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Authors
Cannon, R.M.
Fisher, R.M.
Evans, A.G.

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R.M. Cannon, R.M. Fisher, and A.G. Evans

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Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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DECOHESION OF THIN FILMS FROM CERAMIC SUBSTRATES

R.M. Cannon, R.M. Fisher and A.G. Evans[@]
Center For Advanced Materials, Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

ABSTRACT

Decohesion of thin films from ceramic or semiconductor substrates is strongly influenced by internal stresses in films and stress concentrations from edges or flaws as well as by interfacial fracture energy. Residual stresses can cause spontaneous delamination, splitting and curling of films under tension or delamination, buckling and spalling of films under residual compression, even with good interfacial bonding. Delamination behavior is considered using simple fracture mechanics models, supplemented with preliminary measurements of interfacial fracture energies. Formation conditions largely control internal stresses in films; whereas fracture energies are dictated by interfacial chemistry and mechanical factors such as plasticity.

INTRODUCTION

Failure of systems having ceramic-metal interfaces is usually brittle or semi-brittle and can be treated using fracture mechanics. This permits quantitative evaluation of behavior and correlation of chemical and mechanical aspects such as sensitivity to cleanliness, processing, or residual stresses.

From a fracture mechanics perspective, factors controlling strength are categorized under: stress state, fracture toughness, and inititating flaw population. The stress state depends strongly upon internal stresses and stress concentrations from edges and from elastic modulus mismatch as well as applied forces. The fracture energy depends upon crack location; it reflects mechanical or microstructural aspects such as plasticity or crack deflection as well as interfacial chemical and structural factors controlling crack tip behavior. Flaw populations are difficult to characterize and impart a statistical aspect to strength; important sources include incomplete interfacial bonding, residual pores, microcracks around reaction products or inclusions, and surface damage from contact or machining. Inhomogeneous plasticity can cause stress concentrations as well as initiate cracks.

This paper addresses the role of several of these factors in thin film delamination. Conventional strength or pull tests (e.g. the "Scotch tape test") are hard to interpret and often poorly reproducible. Thus, simpler limiting situations are emphasized for which film delamination is less sensitive to flaw size, and other techniques are applied.

@Present address, Materials Group, Dept of Mechanical Engineering, Univ of Cal. Santa Barbara, CA 93106

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BACKGROUND

Crack extension is driven by the strain energy release rate which is:

$$G = (-dW/dA + dU/dA)$$

where W and U are, respectively the external free energy and internal strain energy; and A, the crack area. This quantity can be compared to thermodynamic or chemical energies. It is also related to crack stress concentration factors although the relationship is complicated when elastic moduli differ across the crack plane, an important issue with combined tensile and shear loading 1 .

A simple crack extension criterion is that advance occurs at a critical strain energy release rate, G_c. However, growth resistance may depend upon prior crack extension and external atmospheres. Further complexities arise in conjunction with predicting and understanding affects of crack path in these heterogeneous systems. When loading is not purely tensile, as for film delamination, the conditions dictating crack path and extension criteria are uncertain. Alternative criteria reflect the tendencies for cracks to extend normal to the maximum tensile stress or to optimally reduce strain energy, but are modified by heterogeneities in growth resistance. Moreover, the fracture energy, G_c, may increase with the ratio of shear to tensile loading.

Fracture may occur in either adjoining member or at the interface. In all three instances in Fig. 1, some plastic deformation may obtain especially if the metal has a low yield stress. If the plastic zone size is limited by the metal dimensions, as may occur in metal films, G_c depends upon the metal thickness. Moreover, if the plastic zone extends through the film, ductile behavior may ensue for an unconstrained film, requiring a plasticity analysis.

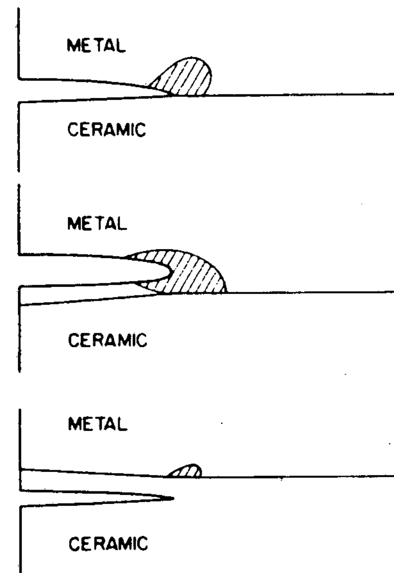


Fig. 1. Possible crack locations.

FRACTURE ENERGIES-TOUGHNESS

Were interfacial fracture reversible, the energy controlling crack growth, G_c, would be the work of adhesion, W_{ad}, i.e. the difference in equilibrium energies of the ceramic and metal surfaces created and the ceramic-metal interface destroyed. This quantity reflects interfacial structure and chemical bonding across the interface including effects of dispersion and image forces, electron sharing, and charge transfer by electrons or ions.

