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ABSTRACT

The kinectics of wetting were studied on several different prepared surfaces of copper (Cu) to simulate the microstructure observed in pre-tinned Cu-clad printed circuit boards. The results illustrate the effectiveness of pre-tinning in maintaining the solderability of Cu surfaces. Pre-tinning with Pb-rich solder (95Pb-5Sn) is particularly effective since solderability is preserved even after a relatively long aging treatment. On the other hand, pre-tinning with eutectic solder risks the loss of solderability during aging or baking due to surface exposure of an ε-phase intermetallic with poor wetting properties. The results also confirm the presence of carbon in pre-tinned specimens due to the use of flux. The effect of carbon on solderability is not yet known.

INTRODUCTION

Pre-tinning of the copper lands on printed circuit boards is widely used in the electronic industry to protect the copper surface from oxidation before assembly.[1-3] Pre-tinning procedure usually consists of cleaning the surface with a flux and then applying a thin layer of solder. The most widely used solder system is lead-tin (Pb-Sn). Lead-tin solder bonds to Cu by forming a layer of Cu-Sn intermetallics at the wetted interface.[4-7] The solderability of a Cu substrate depends on the ease with which the intermetallic can form, and the reliability of the pre-tinned surface is influenced by the integrity of the intermetallic layer.

At normal soldering temperatures the preferred Cu-Sn intermetallic is the η-phase (Cu_6Sn_5). This is the Sn-rich intermetallic in the Cu-Sn system (Figure 1).[8] It is preferred since Sn diffuses rapidly through the liquid solder, so the copper supply at the growing intermetallic interface is the rate-limiting consideration. However, η-phase formation is limited to temperatures below about 400° C in the Cu-Sn binary; the ε-phase (Cu_3Sn) forms when soldering is done at higher temperatures.[9]

The solderability of the pre-tinned surface often deteriorates with long-term storage and/or high temperature baking prior to final processing. It is then sometimes found that the components wet poorly, requiring the rejection or costly re-work of soldered parts. Figure 2 shows the effect of baking at 170°C on a Cu land that was pre-tinned with ~ 10 μm of eutectic solder (63Sn-37Pb). The initial surface has the normal microstructure of eutectic solder which contains primarily eutectic constituent with some Pb dendrites (Figure 2a). After aging for 1 day, the Pb-rich solution has begun to gather into small islands, and the Sn has been replaced by a crystalline material (Figure 2b), which x-ray diffraction and Auger electron spectroscopy reveals to be the η-phase. After 6 days, the Pb-rich solution has gathered into discrete globules on the surface, and the underlying intermetallic has converted into a nearly continuous layer of ε-phase (Figure 2c).

Kumar and Moscaritolo[3], Reed, et al.[10], Sunwoo, et al.[11] have detected high concentrations of carbon at the Cu-intermetallic interface and in the solder by Auger analysis. Reed, et al.[10] have found that the major difference between the good and the bad in the "hot air leveled" (HAL) specimens is the presence of carbon in the solder. Both Kumar and Moscaritolo[3], Reed, et al.[10] conclude that the source of carbon is due to insufficient cleaning of lead-tin etch resist (co-deposited organics) prior to HAL processing.

The present authors, on the other hand, have found that the source of residual carbon is from the flux, which is a complex form of hydrocarbon. As the flux cleans the surface, the decomposed flux may evolve to the surface as dross or may remain in the molten solder. As the impurities in the molten solder increase, solderability is known to decrease.[12] Surface analysis of as-received pre-tinned Cu-clad printed circuit boards using Auger electron survey shows high concentrations of carbon, while other contaminants such as oxygen and chlorine disappear after an initial sputter. Figure 3 shows Auger spectra of a pre-tinned board before and after sputtering for 2 minutes.

The following experiments attempt to provide better understanding of dewetting behavior on the pre-tinned surfaces and suggest possible remedies.

EXPERIMENTAL

The experiments studied the wetting of copper by eutectic Pb-Sn solder (63Sn-37Pb, by weight), using several different surface preparations of the copper to simulate the microstructure observed in Figure 2. The prepared surfaces included (1) clean, bare Cu, (2) Cu pre-tinned with a thin layer of eutectic solder, and (3,4) Cu pre-tinned with eutectic or 95Pb-5Sn solder, then aged at 170°C for 6 days to simulate an aged and baked condition.

All the specimens were made of OFHC Cu sheet cut to 25.4 mm x 25.4 mm x 0.84 mm coupons. Although the actual pre-tinning temperatures varied with the solder composition, the general procedure was the same. The Cu specimens were mechanically polished using a 600 grit silicon carbide paper and chemically microetched with 50% diluted nitric acid until uniform bubbles evolved from the surface. The specimens were rinsed in water and in ethyl alcohol, and were kept in mildly activated rosin-type

(RMA)flux until pre-tinning for approximately 10-20 minutes. To identify the source of carbon, a set of specimens was pre-tinned without using the flux. The solder bath temperature for 63Sn-37Pb solder was 245°C and for 5Sn-95Pb solder was 360°C. The specimens were immersed in the molten solder bath for 5 seconds and then air-cooled, resulting in an average solder thickness of about 10 μm. For aging, the 63Sn-37Pb and 95Pb-5Sn pre-tinned specimens were individually encapsulated in argon-filled quartz tubes and held at 170°C for 6 days.

