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Brown Oxide 형성이 리드프레임/EMC 계면의 파괴인성치에 미치는 영향

이호영, 유 진

한국과학기술원 재료공학과

Effect of Brown Oxide Formation on the Fracture Toughness of Leadframe/EMC Interface

H. Y. Lee and J. Yu

Dept. of Materials Science and Engineering
Korea Advanced Institute of Science and Technology, Taejon, Korea 305-701

Abstract

A copper based leadframe was oxidized in brown-oxide forming solution, then the growth characteristics of brown oxide and the effect of brown-oxide formation on the adhesion strength of leadframe to epoxy molding compound (EMC) were studied by using sandwiched double cantilever beam (SDCB) specimens. The brown oxide is composed of fine acicular CuO, and its thickness increased up to ~150 nm within 2 minutes and saturated. Bare leadframe showed alomost no adhesion to EMC, while once the brown-oxide layer formed on the Surface of leadframe, the adhesion strength increased up to ~80 J/m^2 within 2 minutes. Correlation between oxide thickness, δ and the adhesion strength in terms of interfacial fracture toughness, G_c was linear. Considering the above results, we might conclude that the main adhesion mechanism of brown-oxide treated leadframe to EMC is mechanical interlocking, in which fine acicular CuO plays a major role.

1. INTRODUCTION

As electronic devices become smaller and lighter, thin plastic packages of surface-mounting type are widely used, and the popcorn-cracking phenomena during the solder reflow process become important to the packaging industry[1-4]. These phenomena are caused by the thermal mismatch among different materials and the vapor pressure build-up on pre-existing crack surfaces[5] which lead to cracking along EMC/chip (type I), chip/die-bond adhesive (type II), and leadframe (die pad)/EMC (type III) interfaces. Fig. 1 shows the three types of package cracks.

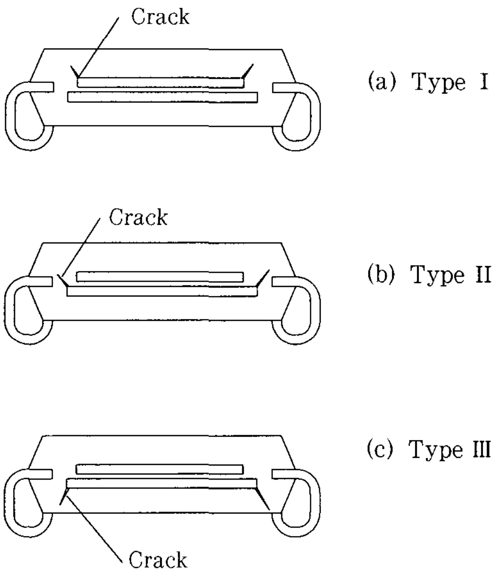

Fig. 1 Three types of package cracks.

Since the adhesion strength of Cu-based leadframe/EMC interface is inherently poor, fracture usually follows the leadframe/EMC interface (type III popcorn crack), and the procurement of a strong leadframe/EMC interface is regarded as a key solution to prevent the popcorn-cracking phenomenon of type III from generating.

In this paper, the adhesion strength of Cu-based leadframe/EMC interface was varied by forming of brown-oxide layer on the surfaces of leadframe before molding with EMC, and the adhesion strength of leadframe/EMC interface was measured in terms of fracture toughness, G_c by using sandwiched double-cantilever beam (SDCB) specimens.

2. EXPERIMENTAL PROCEDURE

2. 1. Formation of Brown Oxide

The Cu-based leadframe (commercial name : EFTEC-64T) sheets with the nominal composition of Cu-0.3Cr-0.25Sn-0.2Zn (wt%) and thickness of 0.15 mm were provided. Organic impurities on the surface of leadframe were removed by ultrasonic cleaning in acetone for 20 minutes and subsequently native oxides on the surface of leadframe were removed by pre-treatment solution (commercial name : Activan #6 offered by Han Yang Chemical Ind. Co. Korea). After the pre-treatment, leadframe sheets were immersed into hot alkaline solution listed in Table I to form brown-oxide layer on the surface[6].

Oxidation treatment typically lasted less than 20 minutes. A schematic diagram of experimental apparatus is shown in Fig. 2. The surface oxide- layers were analyzed by SEM (scanning electron microscope) and glancing-angle XRD (X-ray diffraction). Then, the thickness of oxide layer was measured by the galvanostatic reduction method[7-9].

Table 1. Composition and bath temperature of brown oxide forming solution[6].

