J Mater Sci (2007) 42:9116–9120
DOI 10.1007/s10853-007-2063-2

LETTER

Cracking of densely coated layer adhesively bonded to porous substrates under Hertzian stress

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Received: 27 January 2007 / Accepted: 26 July 2007

Structural components under contact stresses are designed so as to have high damage tolerance. Unexpected degradation of initial strength under the components' actual environmental conditions leads to economic loss, and even potential loss of life, through unanticipated permanent deformation and fractures. Therefore, material design to suppress contact stress is of practical importance in engineering applications, such as for the components utilized in machinery, and bio-, thermal or energy applications [1–4].

Layered composite design has been investigated with consideration of damage tolerance in previous studies [5, 6]. Hard outer layers provide surface resistance against damage from contact loading and soft underlayers contribute to stress redistribution and delayed fracture of the coating layer. An adhesive is sometimes used to bond a hard layer with a soft material in making dental-layered composites. The coating thickness and the elastic modulus mismatch are crucial parameters in geometrical and material designing to suppress Hertzian contact stresses [7]. The design of such layered composites is one of the important issues, because a softer support causes the coating to flex under the constrained contacts.

Recently, we have investigated the cracking of brittle coatings adhesively bonded to substrates with different modulus [8]. A trilayer system consisting of an upper soda-lime glass layer (coating) bonded to a thick glass layer (substrate) with a thin layer of epoxy adhesive facilitated in situ observation of cracks during contact loading. We have investigated the role of substrates of different elastic modulus with respect to crack initiation by in situ observations of cone cracking from the surface and radial cracking from damage at the interface between two layers.

In the present study, we investigate the role of porosity in the substrate on the cracking of a hard-coating layer. To this end, we prepared porous substrates with different porosity and the same epoxy and glass plate. We extended the system to a hard substrate with a high elastic modulus.

Two starting powders were used to prepare the porous substrate, Al_2O_3 (AKP-50, AES-11, ALCOA, Japan), and SiO_2 (SE-8, SO-R31, Tokuyama, Japan). In order to vary the porosity in the porous substrate, we used different powder sizes and also varied the sintering temperature. In Al_2O_3, the starting powders were 1.22 μm, 5.5 μm, and 9.8 μm in size. We varied the sintering temperatures from 1,000 °C to 1,400 °C at an increasing interval of 100 °C. Two types of SiO_2 powders were used, (SE-8, and SO-R31), 10 μm and 1 μm, and the ratio of staring powders was varied, 10 μm: 1 μm = 6:4, 7:3, 8:2, and 9:1, respectively. The powders were sintered at 1,300 °C or 1,350 °C. Therefore, we could vary the porosity and the material. The porosity was controlled in the range of 0.42–42.6% and 8.2–25.4% for Al_2O_3 and SiO_2 substrates, respectively, through the control of sintering temperature and/or starting powder size.

The layered composite systems were fabricated from cover glass with dimensions of 4 × 10 × 0.16 mm bonded to a 4 × 4 × 36 mm substrate with a 10 μm thick layer of epoxy adhesive. The surface was polished to 1-μm diamond finish before bonding, and both the top and bottom surfaces of the glass layers were abraded with a slurry of SiC grit (#600), in order to induce uniform flaw

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distribution. The upper glass and the lower substrate were bonded with epoxy adhesive (Harcos Chemicals, Bellesville, NJ, USA) under light pressure.

Spherical (Hertzian) indentation was used to induce contact stress on the layered composite systems, as shown in Fig. 1 [9–14]. Indentations were made with a universal static testing machine (Microload test system, Unitec., Korea, or Instron 5567, Instron, USA) with a tungsten carbide (WC, J & L Industrial Supply Co., Livonia, MI, USA) ball of radius $r = 3.18$ mm at $P = 150$ N, at a constant crosshead speed of 0.09 mm/min. We have applied the spherical WC indenter ($r = 3.18$ mm) up to 150 N contact load on the layered composites, where a glass coating with both surfaces abraded to ensure uniform flaw density was utilized.

