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Adhesion strength of $Ag/BaTiO_3$ interface

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Abstract

The adhesion strength between a silver electrode and pure barium titanate has been determined by using a blister test. The Ag electrode is a porous layer and the barium titanate substrate is dense. The critical interface crack propagation energy G_{ci} of the $Ag/BaTiO_3$ interface ranges between 1.3 J/m^2 and 4.2 J/m^2.

Keywords: Interface; Adhesion; Ag electrode; Barium titanate

1. Introduction

The characteristics of metal–ceramic interfaces play an important role in many applications, such as electronic packages, multilayer ceramic capacitors (MLCC), wear resistant coatings, thermal barrier coatings, micro-electro-mechanical systems etc. The interfacial strength is an important parameter for all applications. Many different methods have been proposed to measure the adhesion strength of the metal–oxide interface [1]. These methods, however, are very specific and often their results are mutually inconsistent. Furthermore, most methods fail to deliver quantitative results with physical meaning.

The blister test is one of the few methods which can deliver quantitative and meaningful estimation on interfacial strength through the determination of the critical interfacial crack propagation energy. For the test, a rigid substrate with a hole located at the center of the substrate is needed. The substrate, including the hole, is then covered with the film. During the blister testing, the pressure applied to the film through the hole is augmented until the film begins to debond from the substrate. The blister shape before and after debonding is demonstrated in Fig. 1. After the bulging of the self-standing part of the film that covers the hole, a circular blister is formed and grows steadily in diameter. The critical strain energy release rate of the interface crack is determined from the height of blister and the pressure applied during crack growth.

Blister tests are simple and straightforward to analyse only when there is no generalized film yielding before debonding. Another limit of the test is that the crack has to propagate uniformly along the perimeter of the blister. Although the blister test has several limits, it is a reliable method to determine the amount of energy required to debond the film from its substrate, a quantity which characterizes the film adhesion.

The blister test as a standard method for measuring the adhesive strength of thin coatings was first suggested by Dannenberg [2]. The crack propagation energy G_{ci} is calculated directly from the pressure (P_c) vs. volume change (ΔV). The strain energy of the pressurized film is the amount of work required to inflate the film from an initially flat state to a height h, as

$$U_{\text{strain}} = \int_0^h p(h)\,\mathrm{d}V \tag{1}$$

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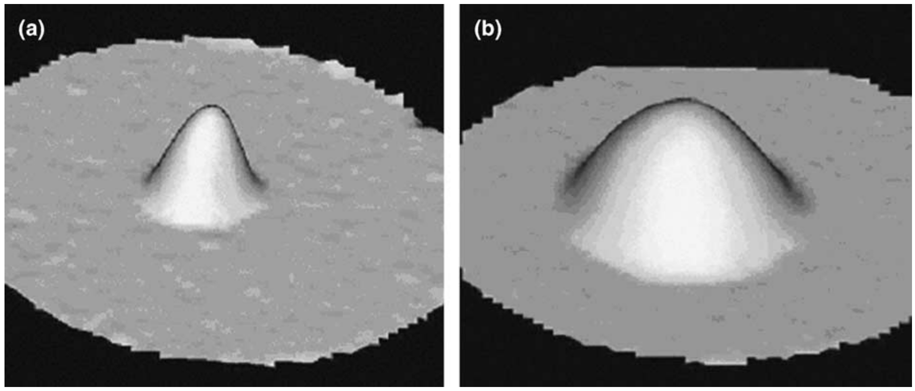

Fig. 1. 3-D-profilometry reconstruction of the Ag electrode: (a) before debonding (the Ag membrane bulge diameter is restricted to the hole) and (b) after debonding during the blister test (blister heights are strongly amplified by 3-D imaging).

The work done on the film by the applied pressure while the blister with radius a growing is

$$\frac{\partial W_{\text{ext}}}{\partial a} = \frac{\partial (pV)}{\partial a} \tag{2}$$

The expression for G can then be approximated as [3]

$$G = C \cdot p \cdot h \tag{3}$$

where C is a dimensionless constant which is a function of the residual stress σ_0 in film, of film biaxial modulus $E/(1-\nu)$ and of the geometrical ratio h/a. As the blister is forming, the equilibrium shape of the blister contour is circular and its ratio h/a is almost constant. The value of C can be taken as a constant during the test; this value is 0.516 for the case of high residual stresses and 0.645 for the case of low residual stresses [3,4].

2. Experimental procedures

A barium titanate powder (Product No. 219-6, Ferro Co., USA) was used in the present study. The purity of the $BaTiO_3$ powder was higher than 99.6%. A disc with a diameter of 25 mm and thickness of 2.5 mm was prepared by die-pressing at 60 MPa. The disc was first pre-fired at 1190 °C for 1 h to obtain a handling strength. A hole with a diameter of 2 mm was then machined into the center of the pre-fired disc by using a steel drill. The disc was then sintered at 1290 °C for 2 h. The relative density of $BaTiO_3$ was then >95%. Finally the disks were ground with fine SiC particles to achieve a flat smooth surface.

A silver paste (Ag 8985, Shoei Co., Japan) composed of silver particles, binder and a small amount of glass particles was used. Screen printing was used to apply the Ag paste onto the flat surface of the $BaTiO_3$ disc. Before screen printing, an adhesive tape patch was applied to cover the central hole of the disc. The $BaTiO_3$ discs with this printed first Ag layer were fired at 600 °C for 1 h to remove the adhesive tape. The discs with electrode including the free-standing membrane over the hole were then screen printed and fired several times until the desired thickness of Ag layer was achieved.

The apparatus used for the blister test consisted of a quadrilateral metal block specimen holder and pressurizing stage, and an optical measurement equipment. A fringe projection device was used to measure the vertical displacement of the specimen surface during the blister test [5]. The test sample was mounted on the top of the blister pressurizing stage. An expanded set of parallel fringes, produced by the interference of two laser beams, was projected under a certain angle on the top of the sample. A CCD camera was fixed above the blister apparatus to photograph the top view of the fringes on the specimen surface, which was then analyzed by a computer. Commercial software (HOLO 3: Fringe Analysis®) was used to analyze the results. The setup of the facilities is illustrated in Fig. 2.

The elastic modulus of porous Ag electrode before and after blister test was determined by using a nanoindenter (XP, MTS, USA). The specimen cross-sectional microstructure was observed by scanning electron microscopy (SEM) on samples before and after the blister test.

3. Results and discussion

The cross-section of a specimen after sintering is shown in Fig. 3. The Ag/$BaTiO_3$ interface is relatively smooth. The free-standing Ag electrode is porous. The relative density of the Ag electrode, as estimated by using image analysis, is around 73%. This density is slightly higher near the interface due to the fact that the electrode near the interface has been fired several times. The thickness of the silver electrode has been changed by between 80 μm and 170 μm. The thickness was measured by a micrometer, with reference to the initial substrate thickness. Five points have been measured and the average was taken as film thickness. Because the pores within the Ag electrode are interconnected, while the film is pressurized by distilled water, water could penetrate through the electrode. Therefore, an adhesive film (about 10 μm) is applied to cover the electrode to make it waterproof. This layer is visible on the top of the electrode, Fig. 3. The influence of this adhesive film is negligible on the Ag/$BaTiO_3$ interfacial strength as long as it is attached firmly to the electrode throughout the blister test.