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Electroless copper deposition on aluminum-seeded ABS plastics

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Abstract We report a method of converting non-conductive plastic surfaces into conductive by coating either aluminum or aluminum-carbon black containing enamel pastes onto acrylonitrile-butadiene-styrene (ABS) plastics to create aluminum-seeded surfaces for a subsequent copper deposition. Through a simple electroless procedure, copper ions were reduced on the Al seeds and deposited on the ABS surface to develop a conductive layer in about 10-min deposition time. We demonstrate that addition of carbon black particles to the pastes shorten the time to reach the maximum conductivity and enhance the adhesion of electrolessly deposited copper layer to the ABS substrate surface. The electroless copper deposition process developed in this study may open up a new route of plating on plastics (POP) for printed circuit boards, electromagnetic interference shielding, and many other applications.

Introduction

Metallization of non-conductive surfaces is important in many industrial applications as it lowers cost, allows more flexibility in parts design, and reduces weight compared to its metal counterpart [1]. Plating on plastics (POP) therefore has been developed and widely involved in manufacturing printed circuit boards (PCBs) and automobile parts, and in the electromagnetic interference (EMI) shielding application [1–3]. Having excellent electrical conductivity and being relatively inexpensive, copper (Cu) has been widely studied for POP and a variety of plastics have been Cu plated including acrylonitrile-butadiene-styrene (ABS), polypropene, and Teflon [1].

Currently, there are two technologies developed for Cu plating of plastics, *via* the electroless route or through a direct electroplating route. For the first route, a regular electroless plating procedure is needed to place a thin conductive Cu layer on the plastic surface. Such a Cu layer provides sufficiently high conductivity required for the subsequent electroplating to complete the materialization finishing. However, the involvement of a regular electroless plating operation in POP is not desirable because of the disadvantages associated with electroless plating, including the complexity of the plating bath, a time consuming procedure, and the use of costly catalyst and environmentally unfriendly agents [4–7]. Alternatively, direct Cu electroplating on plastics was proposed as a substitute to the electroless route, which involves an essential step of seeding the plastics surface with an electronically conductive catalyst or activator, typically a Palladium (Pd) and/or Tin (Sn) colloid. On adsorption of the catalyst onto the plastics surface, the seeded surface is subjected to a regular electroplating procedure to complete the metallization [8–13].

Although many of the disadvantages associated with electroless plating have been circumvented by excluding this operation from the POP process, the requirement of costly catalyst for the direct electroplating is still

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undesirable. Besides, many operations such as etching, neutralization, activation, and acceleration are needed before the electroplating starts, making the direct electroplating route a multi-step and time-consuming process. Hence, elimination of the use of catalyst and development of simpler and more cost-efficient Cu plating bath with a view to further optimize the POP procedure are desired.

It was reported in the US patent 4,242,369 that a noble metal ion can be reduced and deposited onto a less noble metal substrate based on the simple displacement chemistry [14]. The purpose of that study was to use an inkjet printer to pattern a less noble metal surface with a noble metal, or they targeted at a small quantity of materials (ink droplets) as deposit on small areas (patterns).

Recognizing these, we studied and developed an alternative to electroless deposition of conductive Cu on plastics by seeding aluminum (Al) on the surface as the reducing agent. Al seeds were introduced onto the ABS surface by coating the plastics with Al-containing enamel pastes. The coated plastics were then scoured and subjected to a simple electroless procedure in a bath of 15% copper sulfate ($CuSO_4$) and 5% hydrofluoric acid (HF). Good conductivity was obtained at a 10-min deposition time and leveled off after 20 min. For comparison, Al and carbon black (C) particles containing enamel pastes were prepared and applied to ABS as well, and subjected to the same electroless procedure. It was found that incorporation of C particles into the paste shortened the time to reach the plateau conductivity and enhanced the adhesion of electrolessly deposited Cu layer to the substrate surface. The electroless deposition process developed in this study may open up a route of POP for PCB, EMI shielding, and many other applications.

Experimental

Materials

Copper sulfate ($CuSO_4$), hydrofluoric acid (HF, 48 wt%), aluminum powder (average particle size 20 μm), and carbon black powder (particle size range 2–12 μm) were purchased from Sigma-Aldrich (St. Louis, MO) and used without further treatment. ABS plastic board was purchased from Superior Panel Technology (Pico Rivera, CA). Polane 700 T enamel was purchased from Sherwin-Williams (N. Dartmouth, MA).

Preparation of Al and Al–C pastes and coating

Al powder, C powder, enamel, and distilled water were mixed at different weight ratios and magnetically stirred vigorously for 1 h to form pastes which were called Al–C pastes. The Al–C pastes were then applied on ABS boards that were pre-cut into $\sim 5 \times 5$ cm^2 squares, and pre-cleaned with soap and distilled water. The Al–C paste-coated ABS was allowed to dry overnight at room temperature to be ready for the subsequent experiments. For comparison, pastes without C particles were also prepared by mixing Al powder, enamel, and distilled water and by following the same preparation procedure as that of the Al–C pastes. These pastes were called Al pastes. The Al pastes were applied on ABS boards in the same way as were the Al–C pastes to prepare the Al paste-coated ABS surface.

Electroless copper deposition

The Al- or Al–C paste-coated ABS squares were scoured with 300-grit sandpaper, rinsed with tap water, and dried in an oven pre-heated to 40 °C for 30 min. The scoured ABS squares were then immersed into the electroless Cu deposition bath containing $CuSO_4$ and HF at different concentrations at different times (from 1 to 60 min). In this study, the $CuSO_4$ concentrations varied from 5 to 15 wt%, and those of HF were 5 wt% and 10 wt%. Two types of electroless deposition bath were studied with and without HF and the detailed information of these deposition baths is shown in Table 1. The Cu-deposited ABS squares were then dried in the oven pre-heated to 40 °C for 30 min and kept ready for electrical conductivity measurement.

Electrical performance measurement

An Agilent 34401A 6 1/2 Digital Multimeter was used to measure the resistance of the electrolessly Cu-deposited ABS squares in a 4-wire mode, with the two outer wires fed with a consistent current and the inner two wires served as the probes. Shown in Fig. 1 is a picture of such measurement. The measured resistance values were normalized with the area of the ABS squares and recorded in units of Ohm/cm^2.