The kinetics of wetting were studied using a wetting balance in which Cu samples with prepared surfaces are partially immersed in a molten bath of eutectic solder. The force on the specimen is measured as a function of time after immersion. As the interfacial reactions that accomplish wetting proceed, the solder meniscus climbs on the partially immersed copper surface, and the downward force on the specimen increases. The testing device used was a Multicore Universal Solderability Tester (MUST), which is a commercially available unit. The test machine was interfaced with a computer for data acquisition and control, using software developed at Lawrence Berkeley Laboratory. The test parameters are listed in Table1. Prior to the test, the specimens were dipped in RMA flux. Three specimens were tested for each condition.

The surface characterization was performed using scanning electron microscope (SEM) and Auger electron microscope (AEM). For the cross-sectional optical microscopy, the samples were cut from the tested specimens and mounted in epoxy. A conventional polishing technique was used. The intermetallics were identified by using an X-ray diffractometer.

RESULTS AND DISCUSSION

The wetting curves corresponding to the different surface conditions are shown in Figure 4 and are displayed as a function of the wetting force with time. The time to immersion depth was the same for all specimens, and the buoyancy force is subtracted, so the force plotted is the true wetting force due to the solder meniscus developed at the interface.

The cleaned copper surface is rapidly wet by the eutectic solder, as shown in Figure 4a. Wetting is completed within 2 seconds of immersion, and the wetting force stabilizes at about -0.4 N/m. The irregularities in the wetting curve are primarily due to the action of the flux, which flows into the solder bath from the upper part of the specimen. Good wetting is also obtained for an unaged sample pre-tinned with 63Sn-37Pb (Figure 4b), and the kinetics of wetting resemble that of the bare Cu specimen.

The Cu pre-tinned with 95Pb-5Sn was aged at 170°C for 6 days to simulate the surface with the exposed η-phase, as observed in Figure 2b, which is equivalent to shelf aging and short-term baking. The Cu-Sn phase diagram (Figure 1) suggests that η-phase will eventually convert into the Cu-rich ε-phase. This has not happened after 6 days aging, possibly for kinetic reasons associated with the solder composition.[9] The surface and cross-section of an aged specimen is shown in Figures 5a and 5c, and the respective wetting curve is shown in Figure 4c. The wetting kinetics are nearly the same as, or better than, the bare Cu and 63Sn-37Pb pre-tinned specimens, respectively. The wetting force increases rapidly to asymptote at a value of ~ -0.35 N/m. The difference in the measured asymptotic value of the wetting forces between pure copper and pre-tinned specimens is attributed to experimental error (due, for example, to the alignment of the specimen in the bath) and is somewhat imprecise. The surface state and cross-section after wetting are shown in Figures 5b and 5d, respectively. The surface microstructure resembles a typical eutectic pre-tinned microstructure and the intermetallic layer displays fine nodules of η-phase, which suggests that the original intermetallic is removed and reconstituted during wetting, either by dissolution or thermal spall from the interface.

The microstructure of the eutectic pre-tinned layer changes significantly during aging for 6 days at 170°C, from the microstructure containing primarily eutectic constituent with some Pb dendrites (Figure 2a) to mostly discrete, irregular Pb islands on the interface with a significant fraction of ε-phase (Figure 6a and 6c). The kinetics of wetting are dramatically slowed (Figure 4d). The wetted surface and cross-section are shown in Figure 6b and 6d, respectively. The ε-phase is coated with an irregular layer of the Sn-rich η-phase. The poor quality of bonding at the interface is apparent from the figure.

There are two apparent reasons for poor wetting at the aged interface of specimens pre-tinned with 63Sn-37Pb. First, the ε-phase intermetallic oxidizes on exposure to air and is poorly wet by solder. Wetting requires the breakdown of the oxide coating through the action of the molten solder and flux, and is hence retarded. Second, the Cu-Sn phase diagram shows that the equilibrium phase in contact with a Sn-rich medium is the Sn-rich η-phase rather than the Cu-rich ε-phase. As suggested by the cross-section in Figure 6d, the wetting reaction involves the conversion of ε-phase to η-phase at the wetted interface, which may be a kinetically slow process since it requires the dissolution of ε-phase. The cross-section suggests that good bonding is only attained over those portions of the interface where η-phase has formed. Since the reaction is incomplete, only partial bonding is obtained.

Another possible reason for poor wetting may be due to the presence of carbon from flux, where the flux is needed to enhance wetting, while the residual decomposed flux hinders wetting. During surface analysis, Auger electron survey of all the specimens revealed surface contaminants, but after an initial sputter, the only contaminant present was carbon. To determine the source of carbon, fresh 95Pb-5Sn solder and Cu-clad board were analyzed, as shown in Figure 7. The surface of solder was argon sputtered for 2 minutes and left in the chamber for 15 minutes prior to analysis to determine whether there was any carbon build-up from the chamber. The carbon peak at 272 eV was not observed (Figure 7a). Similarly, the board after a minute sputtering showed mainly the Cu peaks (Figure 7b). Figure 8 shows Auger spectra of pre-tinned specimens made with and without flux. The overall survey of the surfaces is similar except for the carbon peak. For the pre-tinned specimens made with flux, the secondary Pb peaks at 249 and 267 eV have almost disappeared and only the carbon peak is apparent. The small carbon peak seen in the spectrum of pre-tinned specimen made without flux is from the re-used solder. These Auger spectrum confirm that the carbon is from the residual flux and not from the board or the solder. However, they do not indicate the carbon bonding state in the solder, although the shape of the carbon peak resembles graphite more than that of carbide. There is no known copper, tin, or lead carbide formation and the solubility of carbon in tin and lead is almost negligible.

