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Pull-out 시험 후의 표면분석 : 갈색산화물

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Analyses of Fracture Surfaces after Pull-out Test: Brown Oxide

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Abstract

Due to naturally formed copper oxides, the adhesion strength between copper and epoxy resin is often very poor. To improve the adhesion strength between copper and epoxy resin, Cu-based leadframe sheets were oxidized in a brown-oxide forming solution. Then the effect of brown-oxide formation on the adhesion strength of leadframe to epoxy molding compound (EMC) was studied using pull-out specimens. After the pull-out test, fracture surfaces were analyzed using SEM, AES and EDS to determine failure path. The results showed that the failure path lay over inside the CuO and inside the EMC irrespective of the pull strength.

1. INTRODUCTION

In the case of plastic packages, the durability of adhesion between Cu-based leadframe and EMC (epoxy molding compound) is of great importance for package reliability[1-3]. Unfortunately, however, the adhesion strength between copper and epoxy resin is very weak, not only because a copper oxide degrades the epoxy resin at high temperature[4-7], but because the mechanical strength of copper oxide is inherently very weak. According to the previous study[8], the weak nature of the oxide strength Can be attributed to the formation of microvoids at the Cu/Cu_2O interface.

In the real packaging processes, the copper oxidation occurs predominantly due to elevated temperature processes, for instance, die attach, die-bond adhesive curing, and wire bonding process. What is worse, the mechanical strength of the copper-oxide layer formed at high temperature is weaker than that of the copper-oxide layer formed at room temperature[9]. This is because the

growth of microvoids along the Cu/oxide interface as the degree of oxidation increased[8]. However, the microvoid formation mechanism has not been fully establishedyet.

In order to improve the adhesion strength between Cu-based leadframe and EMC, various techniques have been studied[10-12]. In most cases, a good adhesion of metal to polymer has been obtained by the modification of metal surfaces.

In this work, a brown-oxide layer was formed on the leadframe surface before molding with EMC to improve the adhesion strength between Cu-based leadframe and EMC. Since the brown-oxide layer is composed of fine acicular oxide precipitates, it was expected to promote the adhesion strength by mechanical interlocking with epoxy resin in the EMC. The adhesion strength of leadframe/EMC interface was measured in terms of pull strength through pull-out test, and the fracture surfaces were analyzed to find out the failure path by SEM (secondary electron spectroscopy), AES (Auger electron spectroscopy) and EDS (Electron Dispersive Spectroscopy).

2. EXPERIMENTAL PROCEDURE

Cu-based leadframe (commercial name: EFTEC-64T) sheets with the nominal composition of Cu-0.3 Cr-0.25 Sn-0.2 Zn (wt%) and thickness of 0.15 mm were used. Organic impurities on the leadframe surface were removed by ultrasonic cleaning in Acetone for 20 minutes and subsequently native oxides on the leadframe surface were removed by the pre-treat ment solution (commercial name : Activan #6 offered by Han Yang Chemical Ind. Co. Korea). After the pre-conditioning, leadframe sheets were immersed in a hot alkaline solution to form brown-oxide layer on the surface[6]. Oxidation time was typically less than 20 minutes. The oxide layers formed on the leadframe surfaces were analyzed by SEM, TEM (transmission electron microscopy) and glancing-angle XRD (X-ray diffractometry). The thickness of the oxide layer was measured by using galvanostatic reduction method[13-15].

After the oxidation treatment, leadframe sheets were compounded with EMC (commercial name : DMC-20 offered by Dong Jin Chemical Co. Ltd. Korea) in a compression molding under 175℃/6.5MPa condition for 15 minutes. After the molding with EMC, the molded bodies were machined into the pull-out specimens. A schematic diagram of pull-out specimen is shown in Fig. 1. After the machining, all specimens were post-cured at 175 ℃ for 4 hours. Because the epoxy is a thermosetting polymer, post-curing is needed to complete the polymerization reaction.

