the formation of IMC at the interface. There are a number of binary intermetallic Cu–Sn phases [25]. However, the tin plated copper alloy contact in as-received condition exhibits peaks pertaining to Cu_6Sn_5 IMC phase only. Cu_6Sn_5 has a hexagonal structure (NiAs-type structure; lattice parameter: $a = 4.20$ Å and $c = 5.09$ Å; space group P6$_3$/*mmc*) and it can be formed without too much change in the structure of tin and it also follows the empirical rule that the phase which is nearest to the lowest-temperature eutectic will form fist [26]. Hence it is understandable that the formation of Cu_6Sn_5 IMC phase is preferred than other Cu–Sn based IMC.

The XRD patterns of tin plated copper alloy contacts annealed at 85, 155 and 185 °C for 30 min are shown in Fig. 7(b)–(d), respectively. The annealing time is restricted to 30 min, since the fretting corrosion test was conducted only for 18,000 cycles (at 600 rpm). Compared to the XRD pattern of tin plated copper alloy in as-received condition (Fig. 7(a)), there is not much change in the XRD pattern for samples annealed at 85 and 155 °C for 30 min, except a slight increase in the intensity of the peaks following annealing (Fig. 7(b) and (c)). There observed to be a slight increase in the intensity of the peaks pertaining to Cu_6Sn_5 IMC phase (30 and 43.2° 2θ) and a slight decrease in the intensity of the peaks pertaining to tin coating (30.5, 31.88 and 44.80° 2θ) when the annealing temperature is increased from 85 to 155 °C. However, the sample annealed at 185 °C for 30 min clearly reveals that the peaks pertaining to Cu_6Sn_5 IMC phase (30 and 43.2° 2θ) grows at the expense of peaks pertaining to the tin coating (31.88 and 44.80° 2θ) (Fig. 7(d)), suggesting an increase in the thickness of Cu_6Sn_5 IMC phase at the interface with increase in annealing temperature.

Literature reports on the Cu–Sn based IMC suggest the formation of at least two different types of IMC, namely, Cu_6Sn_5 and Cu_3Sn [9,11,14,20,21]. Unlike Cu_6Sn_5, the formation of Cu_3Sn IMC phase occurs only at higher temperatures. Bandyopadhyay and Sen [21] have observed that annealing of Cu–Sn bimetallic couple at 80 °C even for several hours shows only the