Composition	Temperature
$NaClO_2$ (160g/l) NaOH (10g/l)	70 ℃

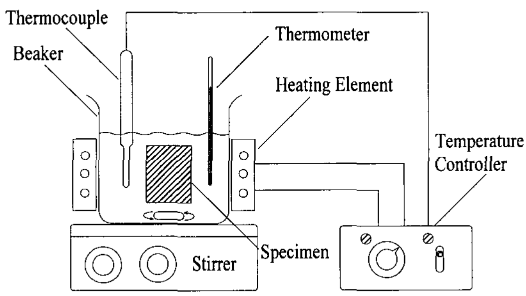

Fig. 2. A schematic diagram of experimental apparatus.

2. 2. Preparation of SDCB specimens and mechanical tests

After the oxidation, leadframe sheets were compounded with EMC, DMC-20 offered by Dong Jin Chemical Co. Ltd. Korea, in a compression-molding system for the 15 minutes at 175 ℃ under the pressure of 6.5 MPa. After molding, SDCB specimens of Fig. 3 were machined, and postcured for 4 hours at 175℃ to complete the polymerization reaction.

Mechanical tests were carried out under ambient conditions on the screw-driven Instron model 4206 with a crosshead speed of 0.5 mm/min, and the critical loads to onset of fracture were recorded to calculate the fracture toughness. Precracks were typically made by pasting correction tape on the oxidized leadframes before molding, which is used for eliminating miswritten letters. The fracture toughness measured in terms of the critical energy-release rate was calculated from[10)]

$$G_c=\frac{12P_c^2a^2}{t^2l^3\bar{E}}\left[3.467+2.315\left(\frac{l}{a}\right)\right]^2 \quad (1)$$

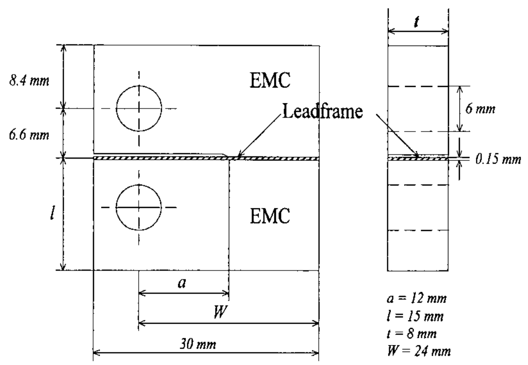

Fig. 3. A schematic diagram showing the geometry of a sandwiched double-cantilever beam (SDCB) specimen used for the fracture toughness test.

where P_c ane $\bar{E}$ are critical load and plane strain tensile modulus defined as $E/(1-\nu^2)$ (ν: Poisson's ratio), a, t, and l are crack length, specimen width, and half specimen-height, respectively. A sandwiched specimen can be regarded as a homogeneous specimen when the inserted layer is sufficiently small compared to the other specimen geometry[11)].

3. RESULTS AND DISCUSSION

3. 1. Characteristics of Brown Oxide

3. 1. 1 SEM Analysis

Scanning electron micrographs of leadframe surfaces treated in the brown-oxide forming solution are presented in Fig. 4 at various oxidation times. Parallel strips due to the cold rolling processes were well preserved even until 20 minutes, and fine acicular oxide precipitates typically 100 ~300 nm in length covered the entire area of surface after one or two minutes. With all the further oxidation, the size and density of the oxide precipitates only increased slightly, and the surface oxides remained more or less the same after 2 minutes. With subsequent X-ray and galvanostatic reduction analyses, the acicular oxide precipitates proved to be cupric oxide (CuO) and the thickness of the oxide layer was in the range of 100~200 nm. The CuO crystals were not only smaller, but also stopped further nucleation once a continuous layer formed on the surface.

3. 1. 2 XRD Analysis

Oxide precipitates on leadframe surfaces were analyzed by glancing-angle X-ray diffraction

