한국표면공학회지
J. Kor. Inst. Surf. Eng.
Vol. 36, No. 4, 2003.
<연구논문>

Irregular Failures at Metal/Polymer Interfaces

Ho-Young Lee

School of Mechanical and Aerospace Engineering, Seoul National University,
Seoul 151-744, Korea.

(Received 27 June, 2003 ; accepted 13 August, 2003)

Abstract

Roughening of metal surfaces frequently enhances the adhesion strength of metals to polymers by mechanical interlocking. When a failure occurs at a roughened metal/polymer interface, the failure prone to be cohesive. In a previous work[1)], an adhesion study on a roughened metal (oxidized copper-based leadframe)/polymer (Epoxy Molding Compound, EMC) interface was carried out, and the correlation between adhesion strength and failure path was investigated. In the present work, an attempt to interpret the failure path was made under the assumption that microvoids are formed in the EMC as well as near the roots of the CuO needles during compression-molding process. A simple adhesion model developed from the theory of fiber reinforcement of composite materials was introduced to explain the adhesion behavior of the oxidized copper-based leadframe/EMC interface and failure path. It is believed that this adhesion model can be used to explain the adhesion behavior of other similarly roughened metal/polymer interfaces.

Keywords : Metal, Leadframe, Oxidation, Polymer, Epoxy, EMC, Adhesion, Mechanical interlocking

1. INTRODUCTION

Copper-based leadframes provide many advantages such as good thermal and electrical performance, and cost effectiveness[2)]. Copper-based leadframes are, however, susceptible to popcorn cracking during the soldering process on the PCB (Printed Circuit Board) due to poor adhesion between copper and EMC (Epoxy Molding Compound)[3)].

To obtain good reliability with copper-based leadframe, prevention of package delamination and cracking are the greatest challenges[4)]. The critical issue for package reliability during reflow soldering is improving adhesion at the copper-based leadframe/EMC interface. A number of attempts on the adhesion improvement between the copper-based leadframe and the EMC have been made[1)].

In a previous work[1)], brown-oxide treatment on the copper-based leadframe was carried out to enhance the adhesion strength between the copper-based leadframe and the EMC, and the strength of the brown-oxide-coated copper-based leadframe/EMC interface was measured in terms of fracture toughness by using sandwiched double-cantilever beam (SDCB) specimens. After the adhesion tests, fracture surfaces (separated leadframe surfaces and separated EMC surfaces) were analyzed by SEM, AES, EDS and AFM to make the failure path clear. The results showed that two types of irregular failures occurred at the interface.

In the present work, an attempt to explain why the irregular failures occurred at the brown-oxide-coated copper-based leadframe/EMC interface was made based on the assumption that microvoids are formed during compression-molding process and on the simple adhesion model developed from the theory of fiber reinforcement of composite materials.

2. FAILURE PATHS

Analyses of the fracture surfaces using SEM, AES, EDS and AFM showed that irregular failures of the brown-oxide-coated copper-based leadframe/EMC interface occurred[1)]. There are two types of irregular failures. When the oxidation time is below 2 minutes, failure occurred near the quasi-macroscopic CuO/

---

*Corresponding author. E-mail : hlee@snu.ac.kr

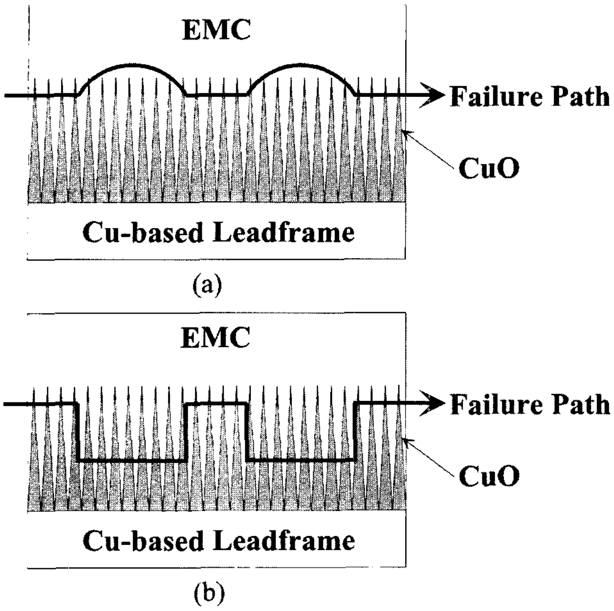


Fig. 1. Schematic illustrations of failure paths for the brown-oxide-coated copper-based leadframe/ EMC joints and their corresponding fracture surfaces. (a) A-type irregular failure, and (b) B-type irregular failure.

EMC interface on the non-debris region of the separated leadframe side in a nearly interfacial mode and occurred inside the EMC on the clod-like debris region of the separated leadframe side in a cohesive mode. The failure occurred at the oxidation times of below 2 minutes was named as '*A-type irregular failure*'. On the other hand, when the oxidation time is more than 2 minutes, failure occurred near the quasi-macroscopic CuO/EMC interface on the convex regions of the separated leadframe side in a nearly interfacial mode and occurred inside the CuO layer on the concave regions of the separated leadframe side in a cohesive mode, respectively. The failure occurred at the oxidation times more than 2 minutes was named as '*B-type irregular failure*'. Schematic diagrams delineating the failure paths are shown in Fig. 1.