Table 1 Electroless Cu deposition bath compositions

Bath #	Electroless Cu deposition bath composition (wt%)	
	$CuSO_4$	HF
1	5	0
2	10	0
3	5	10
4	10	6.7
5	10	10
6	5	15

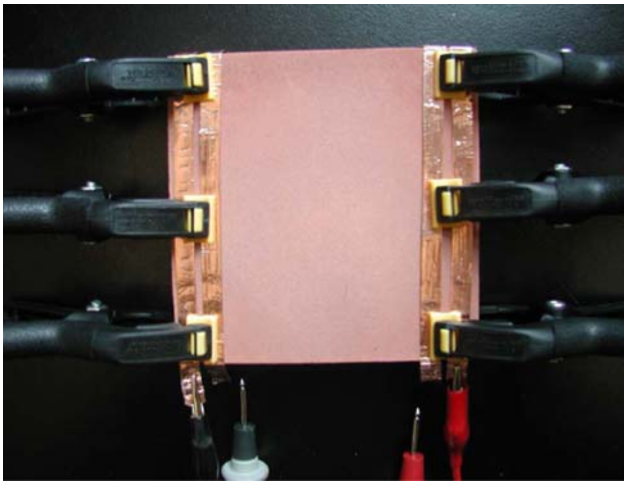

Fig. 1 4-wire mode measurement of the electrical resistance of Al- or Al–C paste-coated ABS after electroless Cu deposition

Adhesion evaluation

The adhesion of Al and Al–C coatings to the ABS surface and that of the electrolessly deposited Cu layer to the coated surfaces were evaluated using the standard ASTM Scotch-tape test (ASTM D 3359) with minor modifications—a 25-kg weight was placed onto the test surface and allowed to remain for 5 min before the tape was pulled off. The resulting surface was examined to evaluate the adhesion performance.

SEM/EDS characterization

A JEOL JSM-5610 SEM scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDS) was used to examine the appearance and elemental composition of the Al- and Al–C- coated ABS surfaces before and after electroless Cu deposition.

Results and discussion

Selection of paste composition

A series of Al–C pastes were prepared and coated on ABS, followed by the Scotch-tape test to examine their adhesion to the substrate. The paste compositions and the tape-test results are shown in Table 2. Samples that had retained an undamaged surface on removal of the tape were defined as “Pass”, whereas the samples with a noticeable peel-off of the coating upon removal of the tape were defined as “Fail”. We can see from Table 2 that varying the composition of the pastes results in different adhesion performances of the coating, with Paste #2, 4, 6, 7, and 11 as “Passes” and Paste #1, 3, 5, 8, 10, and 12 as “Fails”. Pictures shown in Fig. 2 give the appearance of two typical examples that fail or pass the test. Whereas it was not conclusive from the data of Table 2 in regard to which component(s) in the paste is more responsible than others for the resulting adhesive strength, it helped us, however, to choose the tape-test-passed pastes for the subsequent electroless Cu deposition experiments.

Table 2 Tape test results of Al–C paste-coated ABS

Paste #	Paste composition (wt%)				Tape test result
	Al	C	Enamel	H_2O	
1	25	2	30	43	Fail
2	25	3	42	30	Pass
3	25	3	44	28	Fail
4	30	3	40	27	Pass
5	30	5	40	25	Fail
6	30	5	40	25	Pass
7	30	6	50	14	Pass
8	32	6	48	14	Fail
9	32	8	45	15	Fail
10	35	4	40	21	Fail
11	40	3	36	21	Pass
12	40	8	42	10	Fail

Electrical performance of electrolessly Cu deposited ABS

Our experiments indicated that all of the ABS plastic samples coated with the tape-test-passed pastes and then electrolessly deposited in baths without HF (Bath #1 and 2 in Table 1) resulted in much poorer electrical conductivity compared with samples deposited in baths with HF (Baths #3–6, data not shown in this manuscript). In particular, samples coated with Paste #11 and deposited in Bath #6 yielded the best performance. These two formulae were, therefore, chosen for our experiments to study any effect of incorporation of C particles into the paste on the resulting performance of electrolessly deposited Cu layer. As a comparison to Paste #11 (40 wt% of Al and 3 wt% of C), an Al paste without C was prepared having the same enamel and H_2O contents, but 43 wt% of Al and 0 wt% of C.

Shown in Table 3 are the electrical resistance measurements of both Al- and Al–C paste-coated ABS after electroless Cu deposition at different times. At 1-min deposition time, both Al- and Al–C paste-coated ABS samples show immeasurable resistance, indicating their poor conductivity. After 2-min deposition, the Al–C paste-coated ABS becomes conductive with a measured resistance of 846.9 ± 714.4 Ohm/cm^2, while the Al paste-coated sample still yields immeasurable resistance, and it is not conductive until deposited for 5 min (25.1 ± 31.5 Ohm/cm^2). The

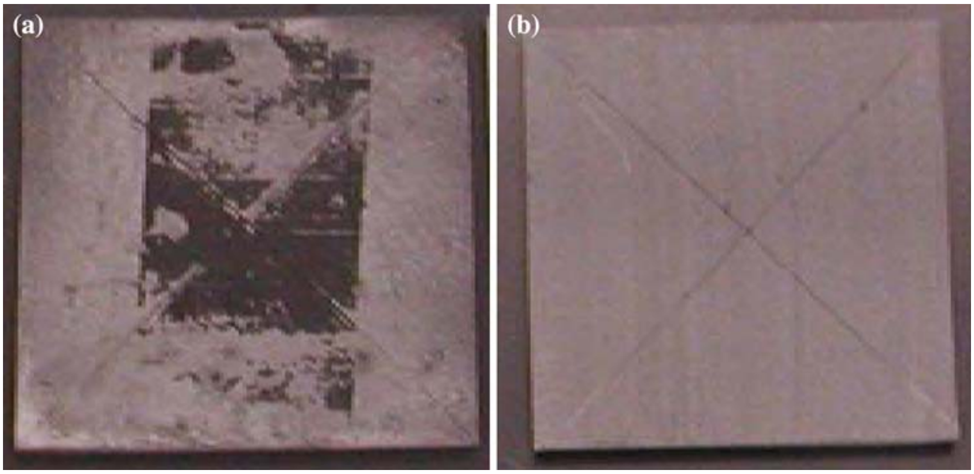

Fig. 2 Appearance of typical tape test failed (**a**, from Paste #9) and passed (**b**, from Paste #3) ABS samples coated with Al–C pastes of different compositions