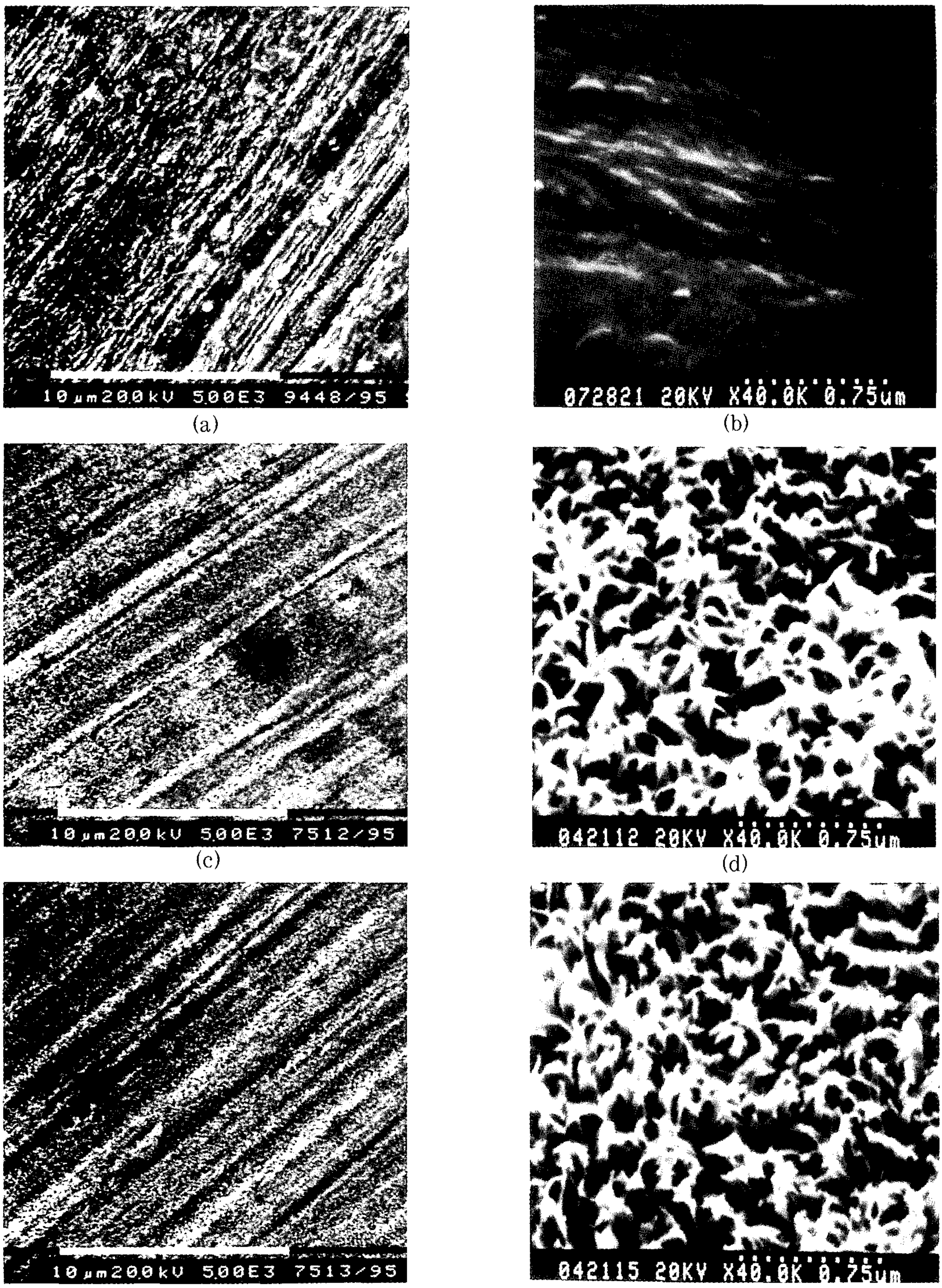

Fig. 4. SEM micrographs of oxidized leadframe surfaces : Oxidation times are (a) 0, as-cleaned, (c) 30 sec, (e) 20 min. (b), (d), (f) are magnified images of (a), (c), (e), respectively.

with the incident angle of 2°and the results are shown in Fig. 5. According to the X-ray results, only CuO phase was found on the surface of leadframe up to 20 minutes without significant changes in the X-ray intensities except for the initial satage of oxidation.

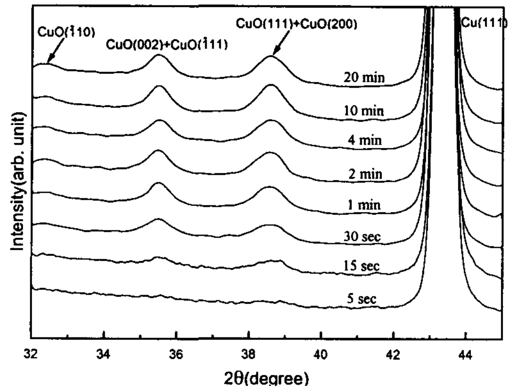

Fig. 5. Glancing-angle X-ray diffraction patterns out of leadframe surfaces at various oxidation times.

3. 1. 3 Thickness Analysis

The thickness of oxide layer was measured by using galvanostatic reduction method[7-9] in which copper oxide is electrochemically reduced under constant current density. Then, the type of oxide was identified from the reduction potential and the thickness of oxide layer were deduced from the reduction time using the Faraday's a law. Results the Faraday's law are presented in Fig. 6. It can be seen that only CuO phase was formed on the surface of leadframe and the average thickness of CuO layer reached ~150 nm after 2 minutes of the oxidation time, and there was no change in thickness with further oxidation time, which is consistent with the results of SEM and X-ray results. Thus, it appeared that there was no further nucleation of CuO precipitates since the CuO layer became continuous, and that the entire covering of CuO precipitates eliminated the contact between the fresh surface and the alkaline solution. For the above reasons, there was no more increase in thickness. A logarithmic plot of the average thickness of CuO layer versus oxidation time $(t < 1.5$ minute) shows that the kinetics of CuO thickening ;