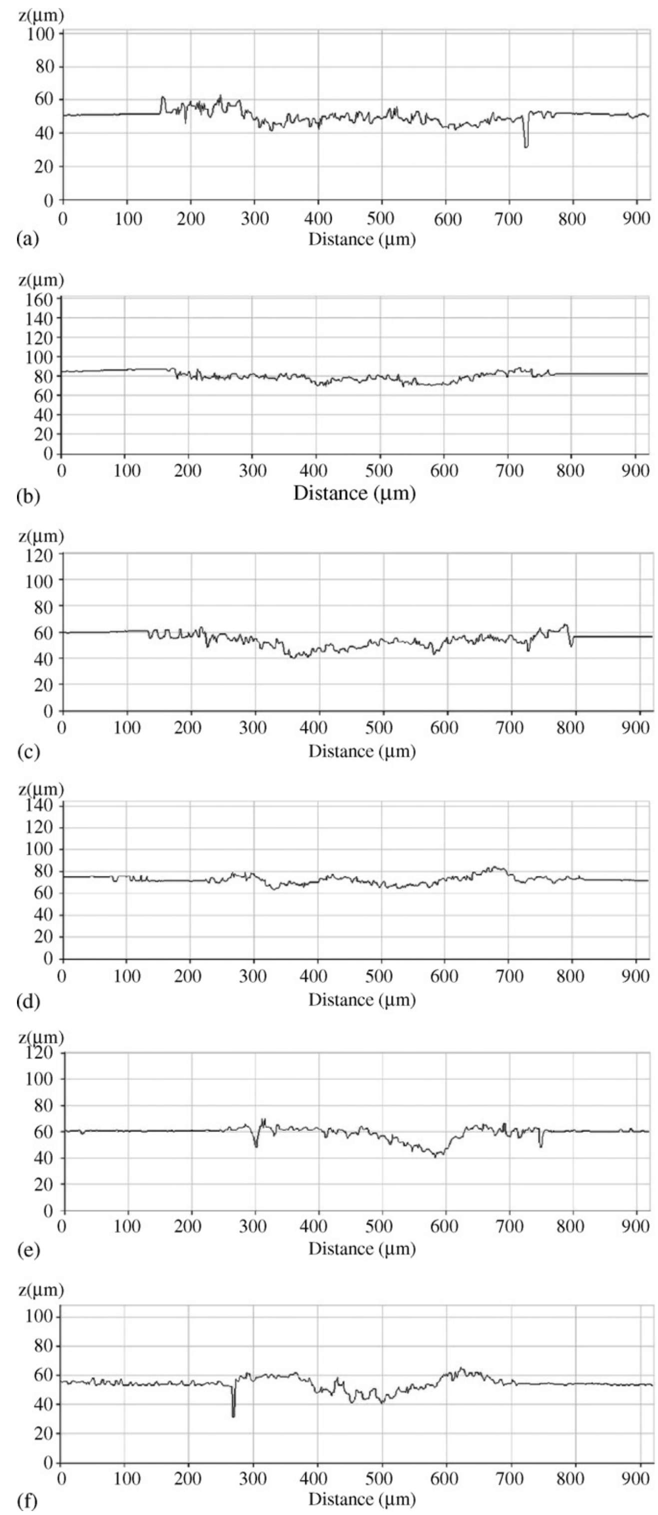

Fig. 6. Surface profile measured across the fretted zone of the tin plated copper alloy sample subjected to fretting for 20,000 cycles at various temperatures (a) 25 °C; (b) 85 °C; (c) 105 °C (d) 125 °C (e) 155 °C; and (f) 185 °C.

presence of Cu_6Sn_5 phase whereas an increase in the annealing temperature from 80 to 150 °C results in the formation of Cu_3Sn IMC phase. According to Tu [20] annealing of Cu–Sn bimetallic thin film above 100 °C results in the formation of Cu_3Sn IMC phase. Based on the findings of these studies and other literature reports on Cu–Sn based IMCs [9,11,14,20,21], it is logical to expect the presence of only the Cu_6Sn_5 IMC phase for tin plated copper alloy contacts annealed at 85 °C for 30 min and the formation of Cu_3Sn IMC phase for samples annealed at 155 and 185 °C for 30 min. However, the peaks pertaining to Cu_3Sn IMC phase is absent in the XRD patterns of tin plated copper alloy samples annealed at 155 and 185 °C for 30 min (Fig. 7(b) and (c)). Liao and Wei [9] have observed that in the Sn (0.19 μm)/Cu (0.2 μm) thin film couple, upon annealing, the intensity of peaks pertaining to Cu_6Sn_5 phase increased and reached a maximum at 128 °C, declined at 184 °C and disappeared at 206 °C whereas the peaks representing Cu_3Sn phase did not show until 184 °C and grew larger at 206 °C. Fig. 7(b)–(d) reveals that there is no reduction in the intensity of the peaks representing Cu_6Sn_5 peaks up to 185 °C. Liao and Wei [9] have suggested that though the nucleation of Cu_3Sn phase occurs at higher temperature, the growth of this phase will be limited due to the competing reaction of Cu_3Sn with Sn forming Cu_6Sn_5 phase. Only in the absence of sufficient supply of tin, the Cu_3Sn phase will grow at the expense of Cu_6Sn_5 phase reacting with the remaining copper. Since the thickness of the tin coating on the copper alloy contacts used in the present study is about 3 μm, it is presumed that the sufficient supply of tin limits the growth of the Cu_3Sn phase and it is not observed in Fig. 7(b)–(d). Similarly, in standard soldering operations, where the amount of tin supply is almost unlimited for the Cu–Sn interfacial reactions, the major IMC being Cu_6Sn_5 phase [9]. Hence it is evident that in tin plated copper alloy contacts, Cu_6Sn_5 IMC phase is formed even at room temperature, the thickness of this IMC phase increases with increase in annealing temperature and the Cu_3Sn IMC phase is absent even for samples annealed at 185 °C for 30 min.