3. ADHESION MODEL

According to another previous work[5)], the brown oxide proved to be composed of merely CuO precipitates and the CuO precipitates have an acicular shape. Acicular shape of the CuO precipitates plays a key role in the adhesion of the brown-oxide-coated copper-based leadframe to EMC. The acicular shape of the CuO precipitates can be confirmed by the cross-sectional transmission electron micrograph of brown-oxide-coated copper-based leadframe shown in Fig. 2.

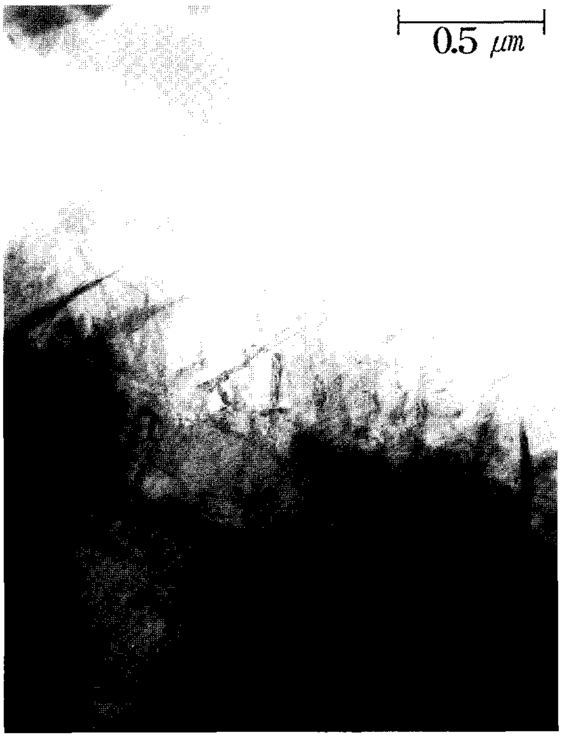


Fig. 2. Cross-sectional transmission electron micrograph of brown-oxide-coated copper-based leadframe. The oxidation time of copper-based leadframe before molding with EMC is twenty minutes.

Based on the acicular shape of the CuO precipitates, it is sufficiently enough to take mechanical interlocking as a main adhesion mechanism between the CuO precipitates and the EMC. When the brown-oxide-coated copper-based leadframe is molded with the EMC, the epoxy resin included in the EMC penetrates into the gaps among the CuO needles. Then, the mechanical interlocking between the CuO needles and the EMC is attained. However, due to the high viscosity of epoxy and the limited wetting angle of the epoxy resin to the CuO, the unoccupied space called microvoids must be formed near the roots of the CuO needles. Furthermore, since we used a compression-molding system instead of a transfer-molding system, there must be trapped air in the EMC near the CuO/EMC interface in the state of microvoids. The presence of the microvoids near the CuO/EMC interface can be confirmed by the cross-sectional transmission electron micrograph of the EMC molded brown-oxide-coated copper-based leadframe shown in Fig. 3.

Apart from the actual situation, the CuO/EMC interface can be simplified as illustrated in Fig. 4(a). The simplified CuO/EMC interface includes only an interlocking zone, Z, defined as in the Fig. 4(a). The

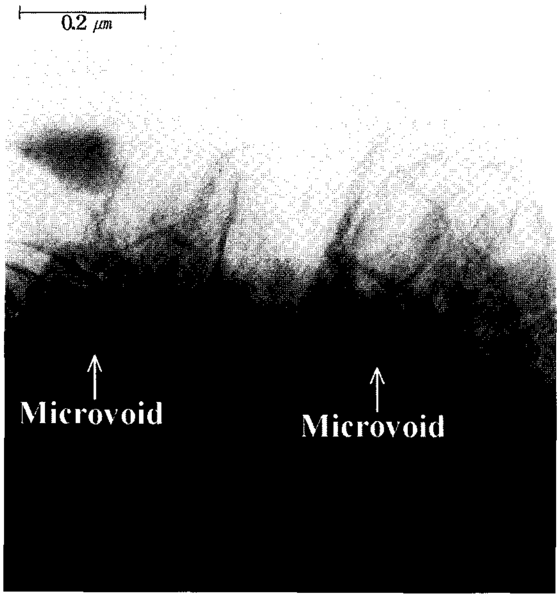
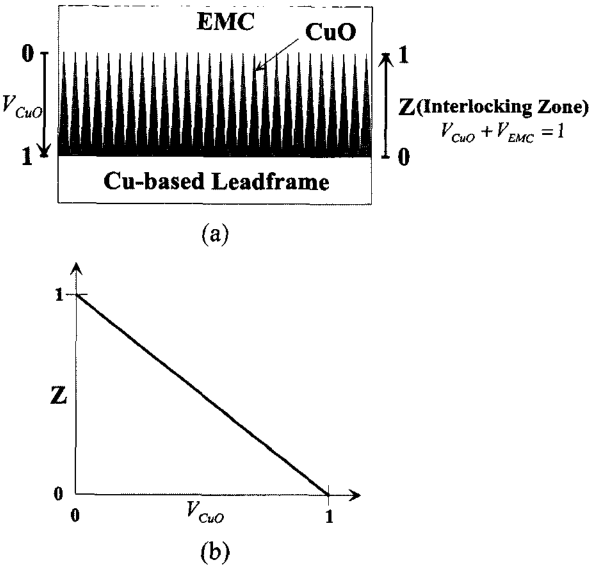


Fig. 3. Cross-sectional transmission electron micrograph of brown-oxide-coated copper-based leadframe molded with EMC. The oxidation time of copper-based leadframe before molding with EMC is twenty minutes.