While the precise effect of carbon contamination on wetting is not yet known, Chang[13] has shown that an amorphous carbon layer (700Å) is extremely effective as a diffusion barrier for Cu, in comparison to gold or nickel, because of the low chemical affinity between Cu and carbon. No out-diffusion of Cu through carbon was seen in his work, even after heat treatments as long as 72 hrs. at 700° C. The carbon/Cu interface also showed adequate bonding. Hence, the presence of carbon can be advantageous if a finite layer of carbon can prevent Cu diffusion to the Cu/intermetallic interface, which will limit the intermetallic growth and maintain the solderability. However, the change in the intermetallic appearance of aged specimens indicates that the carbon bonding state in the pre-tinned layer may differ from the as-deposited carbon layer on Cu.

CONCLUSIONS

The results of the preliminary experiments reported here illustrate the effectiveness of pre-tinning in maintaining the solderability of Cu surfaces. Pre-tinning with Pb-rich solder (95Pb-5Sn) is particularly effective since solderability is preserved even after a relatively long aging treatment. On the other hand, pre-tinning with eutectic solder risks the loss of solderability during aging or baking due to surface exposure of an ε-phase intermetallic with poor wetting properties. The results also confirm the presence of carbon in pre-tinned specimens due to the use of flux. The effect of carbon on solderability is not yet known.

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Table 1: Wettability Test Parameters

IMMERSION TIME:	10 s
IMMERSION DEPTH:	4 mm
IMMERSION SPEED:	15 mm/s
SPECIMEN WIDTH:	25.4 mm
SPECIMEN THICKNESS:	0.84 mm
BUOYANCY FORCE:	6.934E-03 N/m

Figure Captions

Figure 1. A binary Cu-Sn phase diagram.

Figure 2. SEM micrographs showing the surface of Cu sheet pre-tinned with 63Sn-37Pb solder: (a) before aging, the surface exhibits a typical Pb/Sn lamellar distribution; (b) after aging at 170°C for 1 day, the surface changes to islands of Pb and exposed Cu_6Sn_5 (η) intermetallic; (c) after aging at 170° C for 6 days, the surface consists of coarsened Pb islands and exposed Cu_3Sn (ε) intermetallic. XBB 909-7947B

Figure 3. Auger spectra of a pre-tinned Cu-clad printed circuit board: (a) as-recieved; (b) after two minute sputtering.

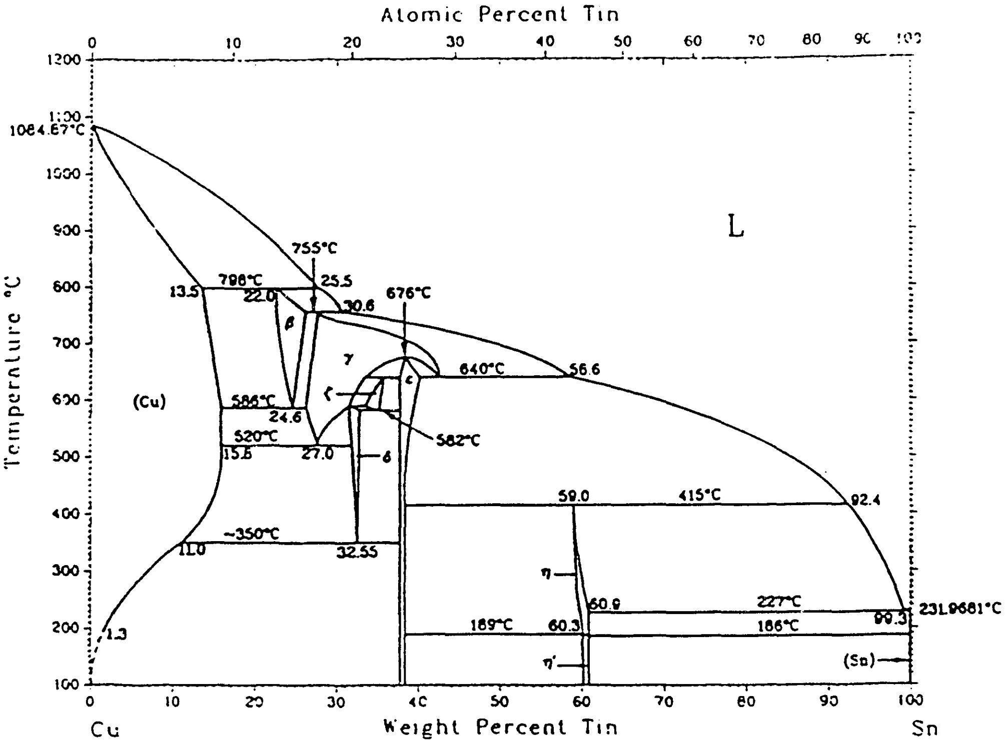
Figure 4. Wetting profiles: (a) clean, bare Cu substrate; (b) Cu pre-tinned with 37Pb-63 Sn; (c) Cu pre-tinned with 95Pb-5Sn aged at 170 κC for 6 days; (d) Cu pre-tinned with 37Pb-63 Sn aged at 170°C for 6 days.

Figure 5. Cu pre-tinned with 95Pb-5Sn aged at 170°C for 6 days: (a) and (b) SEM micrographs of the surface before and after the wetting; (c) and (d) optical micrographs of the cross-section before and after the wetting. XBB 912-1140

Figure 6. Cu pre-tinned with 37Pb-63 Sn aged at 170°C for 6 days:(a) and (b) SEM micrographs of the surface before and after the wetting; (c) and (d) optical micrographs of the cross-section before and after the wetting. XBB 912-1137

Figure 7. Auger strectra of (a) fresh 95Pb-5Sn solder, after two minute sputtering and 15 minutes in the chamber; (b) Cu-clad board, after a minute sputtering.