Since the growth of Cu–Sn based IMC is a function of temperature and time, it is necessary to confirm the growth of Cu_6Sn_5 IMC at 155 °C to meet the requirement of the connectors used in engine compartment. Hence the annealing time was increased from 30 min to 4 h. The XRD pattern of tin plated copper alloy sample annealed at 155 °C for 4 h is shown in Fig. 7(e). A comparison of Fig. 7(c) and (e) clearly indicates that the intensities the peaks pertaining to Cu_6Sn_5 IMC phase (30 and 43.2° 2θ) grows at the expense of tin peaks (30.5, 31.88 and 44.80° 2θ), suggesting an increase in the thickness of Cu_6Sn_5 IMC phase at the interface with increase in annealing time. Increase in the thickness of the IMC film with increase in annealing time has also been reported by Kim et al. [27]. Hence it is evident that annealing promotes diffusion of copper and tin and enhances the growth of the Cu_6Sn_5 IMC in tin plated copper alloy contacts and this effect is well pronounced at high temperatures of the order of 150 °C or more; the extent of IMC formation is also a function of annealing time.

The cross sections taken with the SEM of the tin plated copper alloy samples annealed at 155 and 185 °C for 30 min and at 155 °C for 4 h is shown in Fig. 8(a)–(c), respectively. It is evident from Fig. 8(a)–(c) that upon annealing at 155 and 185 °C the morphology of the tin plated layer becomes irregular. It is difficult to distinctly identify the Cu_6Sn_5 layer at the copper alloy-tin coating interface in all the cases. This could probably be due to the very low thickness of the IMC layer formed at 155