(a)

(b)

Fig. 4. (a) Simplified CuO/EMC interface. (b) Relationship between interlocking zone range, 'Z' and the volume fraction of the CuO needles, V_{CuO}.

interlocking zone length, Z, varies from zero to unity. The interlocking zone was introduced to consider the mechanical interlocking between the CuO needles and the EMC. Actually the CuO needles are tilted as can be seen from Fig. 3, which appears to be attributable to the molding pressure applied during the compression-molding process. However, the degree of tilting is not serious, it is not out of reason to simplify the CuO/EMC interface as presented in Fig. 4(a). The interlocking zone can be regarded as a polymer matrix composite material: the matrix is the EMC (epoxy) and the fiber is the CuO needle. If the z-axis is set normal to the quasi-macroscopic CuO/EMC interface and there are no microvoids near the root of the CuO needles (complete molding assumption), then, the volume fraction of the CuO needles, V_{CuO}, varies in this manner: when $Z = 0$, $V_{CuO} = 1$ and when $Z = 1$, $V_{CuO} = 0$ (see Fig. 4(b)).

A simple micromechanical model for longitudinal tensile strength of a composite material can be developed from the '*rule-of-mixtures*'. For a composite containing continuous fibers, unidirectionally aligned and loaded in the fiber direction (isostrain condition), we can write for the stress in the composite

$$\sigma_{comp} = \sigma_{CuO}V_{CuO} + \sigma_{EMC}(1 - V_{CuO}) \qquad (1)$$

where σ is the axial stress acting parallel to the fiber direction, V is the volume fraction, and the subscripts, *comp*, *CuO*, and *EMC* refer to composite, CuO, and EMC, respectively. Kelly and Davies[6)] showed that a composite must have a certain minimum fiber volume fraction, $V_{CuO}^{\min}$, to obtain actual reinforcement by fibers. This is because below the minimum volume fraction there is an insufficient number of fibers to effectively restrain the elongation of the matrix, so the fibers are rapidly stressed to their fracture point. Assuming that the fibers are all identical and uniform, that is, all fibers have the same ultimate tensile strength, we can calculate the ultimate tensile strength of the composite, σ_{comp}^{UTS}, that will be ideally attained at the strain at which fibers fracture. Thus we can write from Eq. (1)

$$\sigma_{comp}^{UTS} = \sigma_{CuO}^{UTS}V_{CuO} + \sigma_{EMC}^{flow}(1 - V_{CuO}) \quad V_{CuO} > V_{CuO}^{\min} \qquad (2)$$

where σ_{CuO}^{UTS} is the ultimate tensile stress of the fiber in the composite and σ_{EMC}^{flow} is the flow stress of the matrix at the strain corresponding to the ultimate tensile strength of fiber (see Fig. 5(a)). At very low fiber volume fractions, a work-hardened polymer matrix can counterbalance the loss of load-carring capacity as a result of fiber fracture. At such low V_{CuO}, the matrix controls the composite strength. If all the fibers break at the same time, we must satisfy the following relationship in order to attain real fiber strengthening;

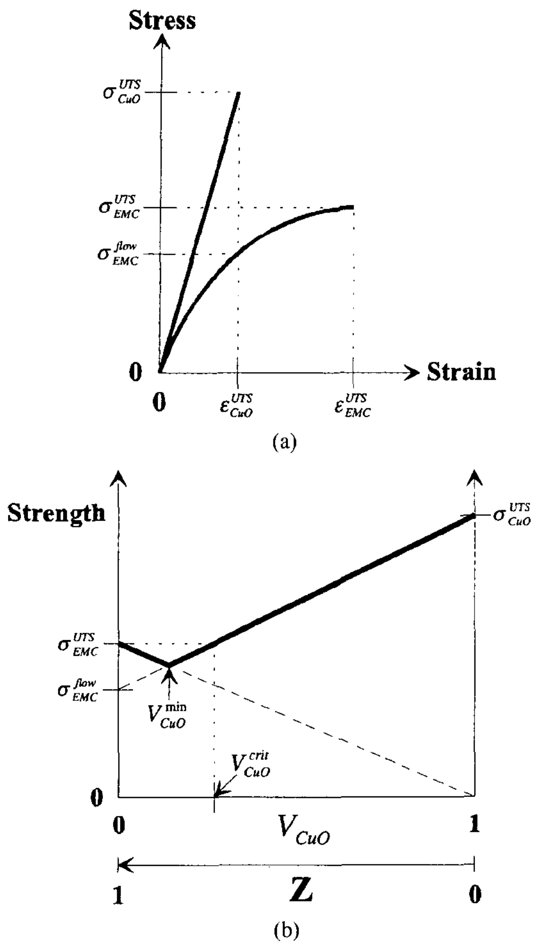


Fig. 5. (a) Stress-strain curves of the CuO and the EMC. (b) Correlation between the strength of the CuO-EMC composite and the volume fraction of the CuO needles, V_{CuO}. Interlocking zone range, 'Z' is also considered.

$$\sigma^{UTS}_{comp} = \sigma^{UTS}_{CuO} V_{CuO} + \sigma^{flow}_{EMC}(1 - V_{CuO}) \geq \sigma^{UTS}_{EMC}(1 - V_{CuO}) \tag{3}$$

where σ^{UTS}_{EMC} is the ultimate tensile strength of the matrix. The equality in this expression gives the minimum fiber volume fraction, $V^{\min}_{CuO}$, which increases with decreasing fiber strength.