Figure 8. Auger strectra of pre-tinned Cu specimens made (a) with; (b) without RMA flux, after seven minute sputtering.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30
40
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70
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90
100
1200
1100
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800
700
600
500
400
300
200
100
Temperature °C
L
755°C
798°C
13.5
22.0
25.5
30.6
676°C
β
γ
ζ
ε
640°C
58.6
(Cu)
586°C
24.6
520°C
15.8
27.0
δ
582°C
59.0
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11.0
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η
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Weight Percent Tin
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Figure 1

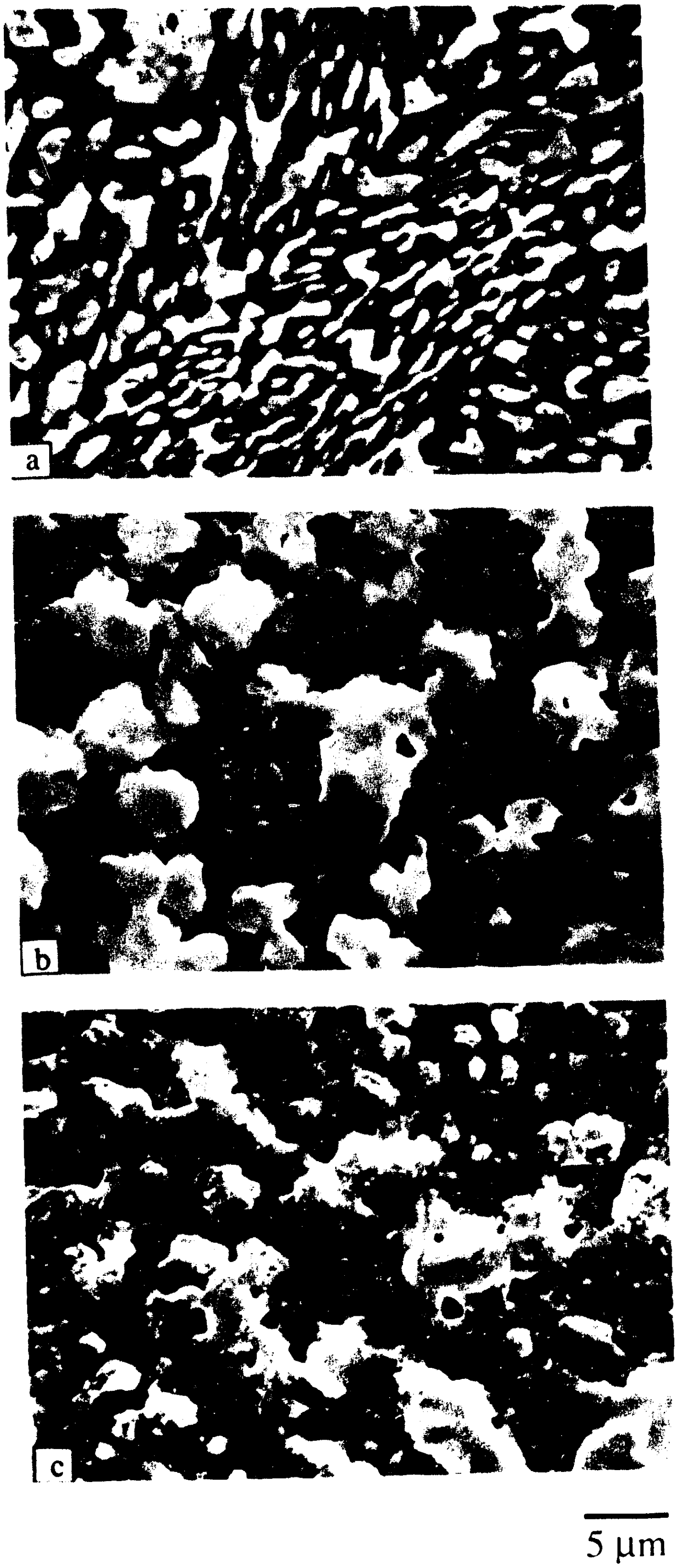

Figure 2

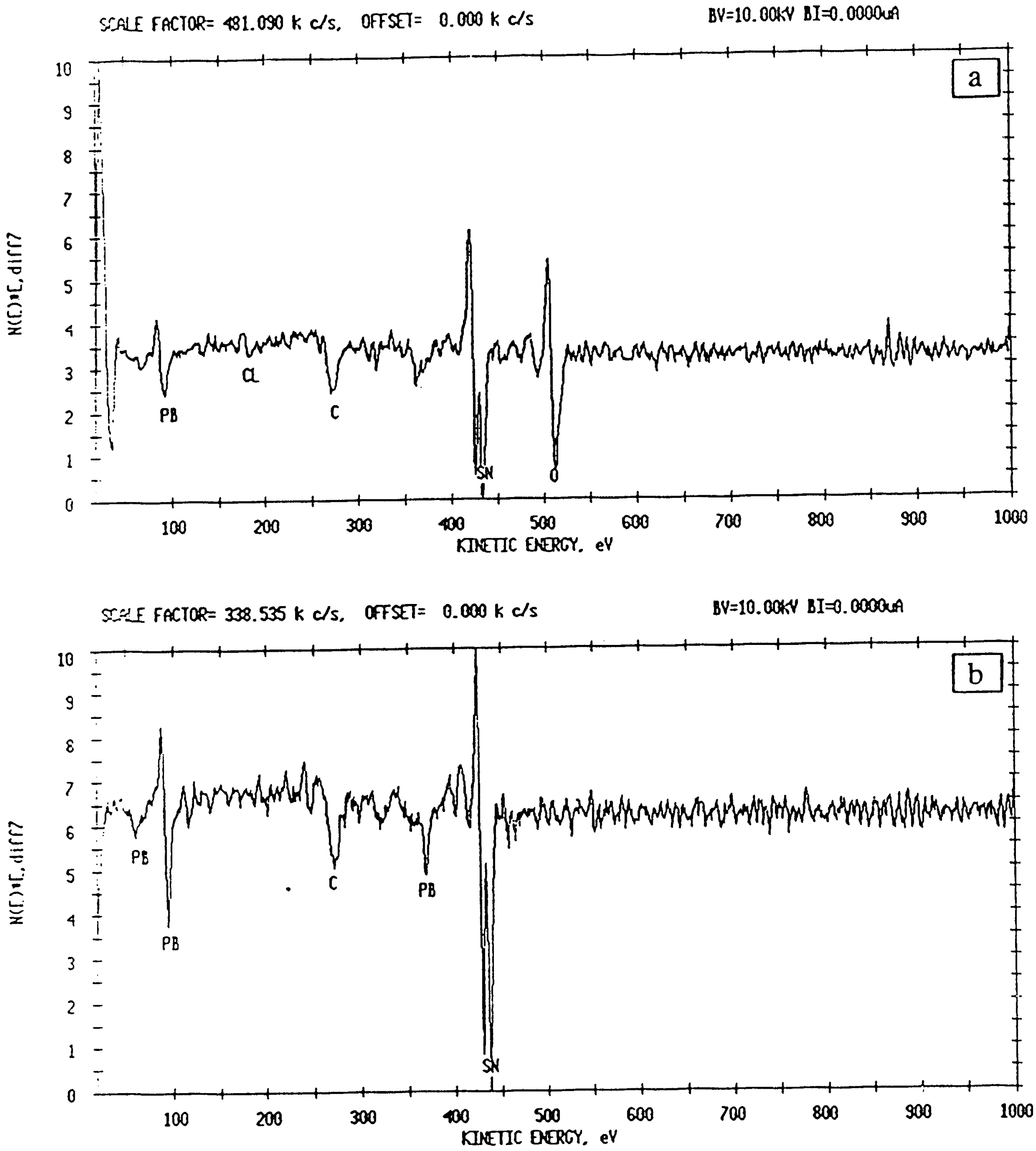
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Figure 3