Mechanical tests were carried out at the ambient conditions on the screw-driven Instron

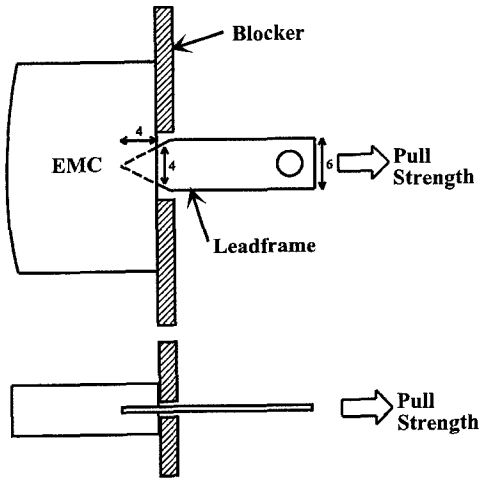


Fig. 1. A schematic diagram showing the geometry of a pull-out specimen.

(Model 4206) with the cross-head speed of 0.5 mm/min, and the critical loads to onset of fracture were recorded to calculate the pull strength, *PS*.

$$PS = \frac{Pc}{A} \quad (1)$$

where, *Pc* is a critical load and *A* is the contact area between leadframe and EMC.

Pull-out test has been considered as a handy method for the evaluation of the adhesion strength of leadframe/EMC interface[9,16-18].

3. RESULTS AND DISCUSSION

3. 1. Oxidation Characteristics

Scanning electron micrographs of oxidized leadframe surfaces treated in the brown-oxide forming solution are presented at various oxidation times.[19] Parallel strips, which were believed to have been formed during the cold rolling processes, were seen from the untreated leadframe surface and were well preserved even up to 20 minutes in the low magnification images. As soon as the oxidation treatment began, fine acicular precipitates started to nucleate on the leadframe surface and covered the entire surface in a few seconds. With all further oxidation, the size and the density of the precipitates increased slightly and remained more or less the same after 2 minutes. By subsequent X-ray analyses and thickness measurement, the fine acicular precipitates proved to be cupric oxide (CuO) and the average thickness of the oxide layer increased until around 2 minutes and remained at around 150 nm[19]. The CuO precipitates were observed to stop further nucleation once they formed a continuous layer on the leadframe surface.

3. 2. Pull Strength

As brown-oxide layer formed on the leadframe surface, the pull strength (*PS*) increased with oxidation time at the initial stage of oxidation. The results of the pull-out test are shown in Fig. 2. For untreated leadframe samples (oxidation time, $t=0$), *PS* was 9 MPa even though nearly mode-I interfacial fracture toughness, G_{IC} was close to zero[20]. This is presumably caused by the mismatch in the CTE (coefficient of thermal expansion) between leadframe and EMC[20]. Once the oxidation treatment started, however, *PS* increased rapidly with the oxidation time and reached the saturation value of around 23 MPa after 1 minute. This is believed to result from the CTE mismatch and the adhesion mechanism (mechanical interlocking).

A cross-sectional TEM micrograph was taken from the 20-minute-oxidized leadframe sheet and presented in Fig. 3. The CuO needles and the gaps among the CuO needles are seen. The real length of CuO needles was estimated at more than

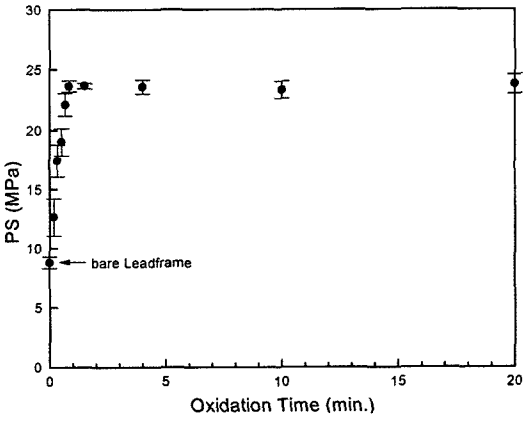


Fig. 2. Variation of pull strength between Cu-based leadframe and EMC with oxidation time.

Fig. 3. A cross-sectional TEM micrograph of 20-minute-oxidized leadframe sheet.

