Improvement of Adhesion Strength between Cu-based Leadframe and Epoxy Molding Compound

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A black-oxide layer was formed on the surface of Cu-based leadframe by chemical oxidation method in order to enhance the adhesion strength between Cu-based leadframe and epoxy molding compound (EMC). Using sandwiched double cantilever beam (SDCB) specimens, the adhesion strength was measured in terms of interfacial fracture toughness, G_{IC}. Results showed that the black-oxide layer was composed of two kinds of layers: pebble-like Cu_2O layer and acicular CuO layer. At the initial stage of oxidation, the Cu_2O layer was preferentially formed and thickened up to around 200 nm within 1 minute of the oxidation time. Then, the CuO layer started to form atop of the Cu_2O layer and thickened up to around 1300 nm until 20 minutes. As soon as the CuO layer formed, the thickness of Cu_2O layer began to reduce and finally reached to around 150 nm. The pre-cleaned and the Cu_2O coated leadframes showed almost no adhesion to EMC, however, as the CuO precipitates appeared and became continuous, G_{IC} increased up to around 80 J/m^2. Further oxidation raised G_{IC} up to around 100 J/m^2.

Keywords : black-oxide layer, Cu-based leadframe, epoxy molding compound, adhesion strength, interfacial fracture toughness.

1. INTRODUCTION

As the electronic devices become smaller and lighter, thin plastic packages of surface mounting type are being widely used. However, the high temperature environment during the solder reflow process, which is a vital process for the surface mounting packages, often gives rise to the popcorn cracking phenomena [1-4]. These are caused by the thermal mismatch among different materials and the vapor pressure build-up on the pre-existing crack surfaces [5]. The popcorn cracking phenomena are classified into three types according to the initial delamination site. Fig. 1 shows the three types of package cracks. The type I is due to the delamination of EMC/chip interface, and the type II and III are due to the delamination of chip/die bond adhesive interface and leadframe (die pad)/EMC interface, respectively.

Since the adhesion strength of Cu-based leadframe/EMC interface is inherently poor, the type III popcorn crack generates more frequently. In order to prevent the type III popcorn crack, the procurement of strong leadframe/EMC interface is indispensible.

To obtain higher adhesion strength between dissimilar materials, several attempts were made so far. One is the plasma treatment [6,7] and the others include the surface treatment [8-10] and the corona discharging [11].

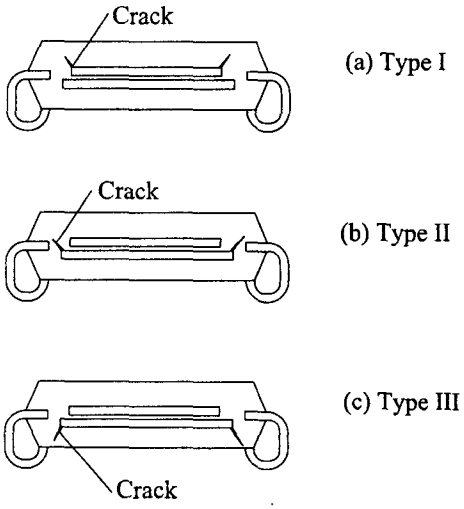


Fig. 1. Three types of package cracks.

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

2. EXPERIMENTAL PROCEDURE

2.1. Formation of Black Oxide

A Cu-based leadframe sheets (commercial name: EFTEC-64T, nominal composition: Cu-0.3Cr-0.25Sn-0.2Zn (wt%), thickness: 0.15 mm) were used. The organic impurities on the leadframe surface were removed in Acetone by ultrasonic cleaning for 20 minutes, and subsequently the native oxides were removed by immersing in the pre-treatment solution (commercial name: Activan #6 offered by Han Yang Chemical Ind. Co. Korea). After the pre-conditioning, leadframe sheets were immersed in the hot alkaline solution listed in Table 1 to form black-oxide layer on the surface [12]. The oxidation treatment was maintained less than 20 minutes. A schematic diagram of experimental apparatus is shown in Fig. 2. The oxide layers were analyzed by scanning electron microscope (SEM) and glancing angle X-ray diffractometry (XRD). The thickness of oxide layer was measured by using galvanostatic reduction method [13-15], which is described in detail in the reference [13].

Table 1. The black-oxide forming condition.