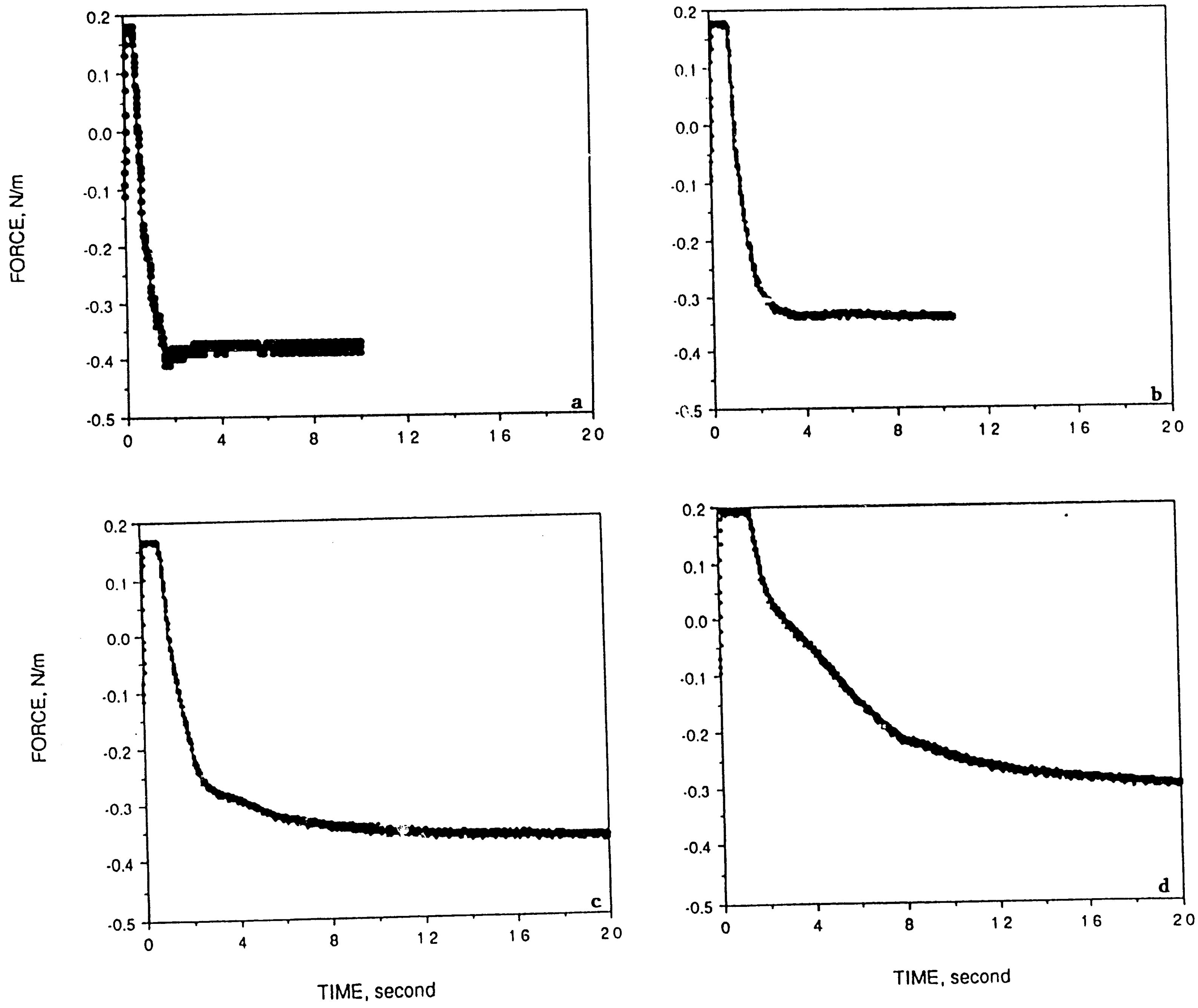


Figure 4