Table 3 Electrical performance of Al- and Al–C paste-coated ABS after electroless Cu deposition for different time

Deposition time (min)	Resistance (Ohm/cm^2 × 10^3)	
	Al paste-coated ABS	Al–C paste-coated ABS
1	>	>
2	>	846.9 ± 714.4
5	25.1 ± 31.5	1.7 ± 1.5
10	26.4 ± 20.4	1.0 ± 0.2
20	1.3 ± 0.6	0.8 ± 0.4
30	0.8 ± 0.4	0.8 ± 0.3
40	1.0 ± 0.6	0.4
50	0.6 ± 0.3	0.6 ± 0.2
60	0.5 ± 0.1	0.7 ± 0.1

resistance change in both groups of samples appears to follow the same pattern—decreasing initially and then reaching a plateau of approximately the same resistance value—but the time needed to reach the plateau differs noticeably. The resistance of the Al–C paste-coated ABS levels off at a deposition time between 10 and 20 min (~0.8 ± 0.4 Ohm/cm^2), while that of the Al paste coated ABS becomes plateau from 20 to 30 min of the deposition time (0.8 ± 0.4 Ohm/cm^2). These results indicate that incorporation of C into the paste shortens the time to reach the maximum conductivity of the deposited Cu layer.

SEM and EDS characterization

The Al paste-coated ABS squares after being electrolessly Cu deposited for different times were examined with SEM (Fig. 3). Also shown in Fig. 3 are the SEM images of the Al paste-coated ABS before and after scouring. The scoured ABS surface at 1-min deposition time appears to be poorly covered by the electrolessly deposited Cu layer, especially the circled area in Fig. 3c, while the samples at 2-, 5-, and 20-min deposition time show improved coverage. Furthermore, the samples at 30-min and longer-deposition times show an even more sufficient surface coverage. Such a surface coverage changing pattern agrees with the resistance changing pattern where dramatic decrease in resistance took place at a time between 2 and 5 min, and the minimum resistance was obtained at about 30-min deposition time (see Table 3).

The SEM images of Al–C paste-coated ABS samples before and after electroless Cu deposition for different times shown in Fig. 4 indicate a slightly different appearance. Both the 1- and 2-min samples have the poorest surface coverage, while all other samples appear to be the same and sufficiently covered by the Cu layer. We have shown previously that a dramatic resistance decrease occurs at a deposition time between 1 and 2 min for the Al–C paste-coated ABS samples (Table 3). It is likely that the incorporated C particles serve as conductive liaison in areas where the deposited Cu layer becomes discontinuous because of an insufficient deposition time, resulting in a measurable conductivity even at a poor surface coverage. A separate study based on such a hypothesis is underway to investigate the role C plays in enhancing the conductivity of electrolessly Cu-deposited ABS at short deposition time.

The EDS analysis reveals the composition changes in both the Al- and Al–C paste-coated ABS surfaces after electroless Cu deposition for different times. As seen from Fig. 5, the EDS spectrum of the scoured ABS surface is dominated by Al at 1.487 keV (Kα, red arrows in Fig. 5a and b). With the increase of deposition time, the Al peak decreases and is replaced by three Cu peaks at 0.930 keV (Lα), 8.041 keV (Kα), and 8.905 keV (Kβ), and at the 60-min deposition time, the entire surface appears to be dominated by Cu (blue arrows in Fig. 5a and b). It is evident that Cu^{2+} has been reduced by the Al particles