0.5 μm on the basis of this TEM micrograph. Comparing between the average thickness of CuO layer measured by using galvanostatic reduction method, 0.15 μm[19], and the real length of CuO needle, 0.5~0.8 μm, it is instantly clear that most part of CuO layer (browh-oxide layer) is filled with gaps. Such gaps may play an important role in the penetration of epoxy resin. This is the reason why the mechanical interlocking is achieved between CuO needles and epoxy resin during the molding process.

According to the previous section, the oxide layer thickened to around 150nm until about 2 minutes and further oxidation did not increase the thickness of the oxide layer. When the oxidation time was 1 minute, the thickness of the oxide layer was about 100 nm. Note that the measured thickness of the oxide layer by using galvanostatic reduction method is average value and there are a lot of empty spaces (gaps) among CuO needles.

Therefore, the reason why the PS was saturated at around 1 minute is presumed to be as follows. Even though the average thickness of the oxide layer is 100 nm, it may be good enough to give rise to maximum PS owing to the mechanical interlocking and the adhesion enhancement by CTE mismatch[20].

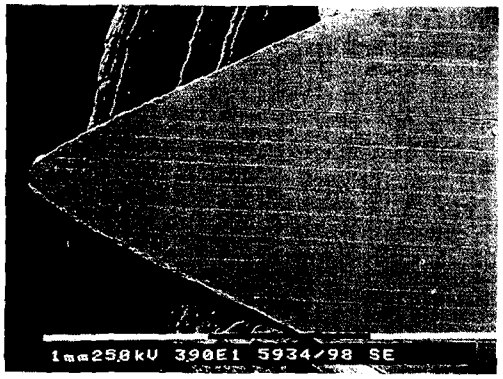
It seems that the overall trend is more or less similar to that of SDCB (Sandwiched Double-Cantilever Beam) specimens[20], but it is notable that PS is saturated slightly earlier than G_{IC}. Such Slightly different results can be ascribed to the dissimilar nature between two test methods[20]
In case of pull-out test, the extra friction-force induced by CTE mismatch is acting on the leadframe/EMC interface, thus the apparent adhesion strength measure by pull-out test is higher as compared with that measured by SDCB test. Moreover, the different nature of stresses acting on the leadframe/EMC interface may during the mechanical test contributed to the slightly different characteristics.

3. 3. Analyses of Fracture Surfaces

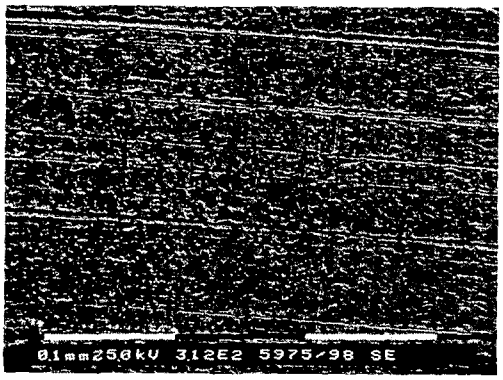
The adhesion strength is closely related to the fracture behavior, and the fracture behavior is dictated by the material failure mechanisms. Consequently, the adhesion strength must be concerned with the material aspect of failure. A vital aspect of that concern is fractography, in part because of the information which can be provided the details of the fracture process. The characterization of the fracture surface may comprise nothing more than assignment of a descriptive term called *failure path*, although even that assignment may pose a complex problem. A process of great significance in most cases is the discovery or identification of individual features on the fracture surface which may provide clues or pointers to the fracture process itself. This section deals with the accurate interpretation of the fracture surface appearance.

In the first place, the fracture surfaces with various PS were examined by SEM. Fig. 4 shows the SEM micrographs of the separated leadframe side oxidized for 30 seconds before molding. In Fig. 4(b), parallel scratches are readily found, which are considered to be formed during the mechanical test. In magnified micrographs (Fig. 4 (b) and (c)), it is notable that there are a lot of debris presumed to come from the EMC side. To confirm this, AES analysis was conducted on the separated leadframe side and the results are presented in Fig. 5. Since a carbon element can be introduced on the surface by contamination, it is necessary to confirm whether the carbon element came from surface contamination or not by Ar ion sputtering for 0.2 minute. The surface contamination can be removed by 0.2 minute Ar ion sputtering. A large amount of carbon element and oxygen element were detected even after 0.2 minute of Arion sputhering. This result represents that the carbon element detected here are evidently from epoxy resin, therefore the cohesive failure of EMC was predominantly occurred. Such a fracture behavior was well preserved until 20 minutes, which is shown in Fig. 6.