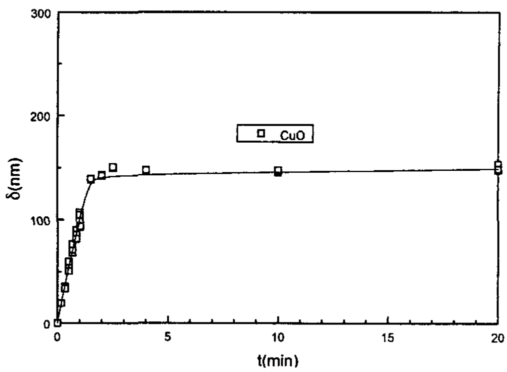

Fig. 6. Variation of oxide thickness with oxidation time.

$$\delta_{CuO} \propto t^{0.86} \quad (2)$$

where δ_{CuO} is the average thickness of CuO layer (nm) and t is time (min).

3. 2. Mechanical Tests

3. 2. 1 Fracture Toughness

With the formation of brown oxide, the fracture toughness of leadframe/EMC interface was changed. The results of the fracture toughness testing using SDCB specimens are presented in Fig. 7. For the leadframe/EMC system, the phase angle which is a measure of the Mode mixity at the crack tip[12] was ~3°. Thus, the loading condition was close to the pure Mode I loading with a slight mode II component.

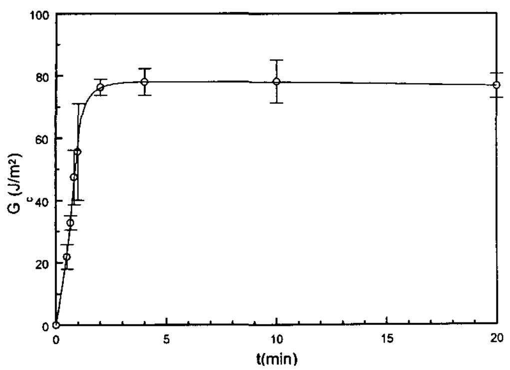

Fig. 7. Variation of fracture toughness of leadframe/EMC interface as a function of the oxidation time. The loading state near the crack tip was quasi-Mode I loading.

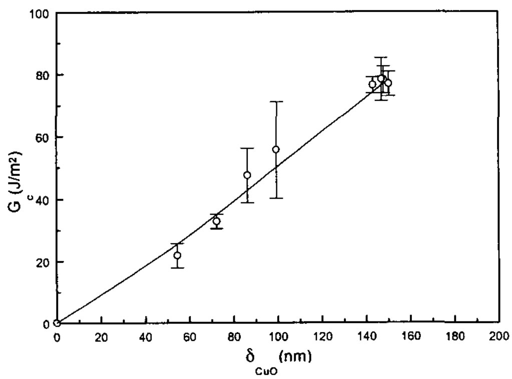

Fig. 8. Correlation between the interfacial fracture toughness and oxide thickness.

The fracture toughness of leadframe/EMC interface measured in terms of the critical energy-release rate, G_c, increased almost linearly with the oxidation time up to a minute and reached the saturation value of ~80 J/m² around 2 minutes. Note that the bare leadframe showed almost no adhesion to EMC. The trend in the G_c variaton is remarkably close to the thickening kinetics of the cupric oxide (CuO) shown in Fig. 6, which suggests that the adhesion between the two materials is directly related to the areal coverage of acicular CuO precipitates over the surface of leadframe and the mechanical interlocking of EMC by acicular CuO crystals.

3. 2. 2 Effect of Oxide Thickness

Previously, we noted the analogy between the variations of oxide thickness and the interfacial fracture toughness with oxidation time, and the correlations between G_c and δ are presented in Fig. 8. In this figure, one can find the proportional increase of G_c with the increase of δ because oxidation treatments longer than 2 minutes did not increase the oxide thickness.

An implication of the present result is that the oxidation treatments of two minutes in brown-oxide forming solutions is good enough to provide superior fracture toughness of leadframe/EMC interface.

4. CONCLUSIONS

1) Brown-oxide treatment of a Cu-based leadframe introduced fine acicular CuO precipitates on the surface and the average thickness of CuO layer increased up to ~150 nm within 1.5 minutes of the oxidation time.

2) Once the CuO layer becomes continuous, there is no change in the average thickness and microstructure of CuO layer. That might be due to the strong passivation property of CuO layer.

3) In a similar manner, the interfacial fracture toughness increased almost proportionally with the thickness of CuO layer and reached a saturation value of ~80 J/m² at two minutes of the oxidation time.

4) Fine acicular CuO precipitates contributed to the increase of fracture toughness of leadframe/EMC interface by mechanical interlocking

with EMC, while pre-cleaned smooth surface plays no role.

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