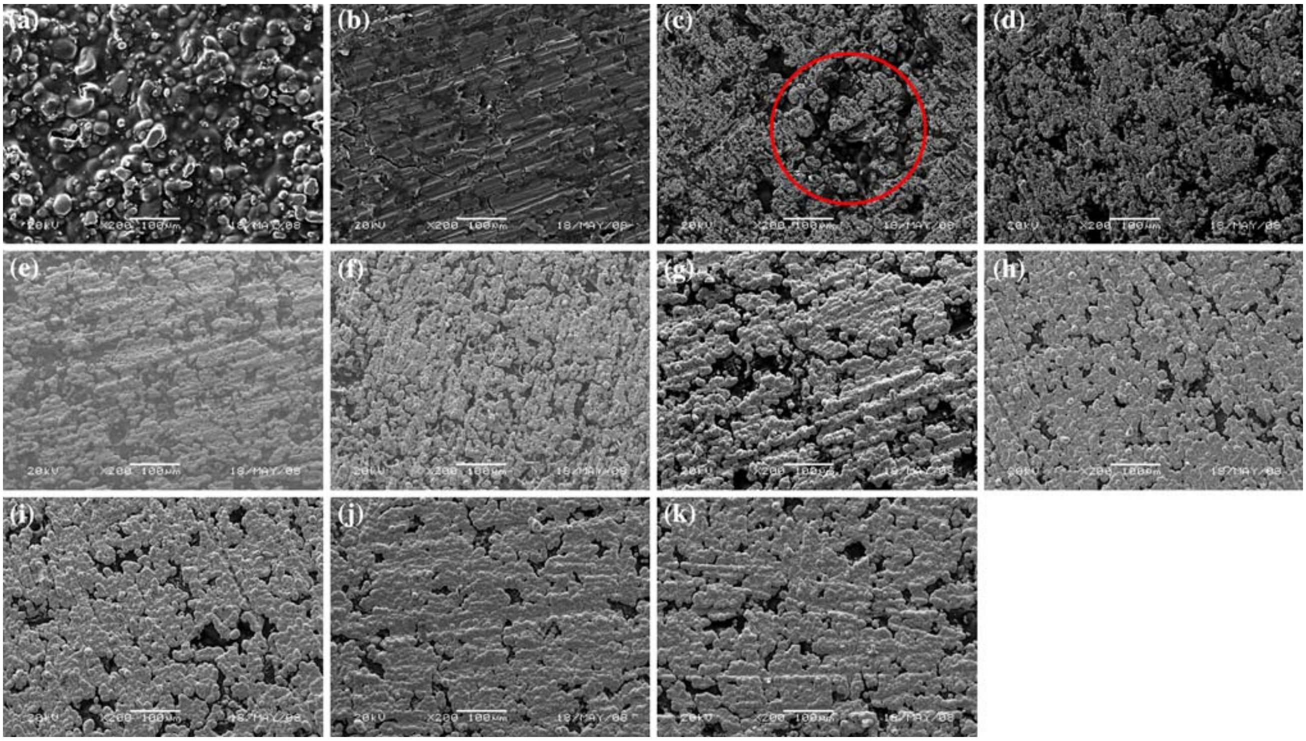

Fig. 3 SEM images of Al paste-coated ABS before (**a**) and after scouring (**b**), and of the scoured ABS after electroless Cu deposition for different times. **c** 1 min, **d** 2 min, **e** 5 min, **f** 10 min, **g** 20 min, **h** 30 min, **i** 40 min, **j** 50 min, and **k** 60 min. Bar length = 100 μm

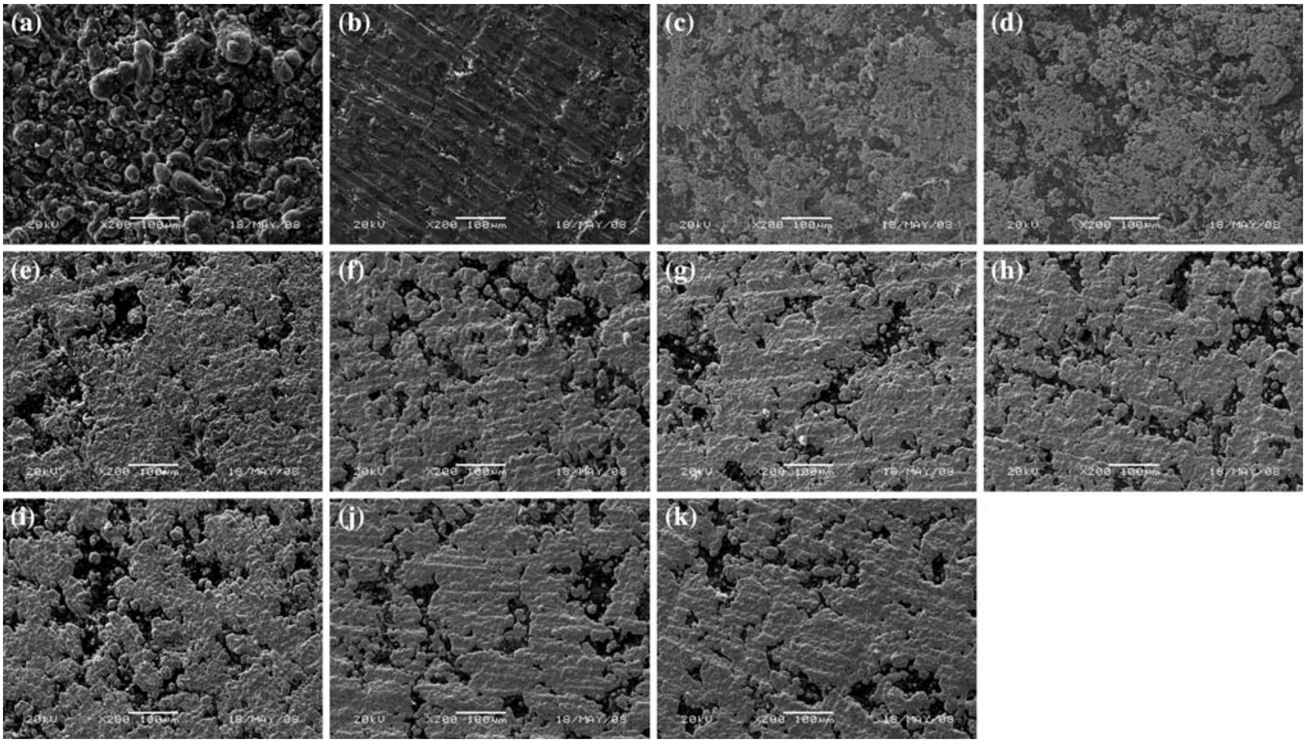

Fig. 4 SEM images of Al–C paste-coated ABS before (**a**) and after scouring (**b**), and of the scoured ABS after electroless Cu deposition for different time. **c** 1 min, **d** 2 min, **e** 5 min, **f** 10 min, **g** 20 min, **h** 30 min, **i** 40 min, **j** 50 min, and **k** 60 min. Bar length = 100 μm

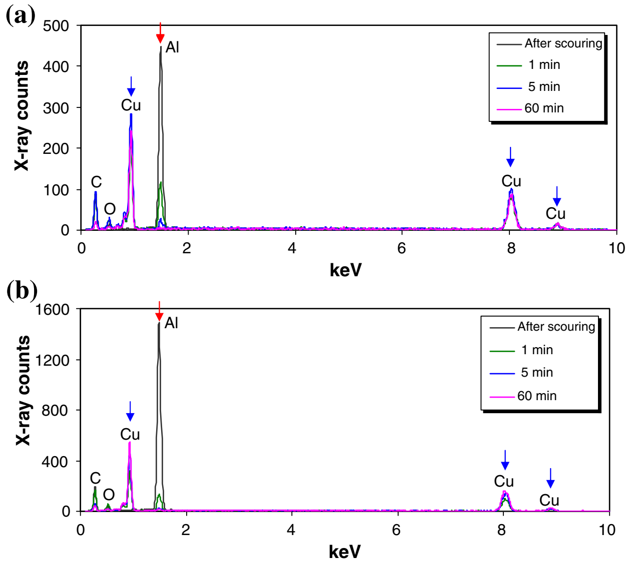

Fig. 5 Typical EDS spectra of Al (**a**) and Al–C (**b**) paste-coated ABS after scouring and of the scoured ABS after electroless Cu deposition for different times