The elastic modulus of each layered material is given in Fig. 2. The graphs in Fig. 2 show the change in the elastic modulus of the substrate monolith according to the porosity in the substrate. The elastic modulus of each layer monolith is measured by acoustic impulse excitation apparatus (Tektronics, 5800PR, USA) and plotted as a function of porosity. The elastic modulus of the coating material monolith and epoxy adhesive are also measured using the same method and included in the graphs. The elastic modulus of porous ceramics such as Al_2O_3 and SiO_2 decreases as the porosity increases, according to the Rice equation [15–17].

$$E = E_o \exp(-bP) \quad (1)$$

where E_o is the elastic modulus of a material with no porosity (0% of porosity), P is porosity, and b an experimentally determined constant [16]. Solid curves are fits from Eq. 1 and the data fall on a theoretical curve.

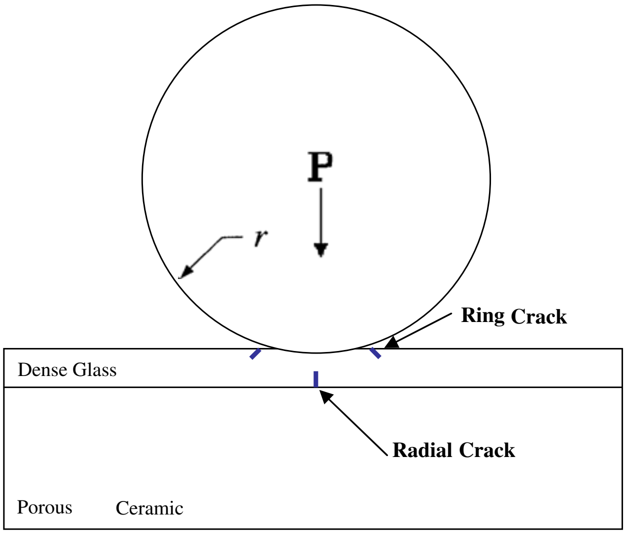

Fig. 1 Schematic diagram of Hertzian indentation test on densely coating/porous-substrate layered composite bonded with thin adhesive

In Fig. 2, it is noteworthy that the elastic modulus of Al_2O_3 is higher than that of the glass-coating layer, and that of SiO_2 is lower than the coating layer. The epoxy adhesive has a low modulus, as compared to the Al_2O_3 and SiO_2. Conversely, Al_2O_3 ceramics with higher porosity present a small elastic modulus mismatch after the layered composite is constructed, and SiO_2 ceramics with higher porosity have a large elastic modulus mismatch. A soft support by epoxy adhesive between the coating and the substrate layer allows the coating to flex beneath the contact. This leads to changes in the fracture patterns in the coating layer, from the mode of surface cracking to subsurface radial cracking, as found in a previous study [8]. The previous study shows that the initiation of radial cracking is related with elastic mismatch, the following equation is applied:

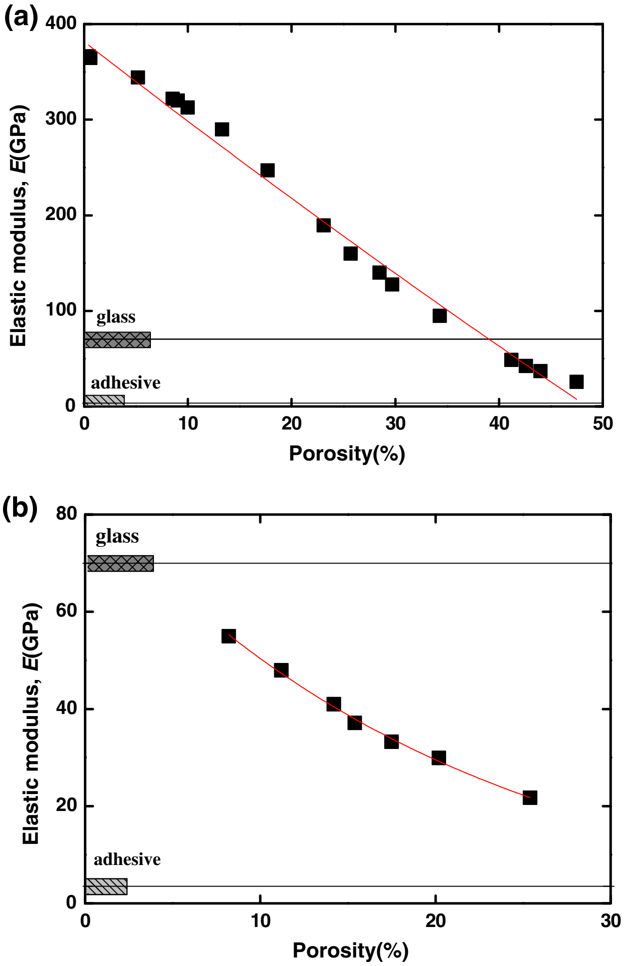

Fig. 2 Plot of elastic modulus of each layer material as a function of porosity for (**a**) Al_2O_3 and (**b**) SiO_2