Composition	Temperature
$NaClO_2$ (37.5g/*l*) NaOH (50g/*l*) $Na_3PO_4 \cdot 12H_2O$(100g/*l*)	95 ℃

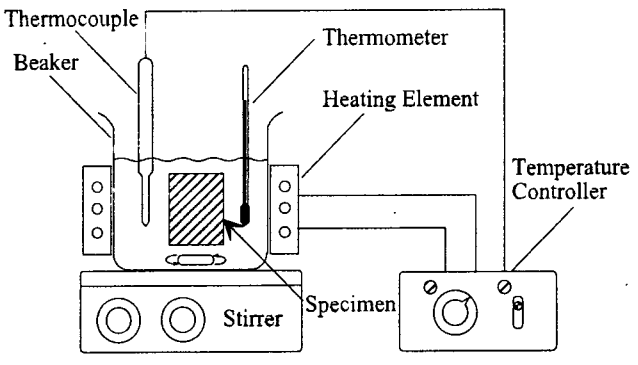


Fig. 2. A schematic diagram of experimental apparatus.

2.2. Preparation of SDCB Specimens and Mechanical Testing

After the surface modification, leadframe sheets were compounded with EMC (commercial name: DMC-20, offered by Dong Jin Chemical Co. Ltd. Korea) in a compression molding system for 15 minutes at 175 ℃ under the pressure of 6.5 MPa. After the molding process, all leadframe/EMC joints were machined into the SDCB specimens. A schematic diagram of SDCB specimen is presented in Fig. 3. The post-mold curing was conducted at 175 ℃ for 4 hours to complete the polymerization reaction of epoxy resin.

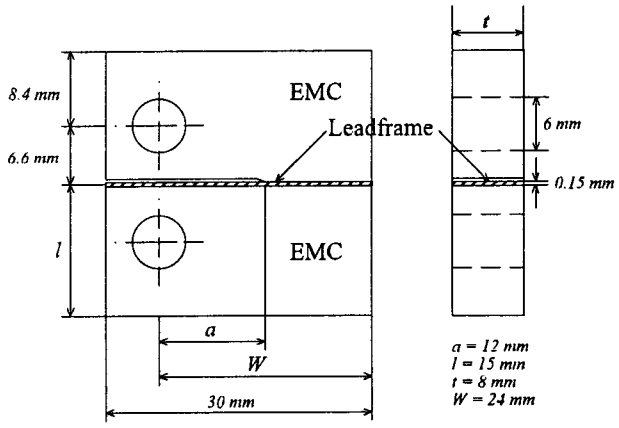


Fig. 3. A schematic diagram of sandwiched double cantilever beam (SDCB) specimen.

Mechanical tests were carried out under the constant crosshead speed of 0.5 mm/min by Instron model 4206. The maximum loads to onset of fracture were taken as critical loads to calculate the interfacial fracture toughness. Pre-cracks were typically made by pasting correction tape on the leadframe surface before molding process, which is used to eliminate miswritten letters. The interfacial fracture toughness, G_{IC}, was calculated by using following equation [16]

$$G_{IC} = \frac{12P_C^2 a^2}{t^2 l^3 \overline{E}}\left[1+\frac{2l}{3a}\right]^2 \quad (1)$$