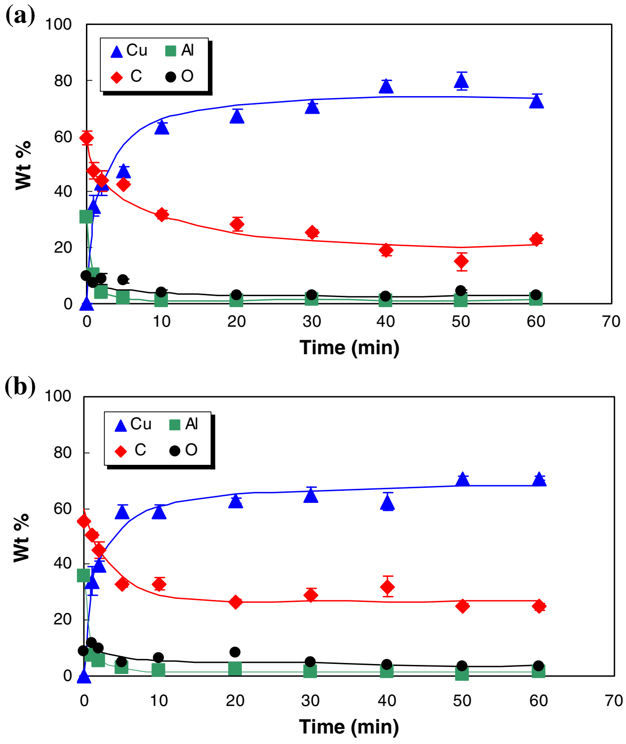

Fig. 6 Composition change of the Al- (**a**) and Al–C paste-coated (**b**) ABS surfaces as a function of electroless Cu deposition time. Three randomly selected areas of each ABS sample were EDS analyzed to obtain the compositions

seeded on ABS and gradually propagated to cover the surface over time until a maximum coverage level is reached leading to the minimum resistance.

The composition change profile of the electrolessly Cu-deposited ABS surfaces is shown in Fig. 6 based on the EDS elemental analysis. First of all, the increase of Cu and the decrease of Al and C over deposition time appear to follow an exponential pattern but in a reverse manner, and a significant change in composition completes within the first 5 min of deposition. Such an observation suggests that reduction of Cu^{2+} to metallic Cu on Al seeds occurs rapidly, and the initial Al- or Al–C paste-coated surface is replaced by the deposited Cu layer within about 5 min. Secondly, the Cu content levels off at about 70 wt%, whereas the Al content becomes tailing at about 1.5 wt% and the C content between 21 and 25 wt%. These results indicate that when the Al seeds applied on the ABS surface are almost completely exhausted and replaced by Cu, there is still a substantial amount of C left on the surface and uncovered by Cu. Presumably, this 21–25 wt% is mainly attributed to the C content in enamel for both Al- and Al–C paste-coated surfaces and little to the incorporated carbon black particles for the Al–C paste coated surface. Thirdly, the content of all of the elements on the Cu deposited surface becomes a constant value at around 20 min, and any prolonged deposition time does not further increase the percentage of Cu or decrease the percentage of Al, C, or O. Apparently, the maximum Cu percentage achievable from this electroless process is about 70 wt%. Yet, the surface with this Cu percentage appears to be sufficiently conductive (Table 3) to allow a subsequent electrolytic procedure for any additional surface finishing or treatment.

The EDS mapping was performed to examine the elemental distribution on Al- and Al–C paste-coated ABS surfaces before and after electroless Cu deposition. The Al paste-coated ABS before scouring shows a “bump and valley” surface topography (Fig. 7a1) in which the “bumps” are Al particles and the “valleys” surrounding the “bumps” are C in the enamel (Fig. 7a2–a3). Scouring appears to truncate the Al “bumps” and turn the “bump and valley” surface topography into a “plain” (Fig. 7b1). The corresponding maps show that Al is more widely distributed on the surface (Fig. 7b2), rather than the appearance of isolated islands seen in Fig. 7a2.

Deposition of Cu on the Al-seeded ABS surface has changed the elemental distribution. Figures 7c1–c4 and 8d1–d4 show the propagation of Cu on ABS surface over deposition time. We can see clearly from Fig. 7c1–c4 that Cu particles start growing on the surface of several Al seeds, but only part of the area of those seeds is covered by Cu at that deposition time. After 60 min, however, a continuous Cu layer has developed to almost fully cover the surface, leaving only a few scattered spots remaining “naked” (Fig. 7d4).