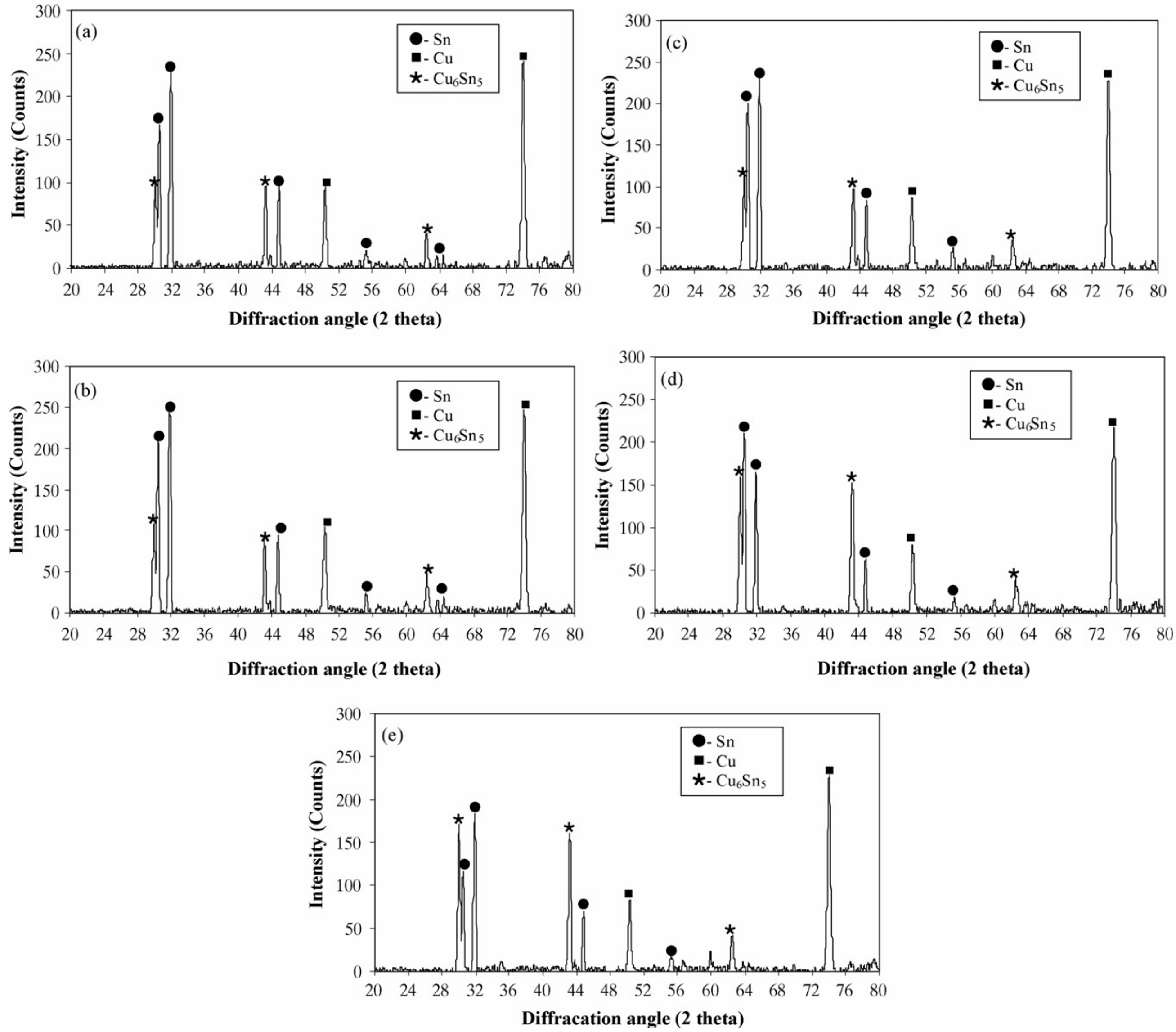

Fig. 7. XRD pattern of tin plated copper alloy contacts in as-received and annealed conditions (a) as-received; (b) 85 °C/30 min; (c) 155 °C/30 min; (d) 185 °C/30 min and (e) 155 °C/4 h.

and 185 °C. To substantiate the formation of IMC, EDX analysis was performed on different spots, marked as A, B and C in the interface (Fig. 8(a)–(c)) and the results of the analysis are complied in Table 2. It is evident from Table 2 that the atomic ratio of copper and tin varies across the interface, suggesting the presence of various phases. Obviously, the region closer to the base metal is richer in copper and vice versa. According to the Cu–Sn phase diagram (Fig. 9), there are at least four different regions in

Table 2
Results of the EDX measurement performed across the copper alloy-tin coating interface on samples subjected to thermal treatment at various temperatures

System studied	Points A			Point B			Point C		
	Cu (wt.%)	Sn (wt.%)	Assignment of phase	Cu (wt.%)	Sn (wt.%)	Assignment of phase	Cu (wt.%)	Sn (wt.%)	Assignment of phase
Tin plated copper alloy heat-treated at 155 °C for 30 min.	79.63	20.37	Cu_3Sn	61.80	38.20	Cu_6Sn_5	47.85	52.15	Cu_6Sn_5
Tin plated copper alloy heat-treated at 185 °C for 30 min.	86.92	13.08	Cu_3Sn	40.97	59.03	Cu_6Sn_5	47.08	52.92	Cu_6Sn_5
Tin plated copper alloy heat-treated at 155 °C for 4 h	91.48	8.52	Cu_3Sn	83.89	16.11	Cu_3Sn	52.59	47.41	Cu_6Sn_5