$$P_{\mathrm{rad}} = B\sigma_{\mathrm{F}}d^2/\log(CE_{\mathrm{c}}/E_{\mathrm{s}}) \qquad (2)$$

where B and C are dimensionless constants, σ_F is the strength of materials, d coating thickness, and E_c/E_s elastic modulus mismatch. The Eq. 2 indicates the coating fracture depends on the elastic modulus of substrate layer material in the layered composite. On the other hand, the initiation of ring cracks, P_{cone}, can be modeled [6, 17] by the following equation for cone cracking:

$$P_{\mathrm{cone}} = A\ r\ G_{\mathrm{c}} \qquad (3)$$

where G_c is the crack resistance, r the radius of indenter, A a dimensionless constant. This critical load does not depend on the elastic modulus mismatch of layered materials. Notably, the above equations are modeled on the results of all dense layered composites.

A plot of the maximum diameter of ring cracks in the coating layers using a WC sphere r = 3.18 mm at a load P = 150 N is plotted in Fig. 3 as a function of porosity for two porous ceramic substrates. Data are only plotted for ring cracks, and the results of crack propagation at P = 150 N of the contact load are shown. Each data point represents the mean and standard deviation of 10 indentations. The solid curves are best fits. The data shows two stages for the porous Al_2O_3 substrate only. In Fig. 3a, the size of contact cracks initially decreases as the porosity increases to a maximum of 20% as shown in stage I, thereafter, the size of cracks increases as the amount of the porosity in the substrate increases to a maximum of 42.6% as in stage II. The optical micrographs of contact damages on the surface for selected conditions are included in the top of the graph. In these micrographs, it is notable that no damages are found for the 25% porosity Al_2O_3 substrate. Extensive damage including multiple cracks is apparent for the 40% porosity Al_2O_3 substrate. Apparent cracking of the layered composite with high porosity in the substrate is found for the SiO_2 substrate, as shown in Fig. 3b. The trend corresponds with that of Al_2O_3 in II.

The result in Fig. 3b indicates that the contact cracking of the coating layer crucially depends on the elastic modulus mismatch, E_c/E_s. We have measured the modulus of the substrate monolith with that of the glass monolith, while the mismatch increases according to the porosity for the SiO_2 substrate as shown in Fig. 2b. The cracking damage in Fig. 3b can be understandable, if we assume that the damage is more apparent at lower P_c, which is predictable from Eq. 2. It is also general that brittle ceramics consist of higher porosity exhibits lower toughness, that is, lower value of G_c in Eq. 3.