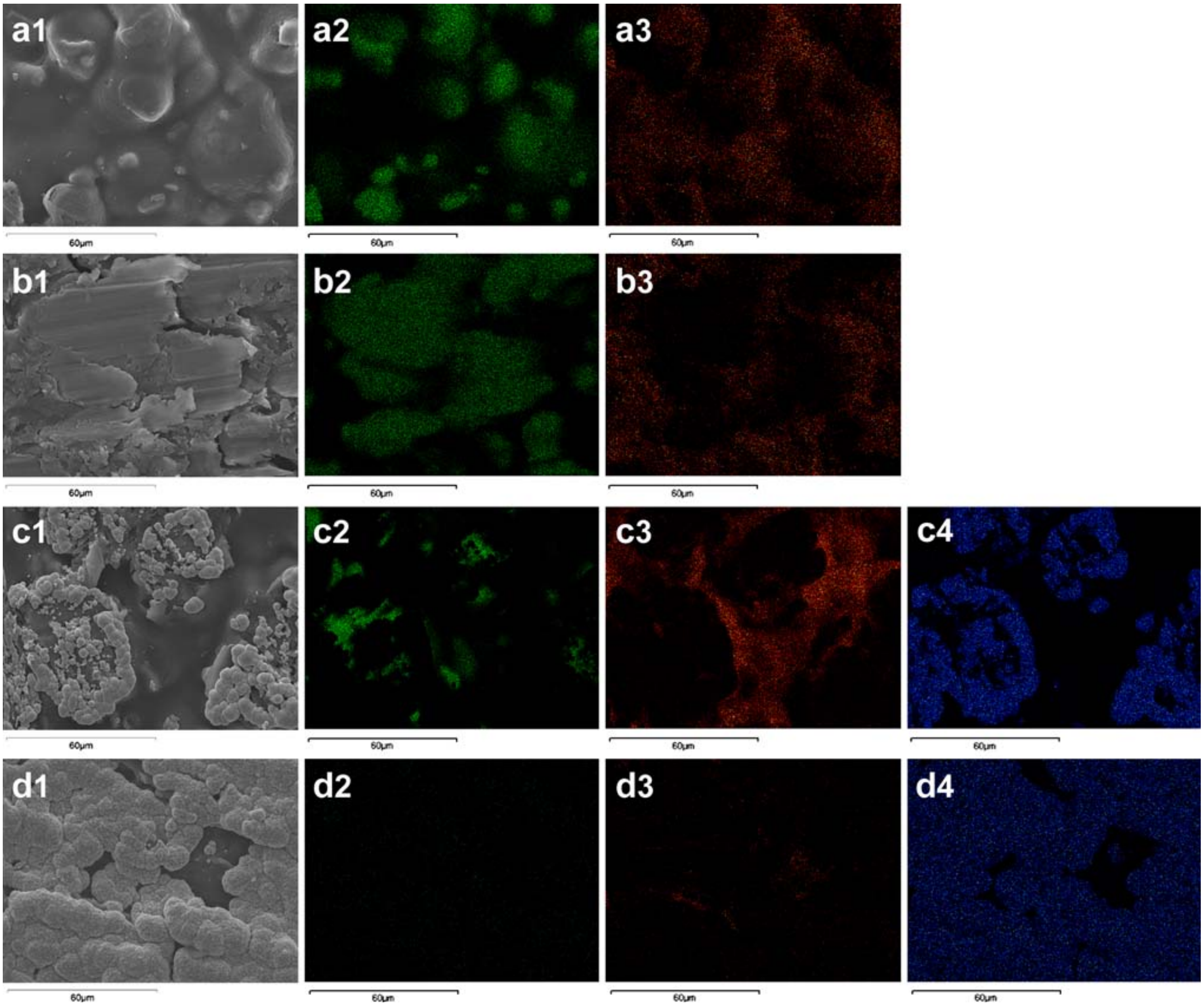

Fig. 7 EDS maps of the Al paste-coated ABS surface before (**a1**–**a3**) and after scouring (**b1**–**b3**), and the scoured ABS surface after 1 min (**c1**–**c4**) and 60 min (**d1**–**d4**) of electroless Cu deposition (Bar length = 60 μm). Green: Al, Red: C and, Blue: Cu (Same for all other EDS maps)

Essentially the same results are observed from the Al–C paste-coated ABS surface (Fig. 8), except for the presence of C particles. Figure 8a1–a3, a11–a13, b1–b3, and b11–b13 show the SEM images and maps of the Al–C paste-coated ABS surface both before and after scouring. We can see that the incorporated C particles are detected in local areas in both cases (Fig. 8a11–a13, and b11–b13), with a size range of 3–6 μm that agrees with the nominal size range (2–12 μm). Increased deposition time yields a surface with increased Cu coverage (Fig. 9c1–c4 and d1–d4).

Cross section of the Al–C paste coated ABS was also EDS mapped (Fig. 9a2–a4). A Cu layer of about 10–15 μm thick has been formed on the top surface (Fig. 9a4), and such a thickness appears to agree with the height of Cu particles, namely, a single layer of Cu particles is deposited on the ABS surface (the SEM cross-sectional images also shown in Fig. 9).

The growth of a Cu particle on an Al seed is captured by SEM imaging and EDS mapping (Fig. 10a–d). The Cu particle has developed a size of about 10–15 μm in a 60-min growth period, forming a cap on the Al head. Presumably, Cu particles appear on individual Al seeds because of the redox reaction, and the individual Cu particles gradually grow and become interconnected, and ultimately develop into a continuous and conductive layer that is responsible for the measured conductivity. A detailed study of the Cu development mechanism will be followed by creating well-isolated Al seeds or islands and sampling at much shorter deposition time intervals, aiming to capture the moments when Cu particles start to nucleate, grow, and eventually become fully ripened.