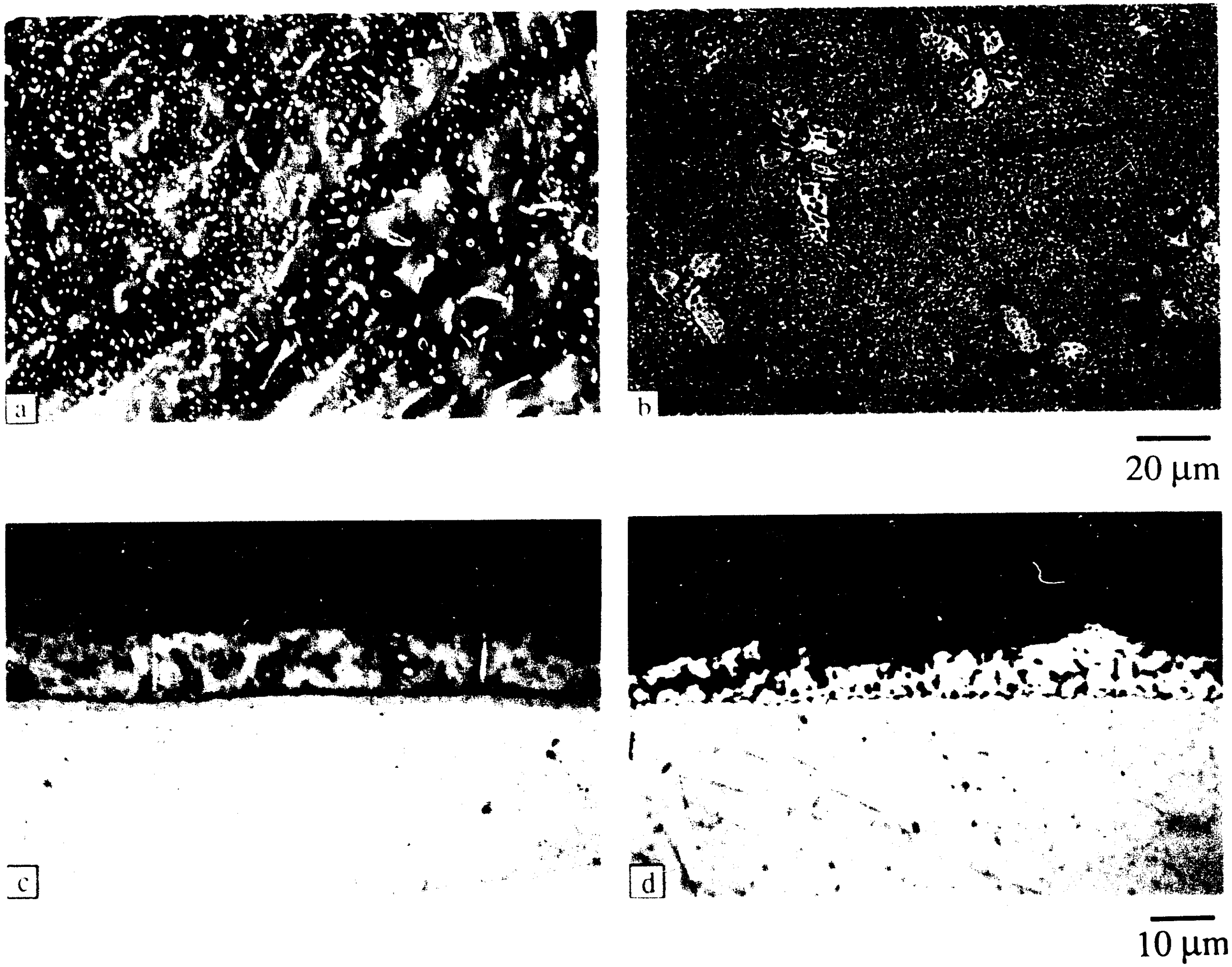


Figure 5

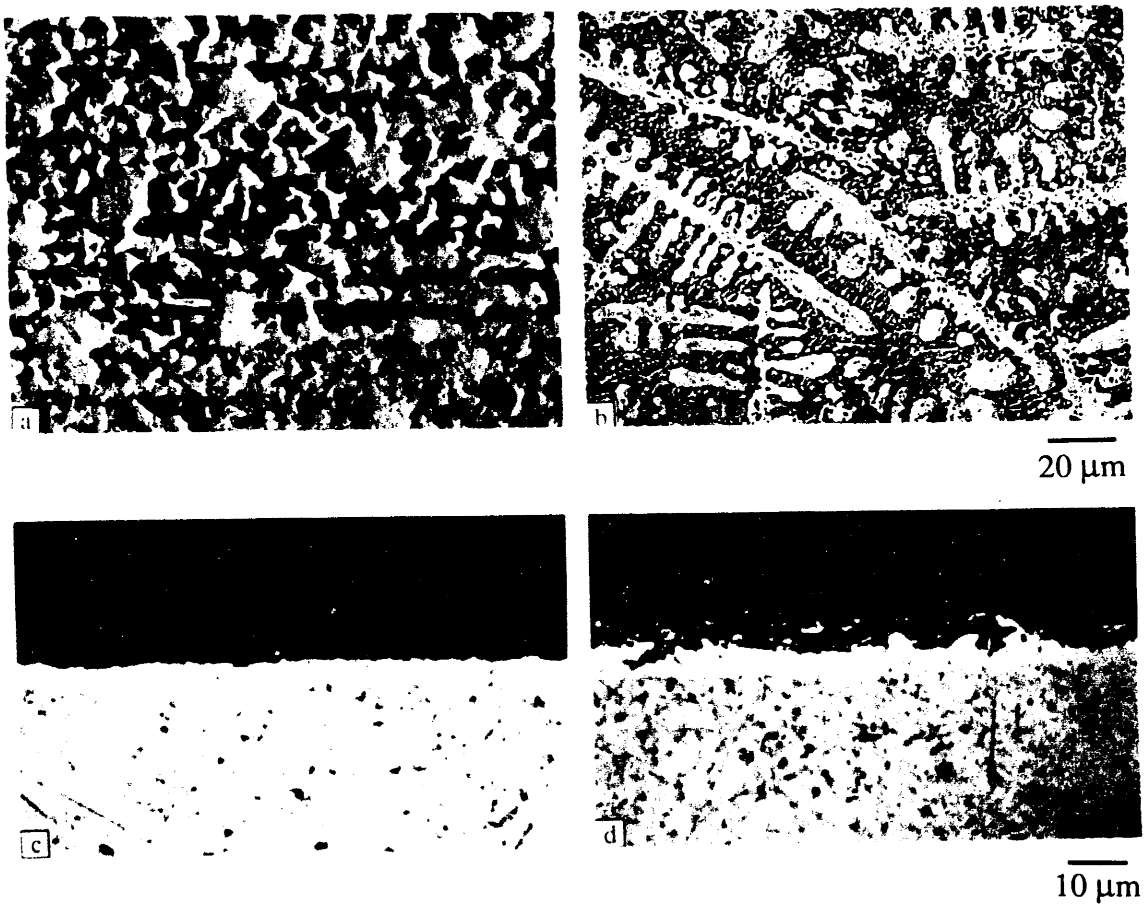