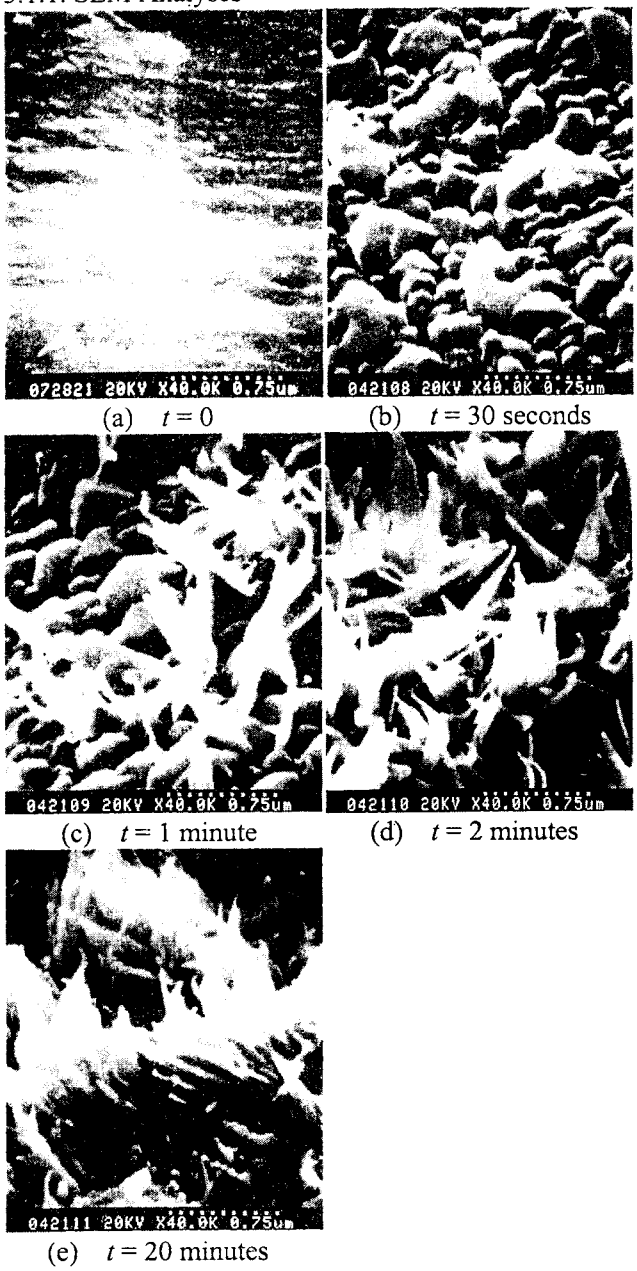
where P_C and $\overline{E}$ are critical load and plane strain tensile modulus defined as $E/(1-\nu^2)$ (ν: Poisson's ratio). a, t and l are crack length, specimen width, and half specimen height, respectively.

A sandwiched specimen can be regarded as a homogeneous specimen when the inserted layer is sufficiently small compared with the other specimen geometry [17].

3. RESULTS AND DISCUSSION

3.1. Characteristics of Black Oxide

3.1.1. SEM Analyses



(a) $t = 0$ (b) $t = 30$ seconds

(c) $t = 1$ minute (d) $t = 2$ minutes

(e) $t = 20$ minutes

Fig. 4. SEM micrographs out of oxidized leadframe surfaces.

Scanning electron micrographs of oxidized leadframe surfaces are presented in Fig. 4 at various oxidation times. It can be seen that there is no remarkable feature in pre-cleaned leadframe surface (Fig. 4 (a)). However, as can be seen from thirty-second-oxidized leadframe (Fig. 4 (b)), pebble-like precipitates were formed and coarsened to the mean diameter of 0.2 μ m. The pebble-like precipitates with smooth facets were later identified as cuprous oxide (Cu_2O). Approximately after one minute, acicular precipitates with 0.5 ~ 1.0 μ m length started to nucleate atop of the Cu_2O layer (Fig. 4 (c)), and patched over the whole surface completely after two minutes (Fig. 4 (d)). The newly formed needle-like precipitates were afterwards confirmed cupric oxide (CuO). Further oxidation made the CuO layer thick and dense, but the size of the forefront CuO needles remained more or less constant (Fig. 4 (e)).

3.1.2. XRD Analyses

The oxide layers on the leadframe surface were analyzed by glancing angle XRD with incident angle of 2° and the results are shown in Fig. 5. According to the X-ray results, the Cu_2O peaks came out as soon as the oxidation treatment initiated. After a minute, the CuO peaks came into existence and increased with oxidation time. With the X-ray data alone, it is difficult to know whether the newly formed CuO precipitates sit atop of the pre-existing Cu_2O layer or intermingled together.

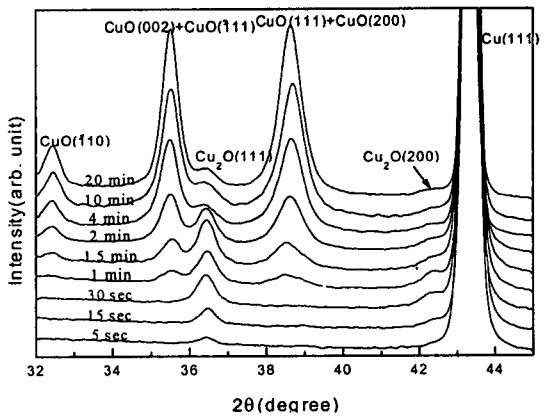


Fig. 5. Glancing angle X-ray diffraction patterns out of oxidized leadframe surfaces.