On the other hand, the examination of the separated EMC side was carried out by SEM, and at the same time copper mapping images were acquired by EDS. The copper mapping images provide us the information about the copper element distribution on the surface. The results are presented



(a)



(b)

(c)

Fig. 4. SEM micrographs of the separated leadframe side : The oxidation time of the leadframe before molding was 30 seconds. (b) and (c) are magnified images of (a) and (b), respectively.

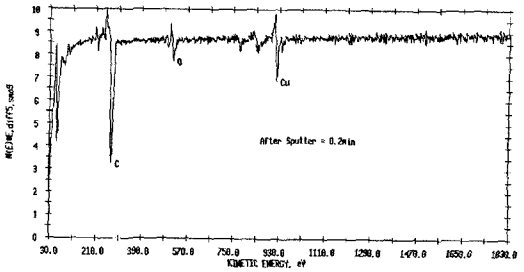
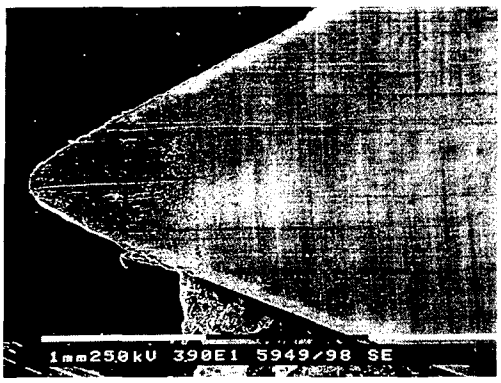


Fig. 5. AES survey of the separated leadframe side : The oxidation time of the leadframe before molding was 30 seconds.

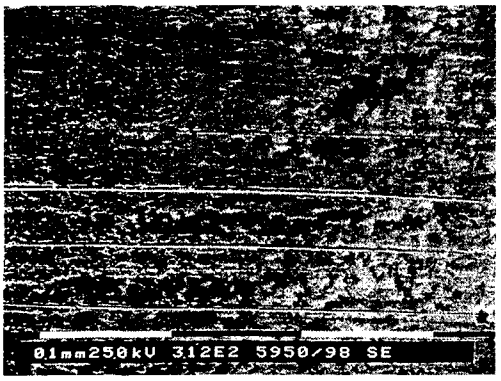
in Figs. 7 and 8 for leadframes oxidized before molding for 30 seconds and 20 minutes, respectively. A number of micro-cracks were seen from the separated EMC side, which were presumed to be formed during the pull-out test. The distribution of copper element was somewhat uniform, which indicates that the CuO needles were broken during the pull-out test, therefore broken needles were remained on the separated EMC side. These microstructural characteristics and copper distribution features were maintained until 20 minutes.

3. 4. Failure Path

From the results of the analyses of the fracture surfaces, it was revealed that the failure path was not changed with the PS because the failure path of the specimen with the PS of 19 MPa (t =30 seconds) was the same that of the specimen with the PS of 23 MPa (t =20 minutes). In addition, it was also revealed that the fracture occurred in a mixed cohesive mode so that the failure path lay over inside the CuO needles and inside the EMC. The schematic diagrams delineating the failure path is shown in Fig. 9.



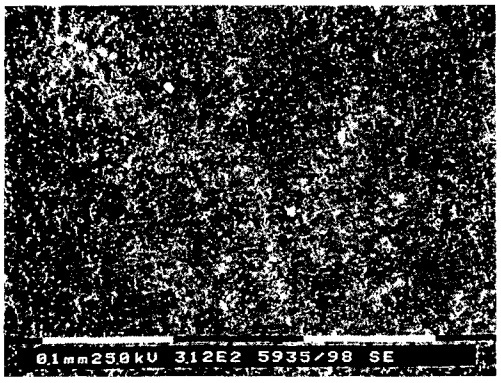
(a)