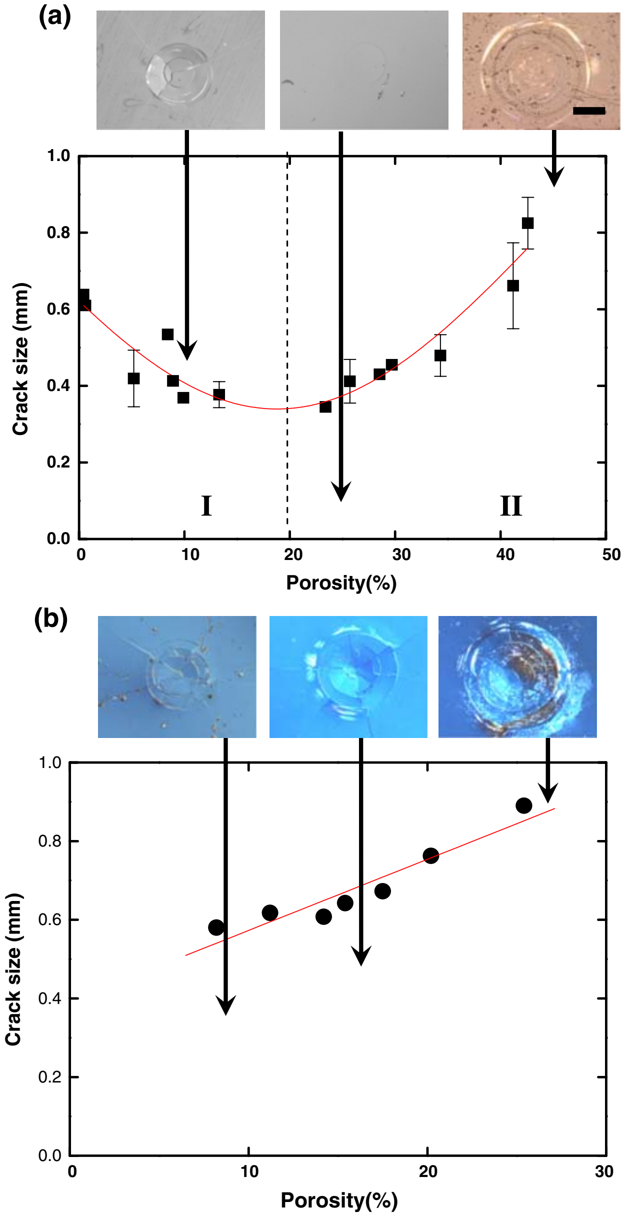

Fig. 3 Plot of the maximum sizes of crack diameter using WC sphere radius r = 3.18 mm at load P = 150 N as a function of porosity for layered composites consisting of glass coatings on porous (**a**) Al_2O_3 and (**b**) SiO_2. The contact damage on the surface for each condition is included in figure. The size of scale bar = 250 μm

Here we can compare the Al_2O_3 substrate monolith in Fig. 3a. Notably, the modulus mismatch generally diminishes at higher porosity for the Al_2O_3 substrate shown in Fig. 2a. Therefore the initial decrease of crack size as the porosity increases to a maximum of 20% as shown in stage I of Fig. 3a is explained by diminishing effect of elastic modulus mismatch. However, the graph in Fig. 3a suggests some range of porosity in the substrate layer can suppress the initiation of ring cracks in the coating layer of layered composite. Moreover, it is noteworthy that the suppression phenomenon of the coating fracture is found at layered composite with stiffer substrate material (Note the included optical micrographs of the contact damage on the surface of the coating for Al_2O_3 substrate is less apparent for cracking than for SiO_2 substrate). The results in Fig. 3a indicate that the contact cracking crucially depends on the porosity, as well as the elastic modulus mismatch.

Therefore, the rigidity of substrate for the layered composite bonded with the substrate controls the initiation and propagation of contact cracks in the coating layer. Strong and stiffer substrates protect coating layers bonded with very-soft adhesive layers ($d = 10\ \mu$m) from cracking caused by flexure stress (a high modulus of substrate delays initiation of subsurface radial cracking according to Eq. 2). This is because the controlling material quantity in Eq. 2 is strength, σ_F, relating with flexure. Plots in Fig. 3a illustrate the beneficial role of well-controlled pores in the ceramic substrate with respect to contact fracture of the coating layer. For small porosity in the substrate (stage I), the pores may suppress cracking by damage re-distribution. On the other hand, radial cracking by flexural stress due to elastic modulus mismatch, especially apparent in the layered composite with SiO_2 substrate as shown in Fig. 3b, causes severe damage to the coating layer. Contact cracks including radial cracking are apparent in the porous SiO_2 support at any range of porosity, because the hard/soft-layered composite has a high elastic modulus mismatch, which strongly influences cracking in the coating layer.

SEM micrographs of section views showing subsurface damages in the brittle substrate monolith as well as crack profiles produced in the coating layers are shown in Fig. 4. Although cracking appears in the coating layer of the glass/Al_2O_3 layered composite with small porosity, it is notable that the damage is not critical in the substrate layer of Fig. 4a and b relative to Fig. 4c. On the other hand, the result suggests that if yielding of the substrate occurs during contact with the higher porosity substrate as shown in Fig. 4c, extensive cracking in the coating layer is produced. An extensive yield in the substrate of the layered composite is observed with more extensive cracking in the coating layer, as indicated in Fig. 4c. The extensive cracking in the coating layer can be appeared if the extensive yielding occurs in the substrate even though the elastic modulus mismatch is diminished. Therefore, the increase of size of cracks as the amount of the porosity in the Al_2O_3 substrate increases to a maximum of 42.6% in stage II of Fig. 3a is closely due to yield of subsurface in the substrate. The determining factor is whether yield occurs in the porous substrate during the contact stress. The result indicates that the substrate should not yield before the coating layer fractures.