3.1.3. Thickness Analyses

The thickness of black-oxide layer was measured by using galvanostatic reduction method [13-15] in which the copper oxide is electrochemically reduced under constant current density. The type of oxide was identified from the reduction potential and the thickness of oxide was calculated from the reduction time by using the Faraday's law. The change of oxide thickness is presented in Fig. 6. Results showed that the smooth-faceted Cu_2O was preferentially precipitated on the leadframe surface and formed Cu_2O layer. Kinetics study revealed that the Cu_2O layer increased to around 200 nm till one minute obeying following equation.

$$d_{Cu_2O} \propto t^{0.89} (t < 1\,\text{min.}) \qquad (2)$$

where d_{Cu_2O} is the average thickness of Cu_2O layer and t is the oxidation time. After one minute, the CuO precipitates began to appear and grew. It seemed that the acicular CuO precipitates nucleated as the thickness of Cu_2O layer became saturated. After two minutes, the CuO layer took over the entire Cu_2O layer and continued to grow. Kinetics study indicated that the CuO layer grew parabolically with oxidation time obeying equation (3), thus, its thickness reached around 1300 nm at 20 minutes of the oxidation time.

$$d_{CuO} \propto t^{0.67} (2 < t < 20 \text{min.}) \quad (3)$$

where d_{CuO} is the average thickness of CuO layer and t is the oxidation time.

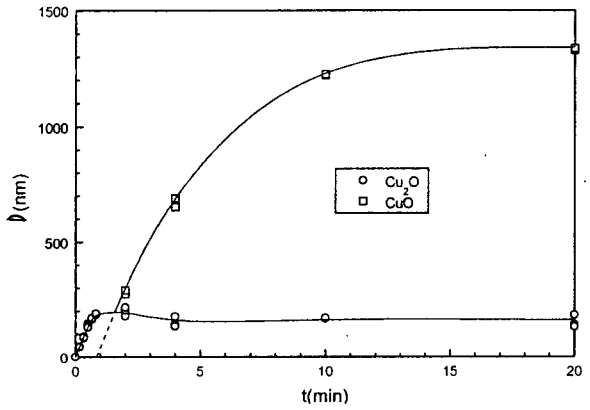


Fig. 6. Variation of oxide thickness with oxidation time.

With the experimental results of the SEM, XRD, and thickness analyses, it can be stated that the experimental results were well matched with each other, and consequently the growth mechanism of the black-oxide layer was disclosed: layer by layer growth.

3.2. Mechanical Testing

3.2.1. Fracture Toughness

The fracture toughness of leadframe/EMC interface was measured by using SDCB specimens, and the results are shown in Fig. 7. For the leadframe/EMC system, the phase angle [18] which is a measure of the Mode mixity at the crack tip was about 3° [17]. Thus, the loading condition was close to the pure Mode I loading with a slight Mode II component (quasi-Mode I loading condition).

Pre-cleaned leadframe/EMC interface showed almost no adhesion ($G_{IC} \cong 0$ J/m^2), and this value was preserved up to one minute. However, as soon as the acicular CuO precipitates turned up, the G_{IC} went into increasing. So, the G_{IC} amounted to 80 J/m^2 at two minutes and reached the saturation value of 100 J/m^2 at around 10 minutes. It was found out that the presence of pebble-like Cu_2O precipitates with smooth facets played no role in the adhesion, thereby, provided no fracture resistance to the Mode I loading. However, the acicular CuO precipitates enhanced fracture resistance.

From the above results, it can be concluded that the adhesion between CuO coated leadframe and EMC is attained through the mechanical interlocking of CuO needles into epoxy resin. It was well reflected in the G_{IC} variation with the oxidation time, which is quite analogous to the thickening kinetics of CuO layer shown in Fig. 6.