In reality, we want the composite strength to be greater than the matrix ultimate strength in isolation. For this to be true, we can define a critical fiber volume fraction, V^{crit}_{CuO}, that must be exceeded. Thus

$$\sigma^{UTS}_{comp} = \sigma^{UTS}_{CuO} V_{CuO} + \sigma^{flow}_{EMC}(1 - V_{CuO}) \geq \sigma^{UTS}_{EMC} \tag{4}$$

From the equality in Eq. (4)

$$V^{crit}_{CuO} = \frac{\sigma^{UTS}_{EMC} - \sigma^{flow}_{EMC}}{\sigma^{UTS}_{CuO} - \sigma^{flow}_{EMC}} \tag{5}$$

V^{crit}_{CuO} increases with increasing degree of matrix work-hardening $(\sigma^{UTS}_{EMC} - \sigma^{flow}_{EMC})$. Figure 5(b) shows the graphically determined $V^{\min}_{CuO}$ and V^{crit}_{CuO}. It is noticed that V^{crit}_{CuO} is greater than $V^{\min}_{CuO}$ because σ^{UTS}_{CuO} is greater than σ^{UTS}_{EMC}.

According to the above-mentioned simple micromechanical model for longitudinal tensile strength of a composite material developed based on the '*rule-of-mixtures*', the longitudinal tensile strength of a composite material varies with V_{CuO}, and it is notable that the weakest point which has a minimum strength surely exists somewhere in the interlocking zone satisfying $V_{CuO} = V^{\min}_{CuO}$ (see Fig. 6).

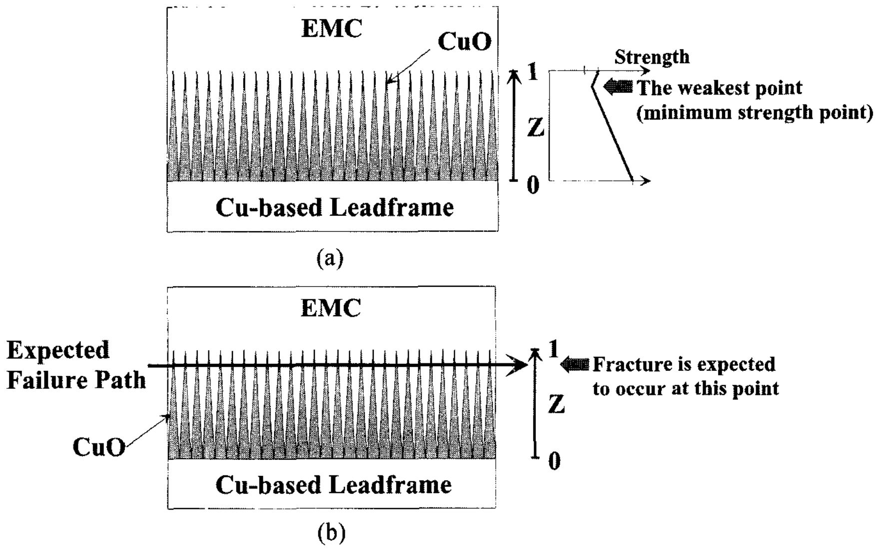


Fig. 6. Failure path expectation based on the simple micromechanical model for longitudinal tensile strength of a composite material developed from on the '*rule-of-mixtures*'. (a) The weakest point which has a minimum strength surely exists somewhere in the interlocking zone satisfying $V_{CuO} = V^{\min}_{CuO}$. (b) Failure path can be expected based on the existence of the weakest point.

4. A-TYPE IRREGULAR FAILURE

The experimental results revealed that when the oxidation time is below 2 minutes, failure occurred near the quasi-macroscopic CuO/EMC interface on the non-debris region of the separated leadframe side in a nearly interfacial mode and occurred inside the EMC on the clod-like debris region of the separated leadframe side in a cohesive mode. This type of irregular failure was named as '*A-type irregular failure*' for convenience.

In the case of the failure occurrence inside the EMC on the clod-like debris region of the separated leadframe side in a cohesive mode, it can be thought that the EMC near the quasi-macroscopic CuO/EMC interface is inherently very weak, and the interface cracks propagate along the weak EMC near the quasi-macroscopic CuO/EMC interface because cracks always select the weakest propagation path. Since the powdered EMC was used for molding and a compression-molding system was used instead of a transfer-molding system, there must be trapped air in the EMC, and the gaps among the CuO needles exist. At the initial stage of oxidation, however, due to the short length of CuO needles[5)] there is not enough room for microvoids formation near the roots of the CuO needles. Accordingly the air initially trapped in the gaps among the CuO needles may move into the EMC near the quasi-macroscopic CuO/EMC interface during compression-molding process due to the penetration of epoxy resin into the gaps among the CuO needles. The loss of air trapping among the CuO needles indicates almost no formation of microvoids in the CuO layer, which means that actually there is no strength loss of the CuO-EMC composite. It is well known that voids in solids weaken the strength of the solids because the solids with voids tend to behave like porous materials. As a rule, the strength of porous materials is lower than that of firm materials. The microvoids in the EMC near the quasi-macroscopic CuO/EMC interface formed by air trapping may coalesce each other due to the hydrostatic stress field arises from the molding pressure during the compression-molding process. Eventually, the coalescence of microvoids may form microscopic cracks in the EMC near the quasi-macroscopic CuO/EMC interface. The migration of air initially trapped in the gaps among the CuO needles into the EMC near the quasi-macroscopic CuO/EMC interface during compression-molding process may cause formation of excess amount of microvoids in the EMC near the quasi-macroscopic CuO/EMC interface. This indicates the local weakening of EMC near the quasi-macroscopic CuO/EMC interface, thus failure is likely to occur in the EMC near the quasi-macroscopic CuO/EMC interface because cracks always select the weakest propagation path. This supports the failure occurrence inside the EMC on the clod-like debris region of the separated