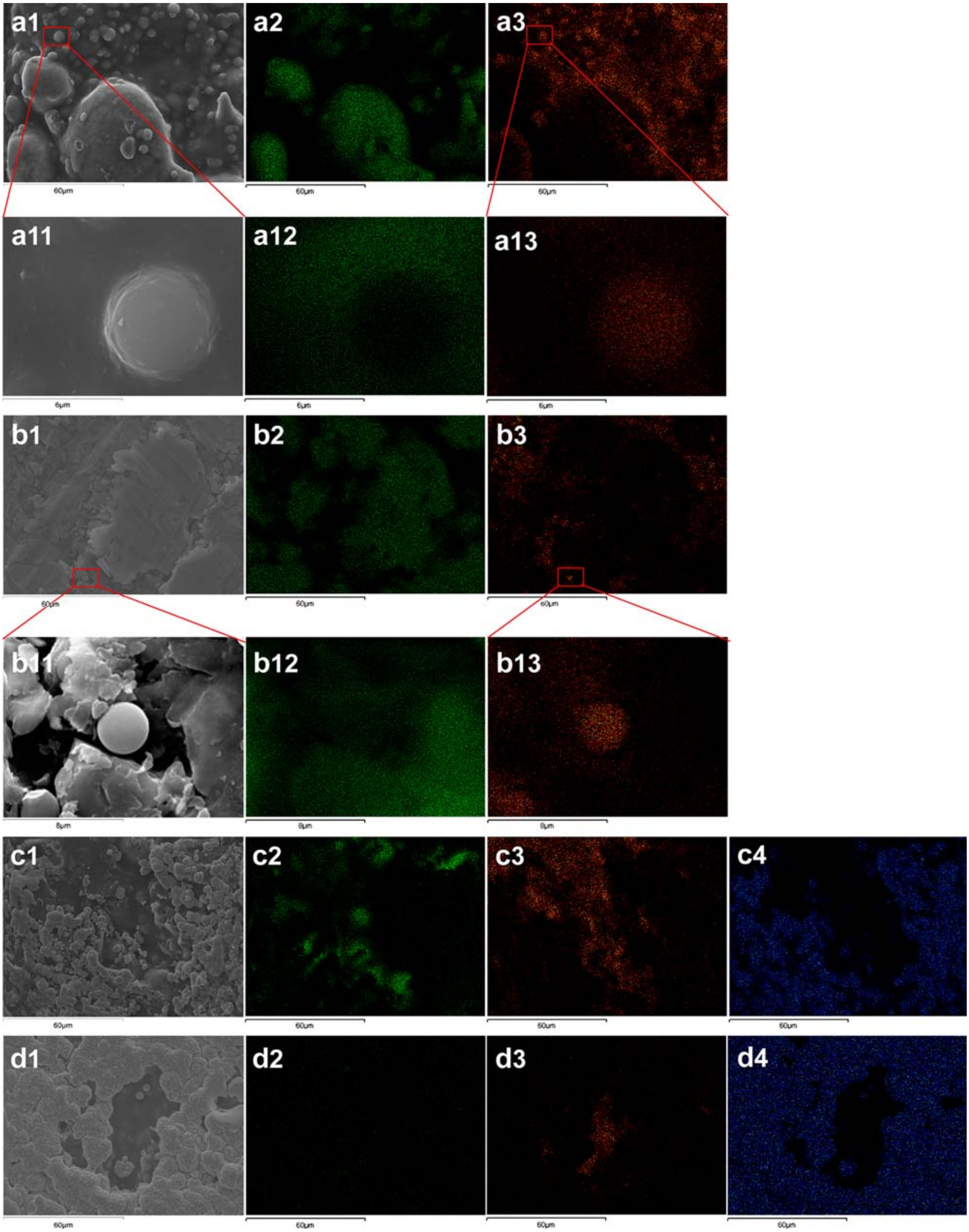

Fig. 8 EDS maps of the Al–C paste-coated ABS surface before (**a2–a3**) and after scouring (**b2–b3**), and the scoured ABS surface after 1 min (**c2–c4**) and 60 min (**d2–d4**) of electroless Cu deposition (Bar length = 60 μm). **a12–a13** and **b12–b13** are the EDS maps of two local areas where carbon black particles are located (Bar length = 6 μm)

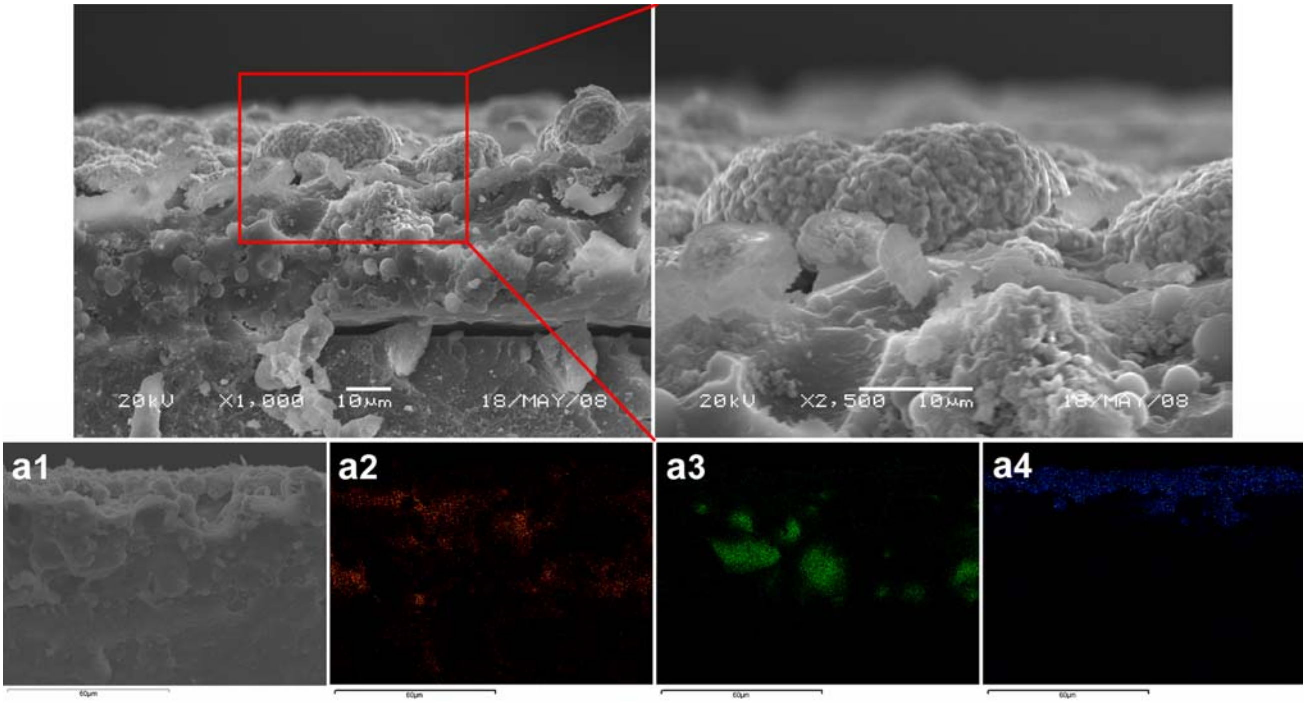

Fig. 9 Cross sectional SEM images and EDS maps of Al–C paste-coated ABS surface after 60 min of electroless Cu deposition (Bar length = 60 μm for the EDS maps)