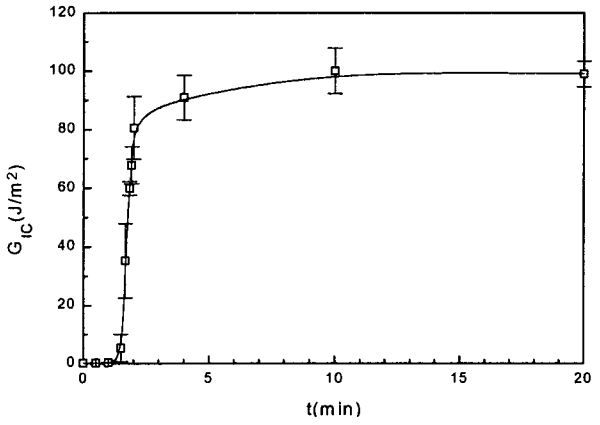


Fig. 7. Variation of fracture toughness of leadframe/EMC interface as a function of the oxidation time.

3.2.2 Effect of CuO Thickness

In this section, the correlation between G_{IC} and d_{CuO} was taken into account, and the results are presented in Fig. 8. There was a linear relationship between G_{IC} and d_{CuO} when the d_{CuO} was in the range between 160 nm and 280 nm. Note that in the early stage of the CuO layer formation, d_{CuO} does not reflect the actual change in the CuO needle length, because the d_{CuO} is the average thickness of the CuO layer.

In the previous SEM observation (section 3.1.1), it was discovered that the CuO layer is discontinuous when the oxidation time is between one minute and two minutes, and it was not until the oxidation time reaches two minutes that the CuO layer became continuous. Thus, thickness increment in the initial stage of the CuO layer formation does not mean the increase of real length of the CuO needles, but the increase of density of the CuO needles.

From those results, it was cleared that the adhesion strength in the beginning of the CuO layer formation is directly related to the areal coverage of the CuO

precipitates on the Cu_2O layer. In addition, considering that the G_{IC} was 80 J/m^2 when the CuO layer became continuous (two minutes of the oxidation time) and there was no remarkable increase in G_{IC} afterwards, it is more important for the CuO layer to become continuous rather than to become dense in the aspect of adhesion.

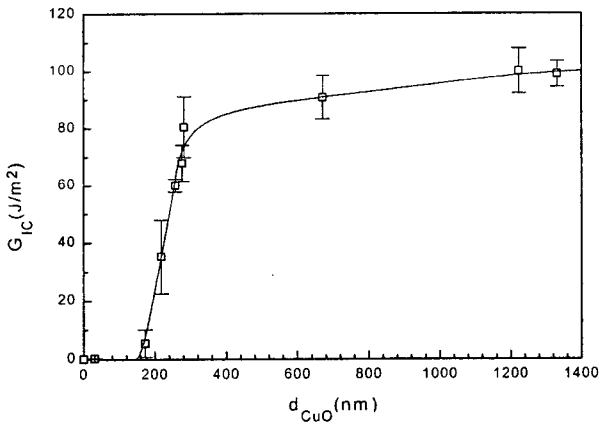


Fig. 8. The Correlation between interfacial fracture toughness and the thickness of CuO layer.

An implication of the present result is that the two minutes of the oxidation time is good enough to provide superior fracture toughness of Cu-based leadframe/EMC interface.

4. CONCLUSIONS

1. A black-oxide treatment on the Cu-based leadframe introduced pebble-like Cu_2O precipitates on the surface at the initial stage of oxidation. The average thickness of Cu_2O layer was increased up to around 200 nm within one minute of the oxidation time. Then, acicular CuO precipitates started to nucleate and thickened up to 1300 nm at the twenty minutes of the oxidation time.
2. The interfacial fracture toughness, G_{IC} was close to zero until the CuO precipitation started after one minute. Then, G_{IC} increased to 80 J/m^2 after two minutes of the oxidation time and reached the saturation value of 100 J/m^2 after ten minutes.
3. The presence of the acicular CuO precipitates contributed to the increment of G_{IC} by mechanical interlocking of CuO needles into epoxy resin, while smooth faceted Cu_2O precipitates did not.
4. Two minutes can be regarded as an optimum oxidation time because it provides superior G_{IC} value in a short time.

REFERENCES

[1] M. Adachi, S. Ohuchi and N. Totsuka, "New Mode Crack of LSI Package in the Solder Reflow Process", *IEEE Trans. on Components, Hybrids, and Manufacturing Technology*, vol. 16, No. 5, p. 550, 1993.

[2] G. S. Ganesan and H. M. Berg, "Model and Analysis for Solder Reflow Cracking Phenomenon in SMT Plastic Packages", *IEEE Trans. on Components, Hybrids, and Manufacturing Technology*, vol. 16, No. 8, p. 940, 1993.