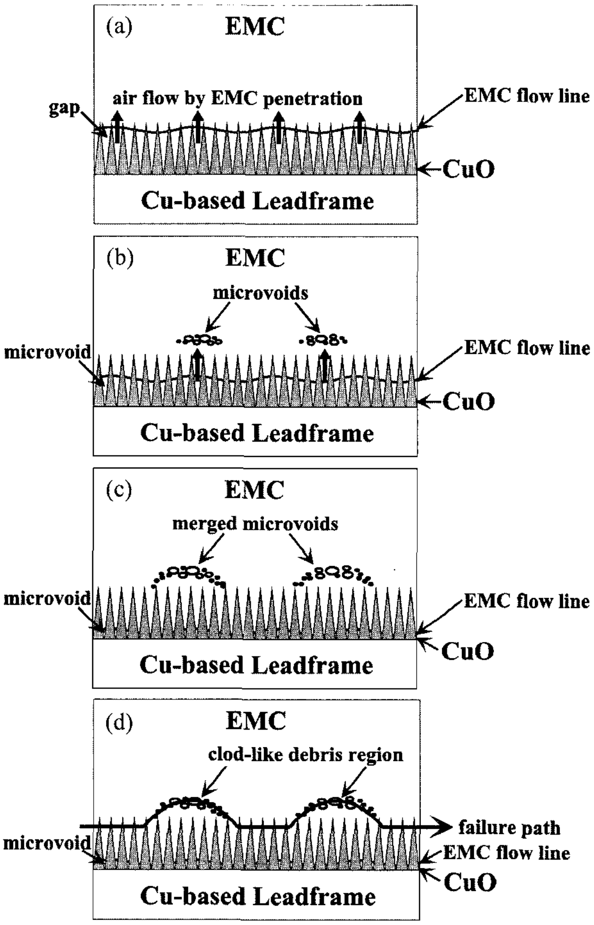


Fig. 7. Schematic diagrams illustrating the failure occurrence inside the EMC on the clod-like debris region in a cohesive mode. (a) As the epoxy resin included in the EMC penetrates into the gaps among the CuO needles, the air trapped in the gaps move into the EMC. (b) As the amount of the air in the EMC increases, microvoids are formed in the EMC. (c) As the compression-molding process goes on, the microvoids coalesce each other and finally compression-molding process is completed. (d) Eventually, the united microvoids may form microscopic cracks in the EMC near the quasi-macroscopic CuO/EMC interface, which indicates the local weakening of EMC near the quasi-macroscopic CuO/EMC interface, thus failure is likely to occur inside the EMC near the quasi-macroscopic CuO/EMC interface because cracks always select the weakest propagation path.

leadframe side in a cohesive mode. The microvoids in the EMC can be seen on the fracture surfaces of the separated EMC sides[1]. The overall situation is delineated in Fig. 7.

On the other hand, in the case of the failure occurrence near the quasi-macroscopic CuO/EMC interface on the non-debris region of the separated leadframe side in a nearly interfacial mode can be explained by the simple micromechanical model for longitudinal tensile strength developed from the '*rule-of-mixtures*'. If there is no excess microvoids in the EMC near the quasi-macroscopic CuO/EMC interface and the roots of the CuO needles, according to the adhesion model developed based on the '*rule of mixtures*', it is expected that failure may occur somewhere in the interlocking zone that satisfies $V_{CuO} = V_{CuO}^{\min}$ (see Fig. 8) because failure always occurs at the weakest point. It was confirmed by XPS (X-ray Photoelelctron Spectroscopy) analyses. The XPS analyses of separated leadframe side as well as separated EMC side were carried out to investigate the amount of CuO on each side. The XPS analyses results are shown in Fig. 9. The XPS anayses were conducted for both before Ar ion sputtering for 30 seconds and after Ar ion sputtering for 30 seconds. The surface state of the before Ar ion sputtering for 30 seconds was as-received surface state which means there are contaminants from air such as CO_2, H_2O etc. on the surface. Thus it is actually impossible to know exactly how much CuO are on the as-received surfaces. The contaminants on the as-received surface can be eliminated by Ar ion sputtering for 30 seconds, and it becomes possible to get exact information on the surface. The XPS analyses results revealed that Ar ion sputtering was effective for removing contaminants and there was CuO on each separated side.