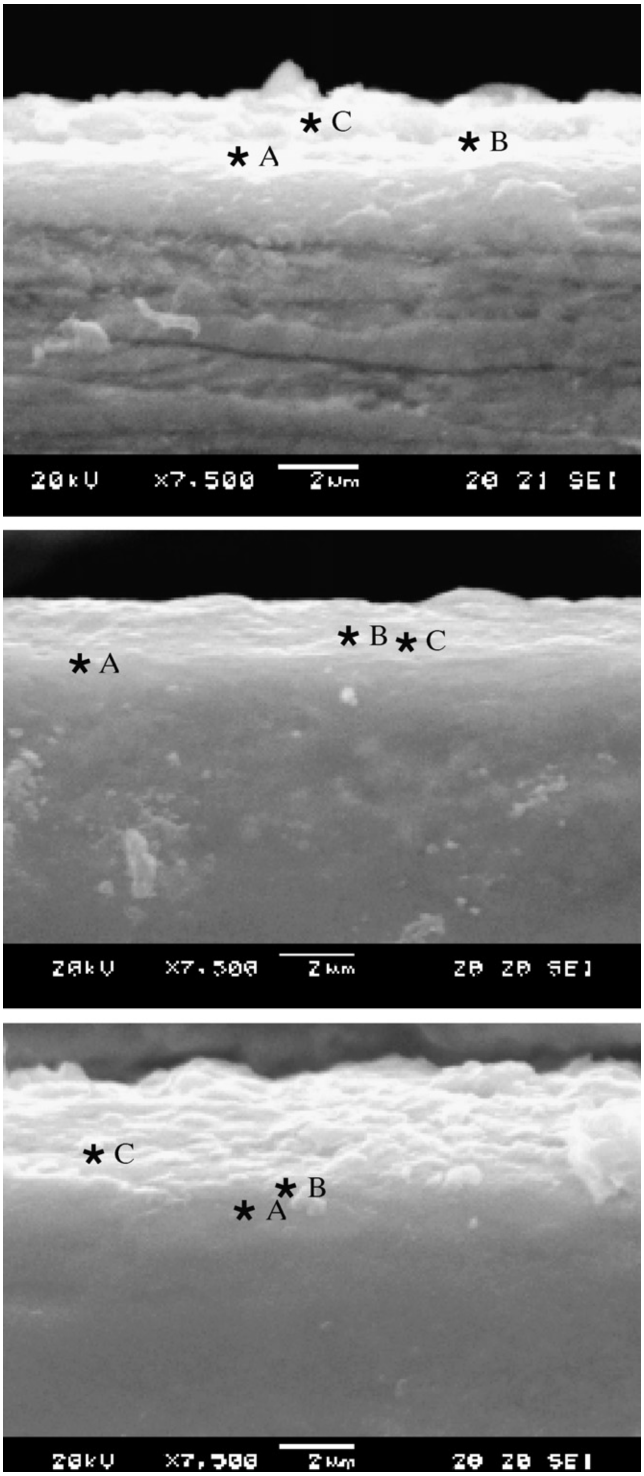

Fig. 8. The cross sectional view taken with the SEM of tin plated copper alloy samples after annealing (a) 155 °C/30 min.; (b) 185 °C/30 min and (c) 155 °C/4 h.

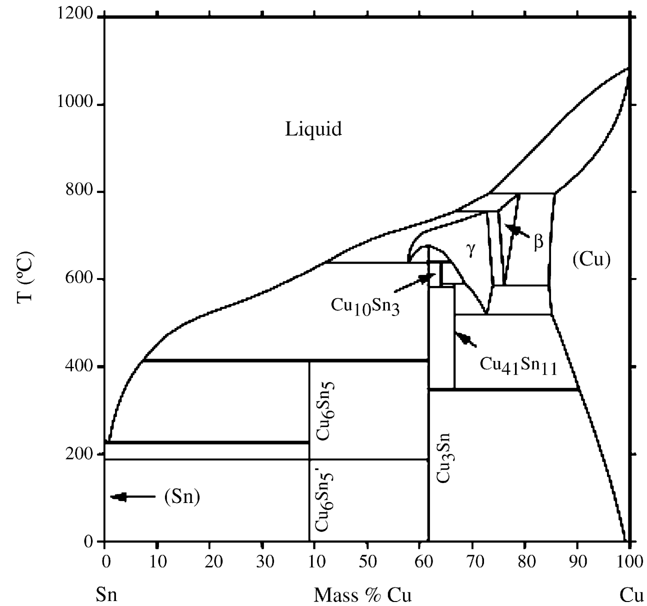

Fig. 9. Cu–Sn phase diagram (source: http://www.metallurgy.nist.gov/phase/solder/cusn.html).

the temperature range of 150–200 °C. Other than the copper rich and tin rich regions at the two ends, two major regions represent the IMCs, Cu_6Sn_5 and Cu_3Sn. Based on the amount of tin and copper, the possible phases that could be present at the interface are proposed (Table 2). Obviously, the region closer to the base metal indicates the Cu_3Sn phase and the region closer to the tin coating indicates tin with a middle layer consisting of Cu_6Sn_5 phase.