[3] A. A. O. Tay, G. L. Tan, and T. B. Lim, "Predicting Delamination in Plastic IC Packages and Determinating Suitable Mold Compound Properties", *IEEE Trans. on Components, Packaging, and Manufacturing Technology - Part B: Advanced Packaging*, vol. 17, No. 2, p. 201, 1994.

[4] N. Tanaka, M. Kitano, T. Kumazawa, A. Nishimura, "Evaluating IC-package interface delamination by considering moisture-induced molding-compound swelling", *IEEE Trans. on Components, Packaging, and Manufacturing Technology - Part A*, vol. 22, No. 3, p. 426, 1999.

[5] M. Kitano, A. Nishimura and S. Kawai, "Analysis of Package Cracking during Reflow Soldering Process", *Proc. International Reliability Physics Symposium*, p. 90, 1988.

[6] J.-H. Lee, Y.-H. Hwang and K.-C. Lee, "A Study on the Adhesive Improvement of Glass-cloth/Epoxy Composite Insulating Materials(1) - For Improvement of Wettability on the Interface -", *The Journal of the Korean Institute of Electrical and Electronic Material Engineers*, vol. 8, No. 2, p. 136, 1995.

[7] S.-T. Kim, Y.-H. Hwang, H.-T. Park, M.-S. Eom, K.-C. Lee and J.-H. Lee, "A Study on the Adhesive Improvement of Glass-cloth/Epoxy Composite Insulating Materials(2) - For Improvement of Dielectric Characteristics -", *The Journal of the Korean Institute of Electrical and Electronic Material Engineers*, vol. 8, No. 4, p. 434, 1995.

[8] C. Lee and A. Parthasarathi, "Investigation of a novel leadframe treatment for "dry-pack" free packaging", *Proc. 47th Electronic Components and Technology Conference*, p. 1049, 1997.

[9] C. Lee, W. Hosler, H. Cerva, R. von Criegern and A. Parthasarathi, "An analytical characterization and reliability testing of an adhesion enhancing Zn-Cr leadframe coating for popcorn prevention", *Proc. 48th Electronic Components and Technology Conference*, p. 1154, 1998.

[10] C. Q. Cui, H. L. Tay, T. C. Chai, R. Gopalakrishan and T. B. Lim, "Surface treatment of copper for the adhesion improvement to epoxy mold compounds",

Proc. 48th Electronic Components and Technology Conference, p. 1162, 1998.

[11] M. R. Kim, "Surface Treatment of Polyethylene Terephthalate Films by Corona Discharge", *The Journal of the Korean Institute of Electrical and Electronic Material Engineers*, vol. 8, No. 3, p. 316, 1995.

[12] H. K. Yun, K. Cho, J. H. An and C. E. Park, "Adhesion Improvement of Copper/Epoxy Joints", *J. Mater. Sci.*, vol. 27, p. 5811, 1992.

[13] J. R. G. Evans and D. E. Packham, "Adhesion of Polyethylene to Copper : Reactions between Copper Oxides and the Polymer", *J. Adhesion*, vol. 9, p. 267, 1978.

[14] V. Ashworth and D. Fairhurst, "The Anodic Formation of Cu_2O in Alkaline Solutions", *J. Electrochem. Soc.*, vol. 124, No. 4, p.506, 1977.

[15] H.-H. Strehblow and B. Titze, "The Investigation of the Passive Behavior of Copper in Weakly Acid and Alkaline Solutions and the Examination of the Passive Films by ESCA and ISS", *Electrochemica Acta*, vol. 55, p. 839, 1980.

[16] T. S. Oh, R. M. Cannon and R. O. Ritchie, "Subcritical Crack Growth along Ceramic-Metal Interfaces", *J. Am. Ceram. Soc.*, vol. 70, No. 12, p. C-352, 1987.

[17] Z. Suo and J. W. Hutchinson, "Sandwich Test Specimens for Measuring Interface Crack Toughness", *Mater. Sci. and Eng.*, vol. A107, p. 135, 1989.

[18] J.-S. Wang and Z. Suo, "Experimental Determination of Interfacial Toughness Curves Using Brazil-nut-sandwiches", *Acta Metall. Mater.*, vol. 38, No. 7, p. 1279, 1990.