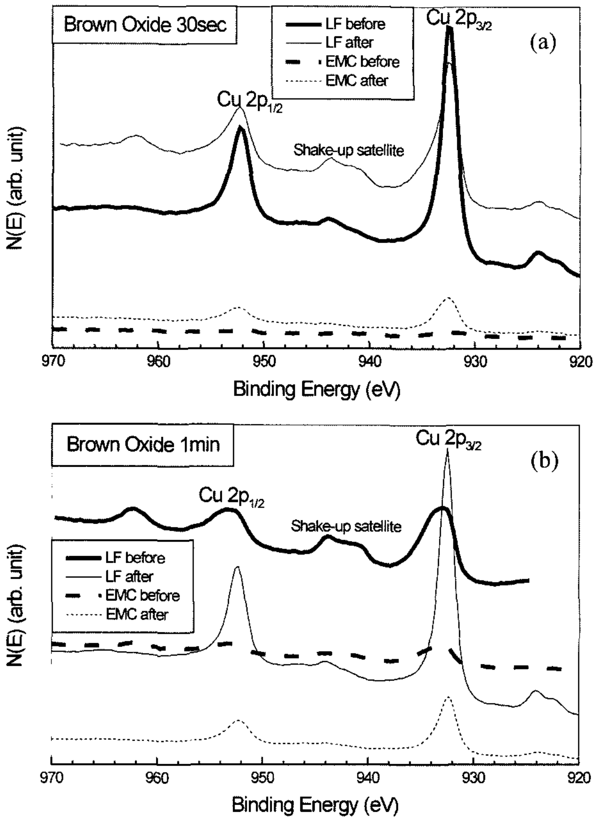


Fig. 9. XPS surveys of non-debris region of the separated leadframe sides and their counterparts, separated EMC sides. 'LF' means 'leadframe' and 'before' means 'before Ar ion sputtering for thirty seconds' and 'after' means 'after Ar ion sputtering for thirty seconds', respectively. (a) The oxidation time of copper-based leadframe before molding with EMC is thirty seconds. (b) The oxidation time of copper-based leadframe before molding with EMC is one minute.

Note that there is smaller amount of CuO on the separated EMC side as compared with the separated leadframe side. This implys that failure occurred

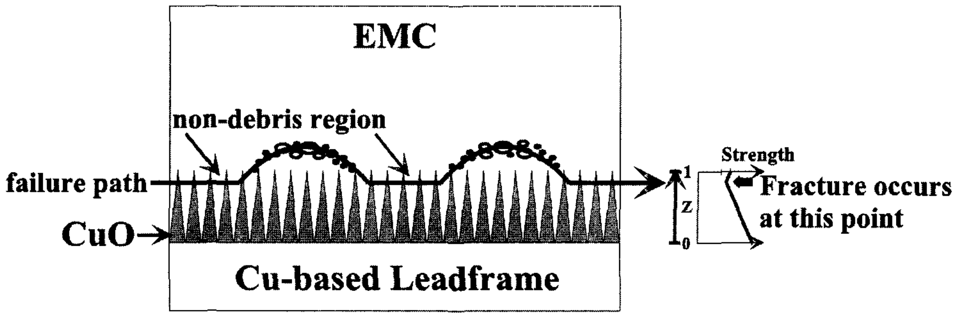


Fig. 8. Failure occurrence near the CuO/EMC interface on the non-debris region of the separated leadframe side and its comparison with the expected failure path based on the simple micromechanical model for longitudinal tensile strength of a composite material developed from the '*rule-of-mixtures*'. The weakest point which has a minimum strength surely exists somewhere in the interlocking zone satisfying $V_{CuO} = V_{CuO}^{\min}$ and failure is expected to occur at the weakest point.

somewhere in the interlocking zone that satisfies $V_{CuO} = V_{CuO}^{\min}$, thus the failure path lies near the quasi-macroscopic CuO/EMC interface with a little deviation from the tip of the CuO needle. In other words, owing to the failure near the quasi-macroscopic CuO/EMC interface with a little deviation from the tip of the CuO needle, it is clear that the amount of CuO is smaller on the separated EMC side than that on the separated leadframe side.

According to the previous work[5], at the initial stage of oxidation (the oxidation time is below 2 minutes) the fracture toughness of the brown-oxide-coated copper-based leadframe/EMC interface increased as the length of the CuO needles grew with a linearly proportional relationship. Aside from the microvoids in the EMC, this seems to be due to the ineffective mechanical interlocking between the CuO needles and the EMC owing to the short length of the CuO needles. On the other hand, the microvoids in the EMC appear to play an important role in the adhesion also at the initial stage of oxidation.

5. B-TYPE IRREGULAR FAILURE

When the oxidation time is more than 2 minutes, failure occurred near the quasi-macroscopic CuO/EMC interface on the convex regions of the separated leadframe side in a nearly interfacial mode and occurred inside the CuO layer on the concave regions of the separated leadframe side in a cohesive mode. This type of irregular failure was named as '*B-type irregular failure*' for convenience.

The failure occurrence inside the CuO layer on the concave region of the separated leadframe side in a cohesive mode is can be explained by using the adhesion model introduced in the previous section. Since the powdered EMC was used for molding and a compression-molding system was used instead of a transfer-molding system, there must be trapped air in the EMC, and the gaps among the CuO needles exist. The air initially trapped in the gaps among the CuO needles may be compressed and finally form microvoids near the roots of the CuO needles during compression-molding process due to the penetration of epoxy resin into the gaps among the CuO needles. It is well known that voids in solids weaken the strength of the solids because the solids with voids tend to behave like porous materials. As a rule, the strength of porous materials is lower than that of firm materials. The microvoids near the roots of the CuO needles may form microscopic cracks, and consequently