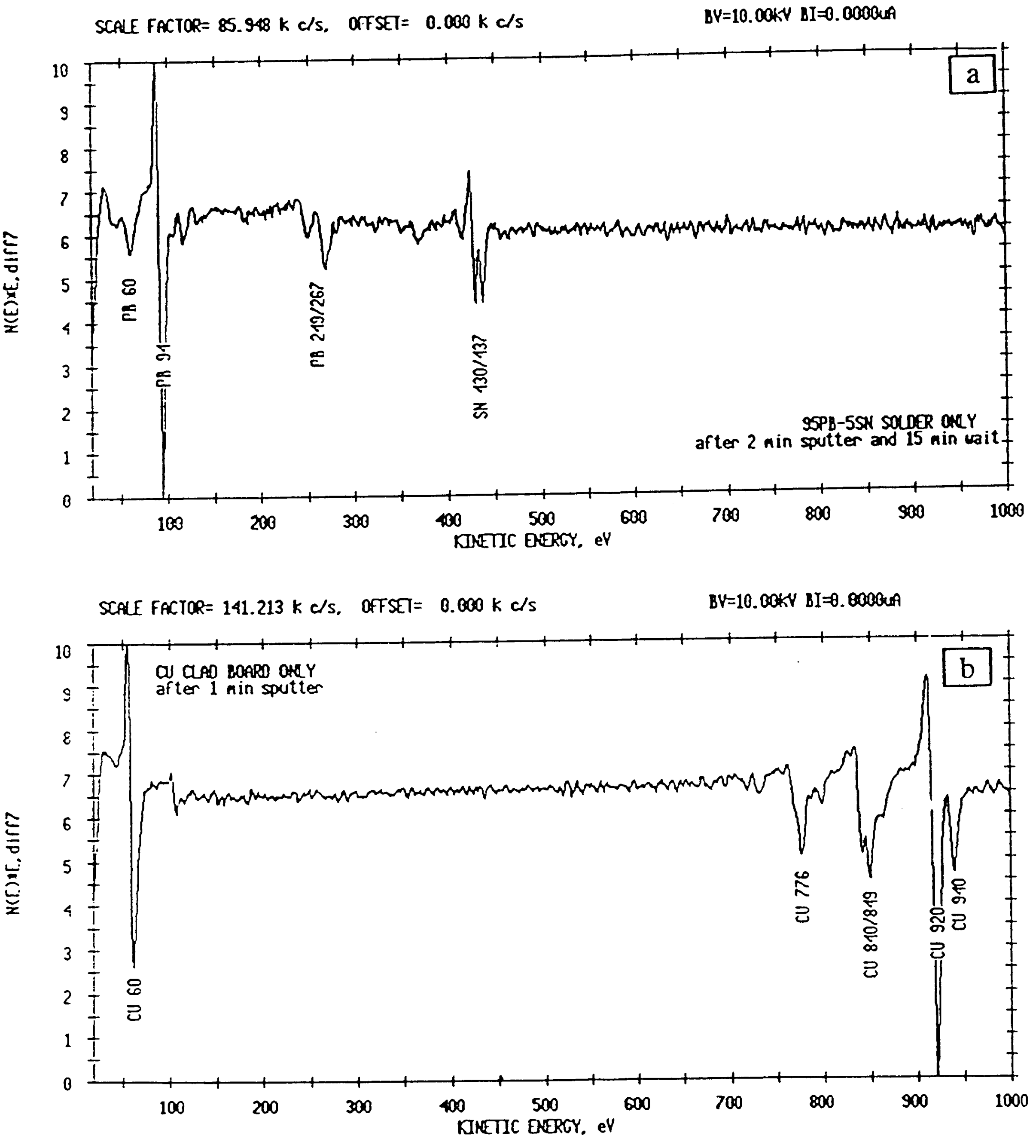