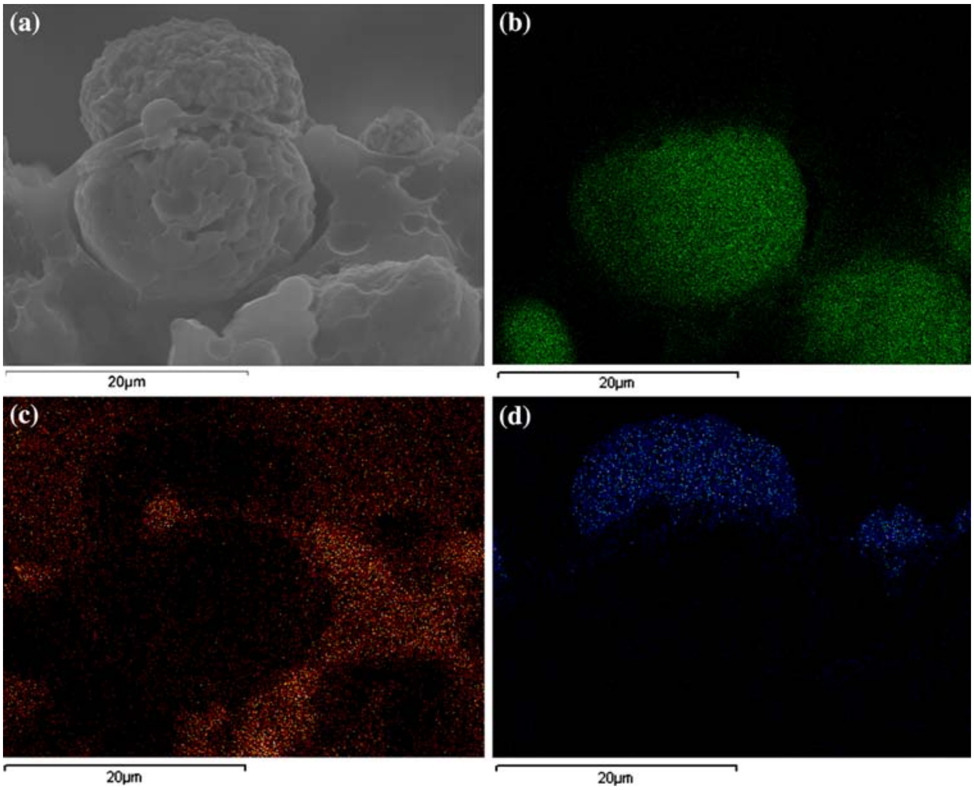

Fig. 10 Formation of Cu particles on Al seeds (Sample from the cross section of Al–C paste-coated ABS after 60 min of electroless Cu deposition, bar length = 20 μm)

Adhesion of electrolessly deposited Cu layer

To evaluate the adhesion of electrolessly deposited Cu layer on ABS surface, standard tape test was performed and the test results are shown in Fig. 11. All Al-coated ABS samples fail the test, which is evidenced either by the peel-off of Cu on the area where the tape is applied (1-min sample, the red square in Fig. 11a), or the peel-off of Cu in the areas around the cross-cut (2-min and longer-deposition time, Fig. 11a). The Al–C paste-coated ABS samples, on the other hand, fail only at the 1- and 2-min deposition time (the red square in Fig. 11b) in which Cu, on the area where the tape is applied, comes off. Any samples of longer deposition time pass the test because no noticeable damage of the surface is observed, especially in the cross-cut areas (Fig. 11b). We believe that the fails at short deposition time for both Al- and Al–C paste-coated samples are attributed to the poor coverage of the deposited Cu layer on surface, while the different performances between the Al- and Al–C paste-coated samples at longer deposition time result because of the incorporation of C particles to the pastes. Exactly how the incorporated C particles enhance the adhesion of electrolessly deposited Cu to the ABS substrate becomes one of our focuses on optimizing the paste formula and therefore the best performance of the resulting conductive Cu layer.

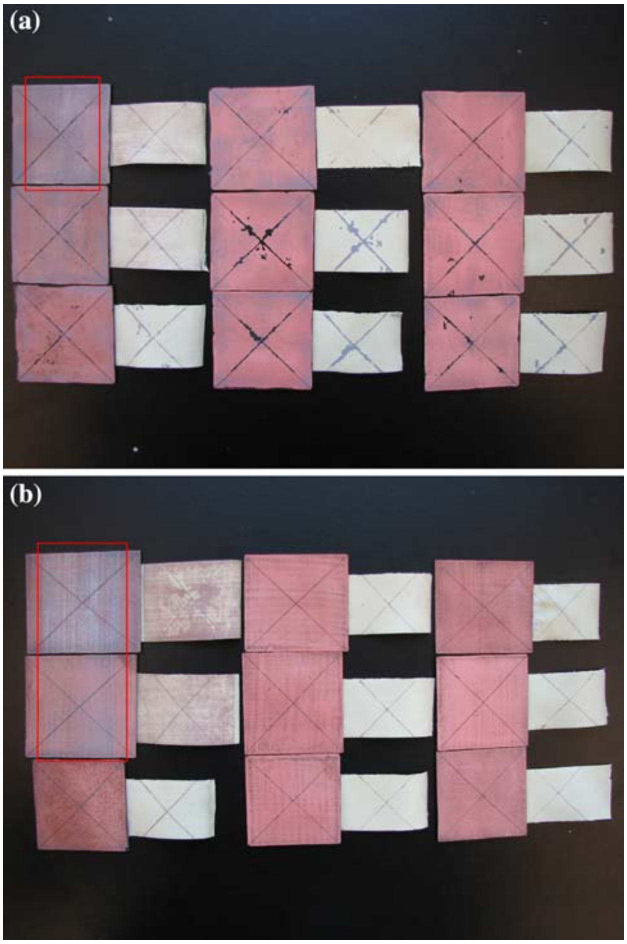

Fig. 11 Standard tape test results of Al- (**a**) and Al–C paste-coated (**b**) ABS after being electroless Cu deposition for different time. Sample identification (from top to bottom): the 1st column: 1 min, 2 min, and 5 min; the 2nd column: 10 min, 20 min, and 30 min and; the 3rd column: 40 min, 50 min and 60 min (same for both (**a**) and (**b**)). Shown on the left side of each sample is the tape after peeled off the sample

Conclusions

Al- or Al–C- containing enamel pastes were coated onto ABS plastic to create Al-seeded surfaces onto which Cu could be readily deposited through a simple electroless procedure, converting the non-conductive plastic surface into conductive. Standard tape test, electrical conductivity measurement, SEM, and EDS were used to characterize the coated ABS surface before and after electroless Cu deposition. It was found that addition of C particles to the pastes shortened the time to reach the maximum conductivity and enhanced the adhesion of electrolessly deposited Cu layer to the substrate. The electroless Cu deposition process developed in this study may open up a new route of deposition on plastics (POP) for printed circuit boards, electromagnetic interference shielding, and many other applications. We realized that the following studies are important to optimize the paste formula and to elucidate the mechanism of Cu growth on the Al seeds:

1. The role HF plays in enhancing the Cu deposition;
2. The role C plays in improving the conductivity at short deposition times and enhancing the adhesion of the deposited Cu layer to the substrate.

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