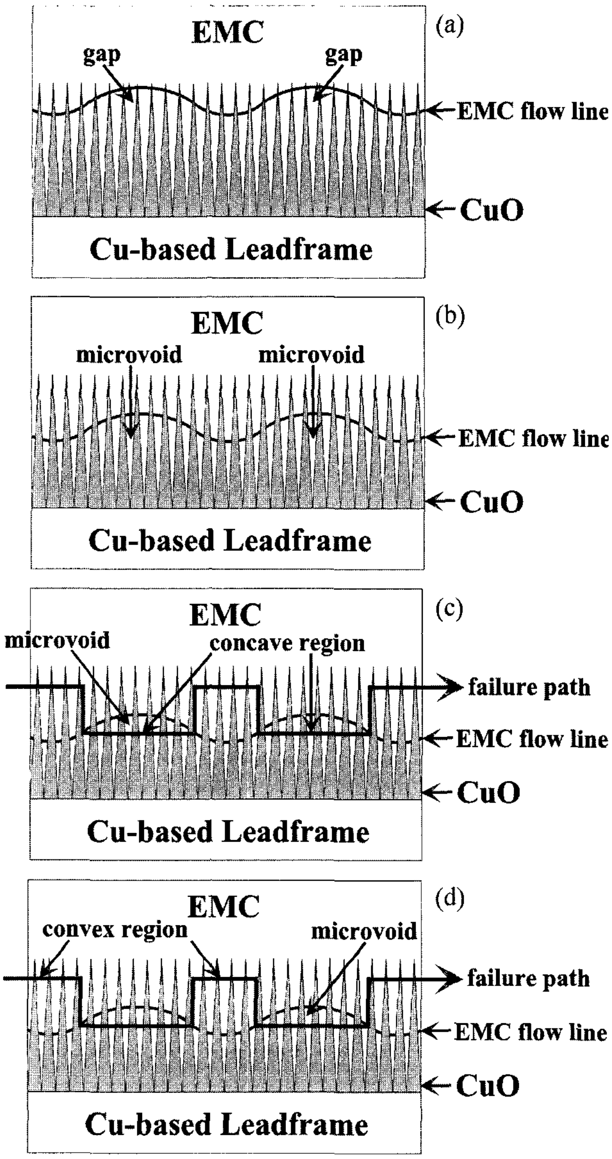


Fig. 10. Schematic diagrams illustrating the failure occurrence inside the CuO layer on the concave regions of the separated leadframe side in a cohesive mode. (a) As the epoxy resin is included in the EMC penetrates into the gaps among the CuO needles, the air trapped in the gaps is compressed. (b) As the EMC flow line advances, microvoids are formed near the roots of the CuO needles. (c) Eventually, the microvoids weaken the local strength of the CuO-EMC composite, thus failure is likely to occur inside the CuO layer on the concave regions of the separated leadframe side in a cohesive mode because cracks always select the weakest propagation path. (d) Failure occurred near the quasi-macroscopic CuO/EMC interface on the convex regions of the separated leadframe side in a nearly interfacial mode. According to the '*rule-of-mixtures*', failure is expected to occur at the weakest point satisfying $V_{CuO} = V_{CuO}^{\min}$. The weakest point is close to the CuO/EMC interface.

they may weaken local strength around the roots of the CuO needles. This indicates the local weakening of CuO layer, thus failure is likely to occur inside the CuO layer because cracks always select the weakest propagation path. This supports the failure occurrence inside the CuO layer on the concave region of the separated leadframe side in a cohesive mode. The overall situation is delineated in Fig. 10. The microvoids around the roots of the CuO needles formed by air trapping during compression-molding process can be seen on the concave region of the separated leadframe side[1]. This upholds the assumption that the microvoids form around the roots of the CuO needles.

The failure occurrence near the quasi-macroscopic CuO/EMC interface in a nearly interfacial mode on the convex region of the separated leadframe side is can be explained by using the adhesion model introduced in the previous section. According to the adhesion model, the composite strength varies with V_{CuO}, and there is the weakest point which has a minimum strength at $V_{CuO} = V_{CuO}^{\min}$. Because failure always occurs at the weakest point, it is expected that the failure would occur somewhere in the interlocking zone that satisfies $V_{CuO} = V_{CuO}^{\min}$ (see Fig. 11). It was also confirmed by XPS analyses. The XPS analyses of separated leadframe side as well as separated EMC side were carried out to investigate the amount of CuO on each part. The XPS analyses results are shown in Fig. 12. As the same way used in the previous section, Ar ion sputtering for 30 seconds was carried to eliminate the contaminants on the surface to get exact information. The XPS analyses results disclosed that there was smaller amount of CuO on the separated EMC side as compared with the separated leadframe side. This indicates that failure occurred somewhere in the interlocking zone that satisfies $V_{CuO} = V_{CuO}^{\min}$, thus the failure path lies near the quasi-macroscopic CuO/EMC interface with a little deviation from the tip of the CuO needle.