In designing the coating/substrate-layered composite, bonding with adhesive requires a higher substrate modulus and hardness with a matching of the substrate, therefore higher damage tolerance. The smaller volumes of pores under the critical porosity range can contribute to delayed cracking if they are not yielded or deformed before coating fracture. More detailed and systematic investigations in this regard should be conducted in future study.

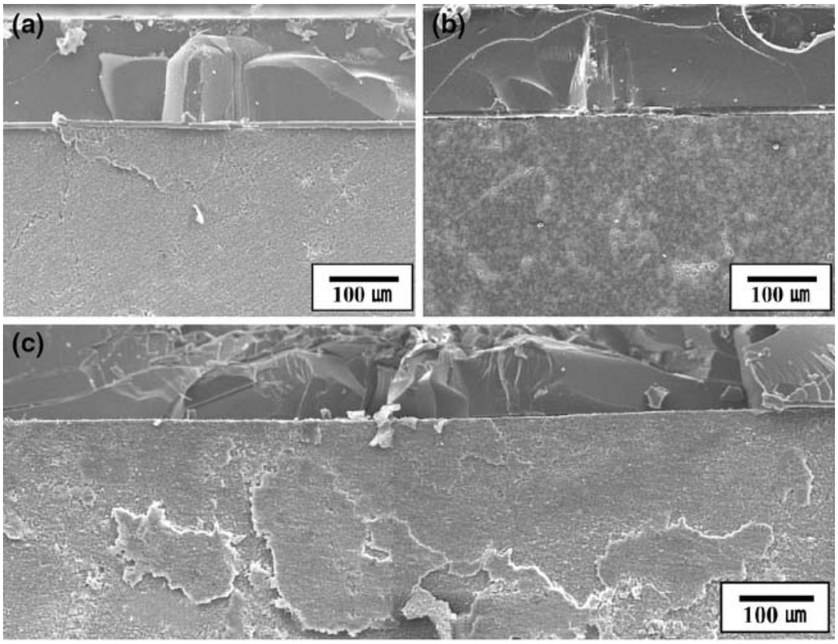

Fig. 4 Section views of SEM micrographs of the glass/Al_2O_3 layered composite from Hertzian indentation at load $P = 150$ N. The porosity of the substrate layer is (**a**) 13.3%, (**b**) 34.3%, and (**c**) 41.2%

Acknowledgements This work was partly supported by Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2004-003-D00002) and partly by a grant from Electric Power Industry R&D Project funded by the Ministry of Commerce, Industry and Energy.

References

1. Lawn BR (1998) J Am Ceram Soc 81:1977
2. Lee KS, Seo DW, Yu JH, Woo SK (2003) J Kor Ceram Soc 40:241
3. Jung HH, Kim DJ, Han JS, Lee DY (2004) J Kor Ceram Soc 41:508
4. Beele W, Marinjiniseen G, van Lieshout A (1999) Surf Coat Tech 120–121:61
5. Lee KS, Lee SK, Lawn BR, Kim DK (1998) J Am Ceram Soc 81:2394
6. Lawn BR, Lee KS, Chal H, Pajares A, Kim DK, Wuttiphan S, Peterson IM, Hu X (2000) Adv Eng Mater 11:745
7. Lee KS, Wuttiphan S, Hu XZ, Lee SK, Lawn BR (1998) J Am Ceram Soc 81:571
8. Lee KS, Lee YW, Blackburn DH, Chai H, Lawn BR (2000) J Mater Res 15:1653
9. Hertz H (1896) Hertz's miscellaneous papers, Ch. 5, 6. Macmillan, London
10. Lawn BR (1993) Fracture of brittle solids, 2 edn. Cambridge Univ. Press, Cambridge
11. Pajares A, Wei L, Lawn BR, Padture NP, Berndt CC (1996) Mater Sci Eng A208:158
12. Lee KS, Wuttiphan S, Hu XZ, Lee SK, Lawn BR (1998) J Am Ceram Soc 81:571
13. Lee KS, Lee SK, Lawn BR, Kim DK (1998) J Am Ceram Soc 81:2394
14. Rhee YW, Kim HW, Deng Y, Lawn BR (2001) J Am Ceram Soc 84:1066
15. Rice RW (1993) J Mater Sci 28:2187
16. Rice RW (1989) Mater Sci Eng A112:215
17. Ha JH, Kim JH, Kim DK (2004) J Jap Ceram Soc 112:1084