Figure 6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7
6
5
4
3
2
1
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PB 60
PB 94
PB 249/267
SN 430/437
95PB-5SN SOLDER ONLY
after 2 min sputter and 15 min wait
100
200
300
400
500
600
700
800
900
1000
KINETIC ENERGY, eV
SCALE FACTOR= 141.213 k c/s, OFFSET= 0.000 k c/s
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b
CU CLAD BOARD ONLY
after 1 min sputter
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10
9
8
7
6
5
4
3
2
1
0
CU 60
CU 776
CU 840/849
CU 920
CU 940
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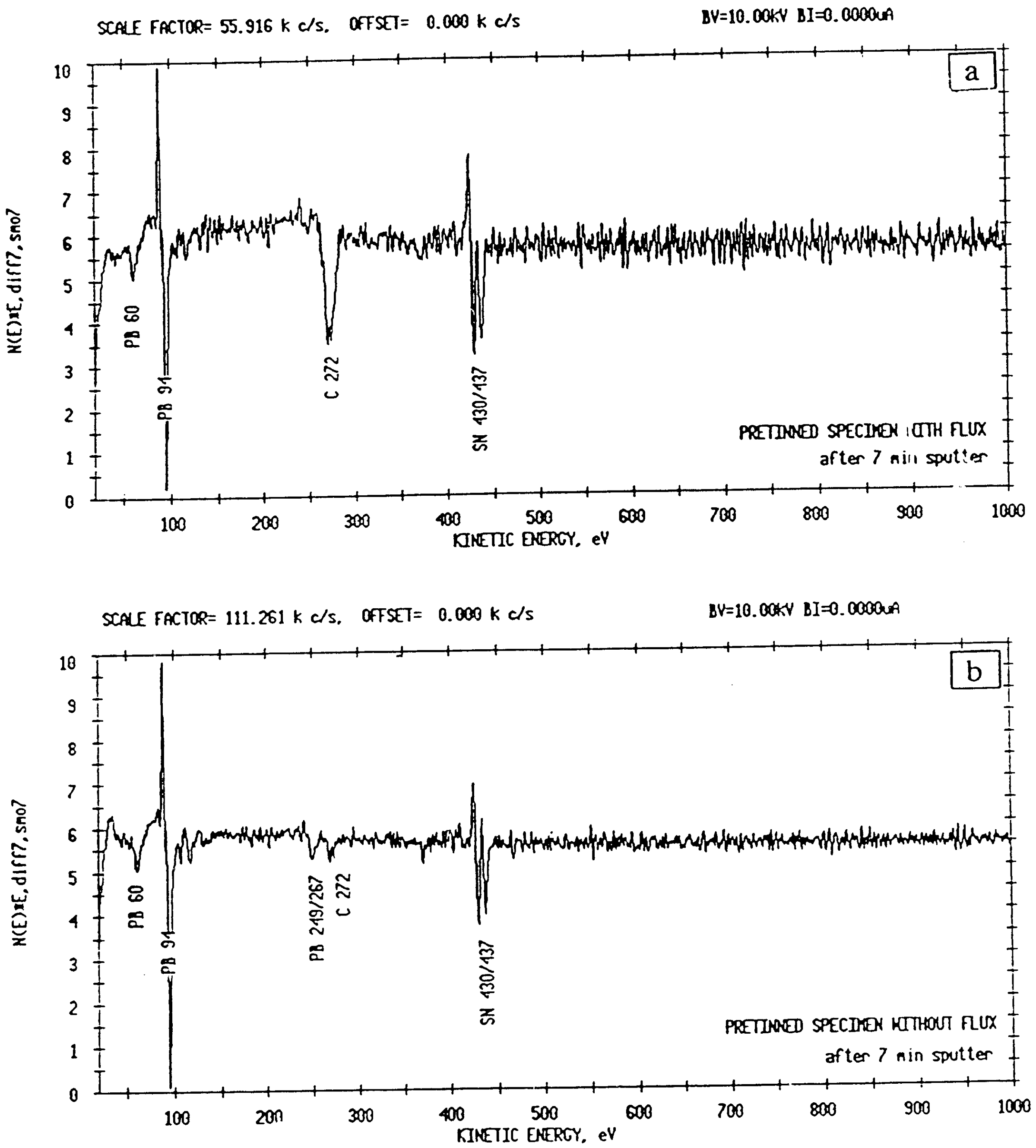
KINETIC ENERGY, eV

Figure 7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PB 60
PB 94
C 272
SN 430/437
PRETINNED SPECIMEN WITH FLUX
after 7 min sputter
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200
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400
500
600
700
800
900
1000
KINETIC ENERGY, eV
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0
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PB 94
PB 249/267
C 272
SN 430/437
PRETINNED SPECIMEN WITHOUT FLUX
after 7 min sputter
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400
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KINETIC ENERGY, eV

Figure 8

END

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