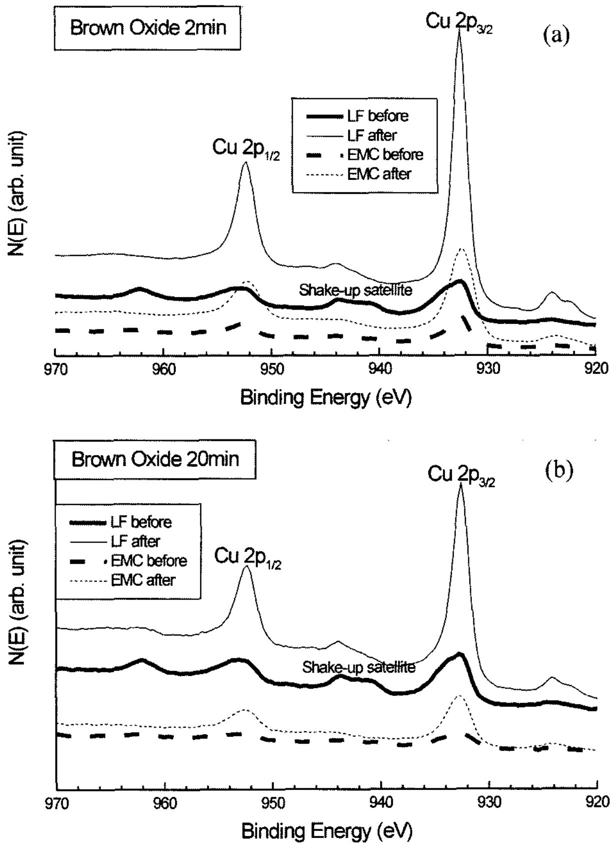


Fig. 12. XPS surveys of on the convex regions of the separated leadframe sides and their counterparts, separated EMC sides. 'LF' means 'leadframe' and 'before' means 'before Ar ion sputtering for thirty seconds' and 'after' means 'after Ar ion sputtering for thirty seconds', respectively. (a) The oxidation time of copper-based leadframe before molding with EMC is two minutes. (b) The oxidation time of copper-based leadframe before molding with EMC is twenty minutes.

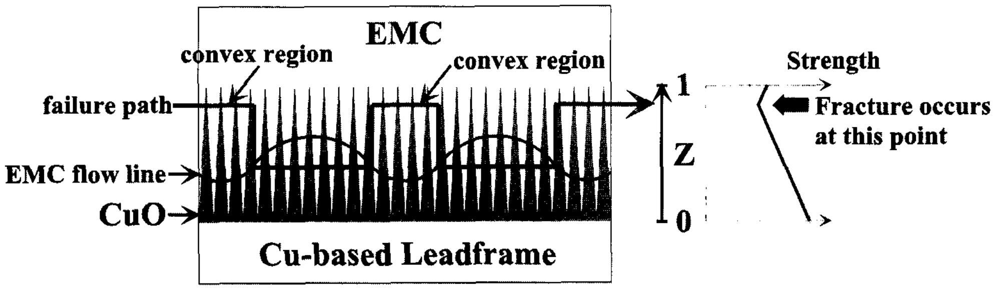


Fig. 11. Failure occurrence near the quasi-macroscopic CuO/EMC interface on the convex regions of the separated leadframe side in a nearly interfacial mode and its comparison with the expected failure path based on the simple micromechanical model for longitudinal tensile strength of a composite material developed from the '*rule-of-mixtures*'. The weakest point which has a minimum strength surely exists somewhere in the interlocking zone satisfying $V_{CuO} = V_{CuO}^{\min}$ and failure is expected to occur at the weakest point.

6. CONCLUSIONS

The practical adhesion strength of the brown-oxide-coated copper-based leadframe/EMC interface was measured by employing sandwiched double-cantilever beam (SDCB) specimens, and the fracture surfaces were analyzed to determine the failure path. Subsequently, in the present work, an attempt to interpret the failure path was made under the assumption that microvoids are formed in the EMC as well as near the roots of the CuO needles during compression-molding process. A simple adhesion model developed from the theory of fiber reinforcement of composite materials was introduced to explain the correlation between adhesion strength of the copper-based leadframe/EMC interface and failure path. The following conclusions were drawn from this study.

1. When the oxidation time, $t < 2$ minutes, failure occurred near the CuO/EMC interface on the non-debris region of the separated leadframe side in a nearly interfacial mode and occurred inside the EMC on the clod-like debris region of the separated leadframe side in a cohesive mode. This type of irregular failure was named as '*A-type irregular failure*'.

2. For the oxidation time, $t \geq 2$ minutes, failure occurred near the quasi-macroscopic CuO/EMC interface on the convex regions of the separated leadframe side in a nearly interfacial mode and occurred inside the CuO layer on the concave regions of the separated leadframe side in a cohesive mode, respectively. This type of irregular failure was named as '*B-type irregular failure*'.

3. The overall experimental results on both '*A-type irregular failure*' and '*B-type irregular failure*' are well explained by the adhesion model developed under the assumption that microvoids are formed in the EMC as well as near the roots of the CuO needles during compression-molding process.

4. The adhesion model introduced in the present work can be used to explain the adhesion behavior of other similarly roughened metal/polymer interfaces which have the same adhesion mechanism, mechanical interlocking, as the the adhesion mechanism used in the present work.

REFERENCES

1. H. Y. Lee, S. R. Kim, J. Korean Inst. Surf. Eng., 33 (2000) 241.
2. K.-S. Choi, T.-G. Kang, I.-S. Park, J.-H. Lee, K.-B. Cha, IEEE Trans. Electron. Packag. Manufact., 23 (2000) 32.
3. B. H. Moon, H. Y. Yoo, K. Sawada, in Proc. 48th Electron. Comp. Technol. Conf., (1998) 1148.
4. Y. Inoue, K. Sawada, N. Kawamura, T. Sudo, in Proc. 46th Electron. Comp. Technol. Conf., (1996) 71.
5. H. Y. Lee, Jin Yu, J. Korean Inst. Surf. Eng., 32 (1999) 531.
6. A. Kelly, G. J. Davies, Metall. Rev., 10 (1965) 1.