Based on the results of the XRD, SEM and EDX measurements, it is evident that tin plated copper alloy contact really possesses a duplex film of IMC/Sn over copper alloy. Increase in annealing temperature and time increases the thickness of the IMC layer. Considering the surface oxidation of tin coating, the system should be considered as copper alloy/IMC/Sn/SnO_2, instead of only the tin coating over copper alloy. Hence the change in contact resistance as a function of fretting cycles measured at different temperatures is largely a function of the nature of the film on the tin plated copper alloy contacts.

Considering the changes that occur during annealing of tin plated copper alloy contacts, as evidenced by the characterization studies, it is obvious that both the rider and flat samples will undergo similar changes. As a result, during fretting corrosion test conducted at elevated temperatures, the diffusion of copper into the tin layer is likely to transform the contact interface from tin-to-tin to tin-intermetallic to tin-intermetallic, once the top surface layers are worn out. As the soft tin plating which is capable of providing a good electrical contact is removed during the initial few fretting cycles, the contact zone will experience a totally different environment and influence the contact resistance and surface roughness accordingly. The hardness of Cu–Sn based IMC is extremely high compared with the tin plating. The bulk Knoop hardness of pure tin and the Cu–Sn IMC has been reported to be 8 and 350 kg/mm^2, respectively [14]. Hence the observed decrease in roughness at 155 and 185 °C is due to the transformation of the contact zone from tin versus tin to tin-IMC versus tin-IMC and the increase in hardness of the matrix. It has been reported that the hard and brittle Cu–Sn IMC is responsible for the apparent cracks developed on the contact area under a certain load during sliding and fretting [15]. Braunvoic [16] showed that the very hard Al–Cu IMC could easily break under pressure and cause severe contact problems. Kim et al. [10] suggests that the growth of Cu/Al IMC could induce a mechanical failure and increase the contact resistance. Braunovic [22] suggests that the difference in the mechanical properties of tin and the IMCs promotes the increase in contact resistance. Hence the rapid increase in contact resistance after a few fretting cycles, observed in samples subjected to fretting corrosion at 125–185 °C is due the hardness of the Cu–Sn based IMCs which induces the mechanical failure at the interface. Shao and Zang [15] and Hammam [28] have also found that when the pure tin layer was removed by wear and the rider slid on the hard and uneven IMC, the contact resistance rose sharply to a relatively high value. Since softening of tin enables a better electrical contact at 85 °C, it is expected that it might help reduce the contact resistance at higher temperatures of the order of 125–185 °C. However, due to the large difference in the melting point of tin (232 °C) and the IMC (630 °C), the tin starts to soften with increase in temperature whereas the IMC will remain hard. As a result, the softened tin will smear out over the contact area, leading to the formation of a thick and tight oxide film and ultimately results in an increase in contact resistance. Besides higher hardness, the high resistance of Cu–Sn IMC could also cause a significant increase in the contact resistance. Liao and Wei [9] also found that the formation of highly resistive Cu–Sn IMC is responsible for the nonlinear increase in resistivity in Cu–Sn bimetallic thin films.

4. Conclusions

The effect of temperature on the fretting corrosion behaviour of tin plated copper alloy contact is studied. The study reveals that temperature has a greater influence on the extent of fretting corrosion of tin plated copper alloy contacts. The softening of tin is responsible for the extended region of low contact resistance observed at 85 °C. The increase in thickness and the resistance of Cu–Sn IMCs at elevated temperatures causes a drastic increase in the contact resistance of the tin plated copper alloy contacts. The formation of IMC is also responsible for the decrease in surface roughness at higher temperatures. The study suggests that the connector system should be considered as copper alloy/IMC/Sn/SnO_2 instead tin plated copper alloy. During fretting corrosion test at elevated temperatures, once the top surface layers are worn out, the contact interface is transformed from tin versus tin to tin-intermetallic versus tin-intermetallic. The high hardness and electrical resistance of IMC causes a rapid increase in contact resistance. Hence it can be concluded that tin plated copper alloy connectors are not suitable for high temperature applications.

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