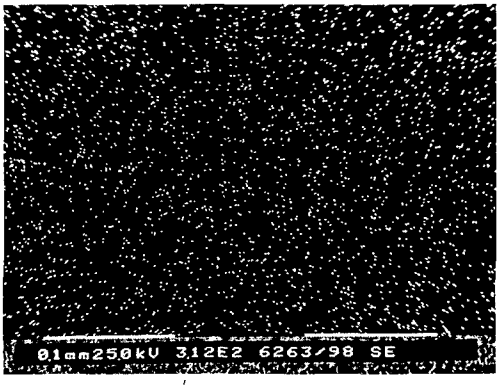
(b)

(c)

Fig. 6. SEM micrographs of the separated leadframe side : The oxidation time of the leadframe before molding was 20 minutes. (b) and (c) are magnified images of (a) and (b), respectively.



(a)



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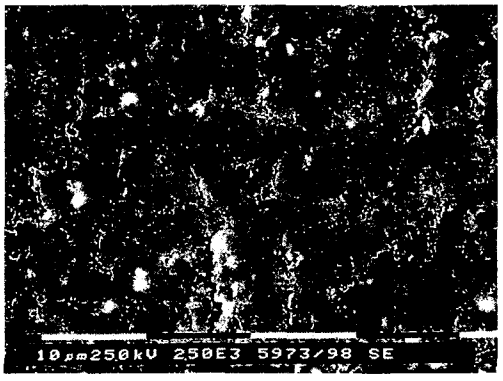
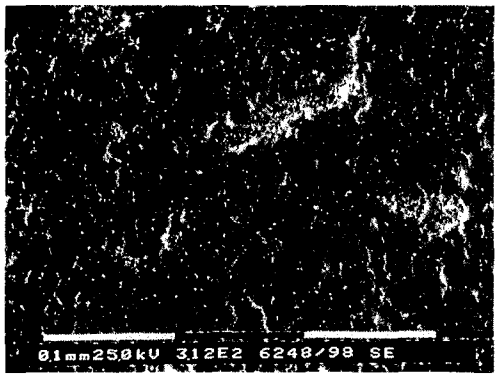


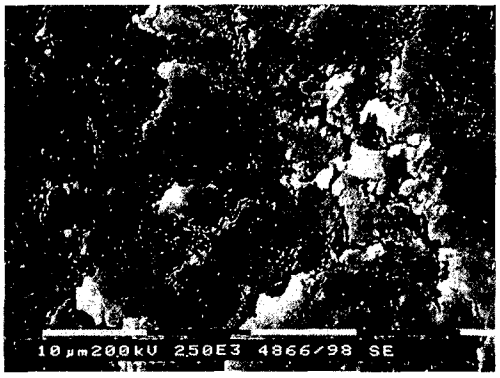
(c)

Fig. 7. SEM micrographs of the separated EMC side : The oxidation time of the leadframe before molding was 30 seconds. (b) and (c) are Cu-mapping image and magnified image of (a), respectively.



(a)

(b)



(c)

Fig. 8. SEM micrographs of the separated EMC side : The oxidation time of the leadframe before molding was 20 minutes. (b) and (c) are Cu-mapping image and magnified image of (a), respectively.

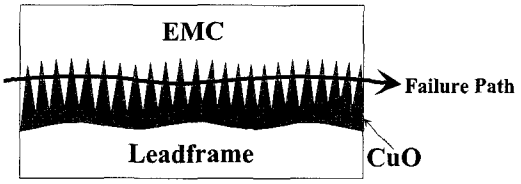


Fig. 9. A schematic diagram describing failure path.

4. CONCLUSIONS

Oxidation of Cu-based leadframe in a hot alkaline solution introduced the brown-oxide layer on the surface. Pull-out specimens were employed to know the effect of the brown-oxide formation on the adhesion strength between leadframe and EMC. After the pull-out test, the fracture surfaces were analyzed systematically using various equipments to unveil the failure path. The pull strength showed an abrupt increase to the saturation value of 23 MPa until 1 minute of the oxidation time and the failure path lay over inside the CuO and inside the EMC irrespective of the pull strength. This can be attributable to the fine acicular shape of CuO precipitates, which may play an important role in the adhesion to the EMC by mechanical interlocking.

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