Irreversible contributions to surface creation are important, even without plasticity. Analysis of oxide crystal and grain boundary cleavage suggests the fracture energy is proportional to a modified work of adhesion, W_{ad}'[2]. The proportionality constant reflects irreversibilities associated with breaking bonds at the crack tip. It is higher for less close packed surfaces, perhaps varying from 1 to 3. Creation of nonequilibrium surfaces raises W_{ad}' and thus, the fracture resistance; this obtains if creating the interface involved diffusional reconstruction relative to the two equilibrium surface structures. If the crystallographic surfaces to be created are not naturally

neutral, as for a dipolar interface between a ceramic and semiconductor or for cleaving the Al_2O_3 basal plane, the crack may be forced from the interfacial plane of lowest bond density, again increasing fracture resistance.

Segregation may significantly alter bond rupture resistance. Prior interfacial segregation usually reduces $-W_{ad}$ although exceptions are important. Reactive environments can induce stress corrosive crack growth.

Plasticity can cause crack blunting, which reduces the crack stress concentration, and crack shielding from closure forces induced by residual stresses from constrained deformation near the crack. In both instances, toughening may increase with decreasing yield stress; however, where the crack opening displacement from blunting is fixed geometrically (e.g. by metal film thickness) or otherwise, toughness increases with yield stress. Crack tip processes are important because plastic zone size and dissipation increase if higher forces are required to break interfacial bonds. Moreover, sufficient interface toughness drives cracks into the weaker neighboring member.

Finally, dissimilar interfaces are often rough, and for many ceramic-metal couples the bonded region involves a reaction zone. Crack tip deflection or other crack interactions with the local microstructure can appreciably inhibit propagation. Increasing far field stresses to overcome local deflections can also increase the plastic zone. Further increases in crack resistance could derive in specific instances from crack shielding from stress induced phase transformation or microcracking around the crack, or from crack branching. Bridging of material across the crack could also be important, especially in the presence of ductile interfacial phases. However, microstructural toughening must be viewed in the context that cracking through any low toughness interfacial phase present would reduce the tip resistance.

With shear loading or for delamination of films with stress gradients, contact can occur across the crack face, especially with rough interfaces; it may be enhanced by elastic modulus differences across the crack plane [1]. Such contact coupled with enhanced plasticity could increase G_c.

Fracture energies have been measured by adapting the double cantilever beam (DCB) method. Samples were prepared by evaporating thin Cu films onto glass slides, bonding two slides together, and bonding grips at one end, Fig. 2. Masking provided precracks. For one method the Cu from two slides was pressure bonded at 400°C. Alternatively, an epoxy bond between the Cu film and a second glass slide permits testing of as-deposited interfaces and films; however, measurable interface toughnesses are limited by the epoxy strength which is marginal for the best Cu/glass couples.

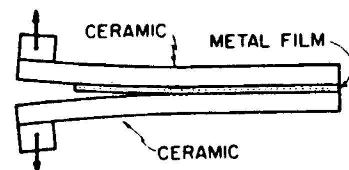


Figure 2.

The highest G_c was about 8 J/m^2, similar to that for glass. It resulted from diffusion bonded, 2 μm thick Cu and sputter cleaned slides. Other, less clean samples, gave values between 0.14 and 4 J/m^2. Subcritical crack growth was easily observed at applied G values below half the maximum for a given sample. Fracture was usually at the Cu/glass interface as judged by optical microscopy. Microscopic and other evidence revealed plasticity contributed to the fracture energies. A very thin Cr flash between the Cu and glass caused a propensity for the crack to run into the glass, suggesting that Cr gives improved atomic bonding at metal-glass interfaces [3].

INTERNAL STRESS-INDUCED DELAMINATION

Large residual stresses in thin films can cause spontaneous delamination even in the presence of good interfacial bonding. Residual stresses which develop during deposition (or from thermal expansion mismatch) are exacerbated by stress concentrations at film edges. The driving force, G, for edge crack delamination increases with crack length to an asymptotic limit, Fig. 3, which is independent of the sign of the stress. (The coefficient is for uniform biaxial stress, σ_r, where ν is Poisson's ratio; differences if σ_r is anisotropic or varies through the thickness are easily derived.) Below a critical film thickness $(G_c E/\sigma_r^2(1-\nu))$, residual stress-driven delamination is unfavorable for any flaw size. Above this thickness, the flaw length to induce delamination need be only 5t or less, at least with tensile stresses. Moreover, edges will be particularly sensitive to damage from impact or grinding. However, the driving force develops more slowly for compression than tension; it is affected by residual bending moments within the film and elastic modulus, E, differences between film and substrate, which affect the extent of crack closure [4]. Unless delamination starts at edges, films must either split (if residual tension) or buckle (if residual compression) to facilitate delamination.

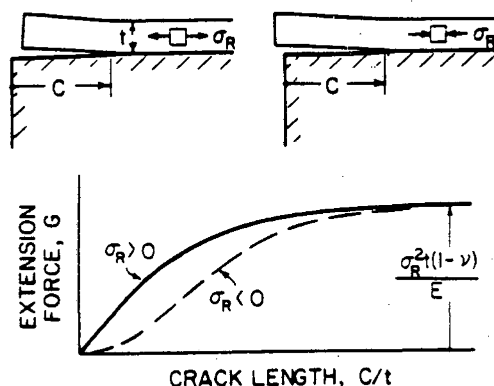
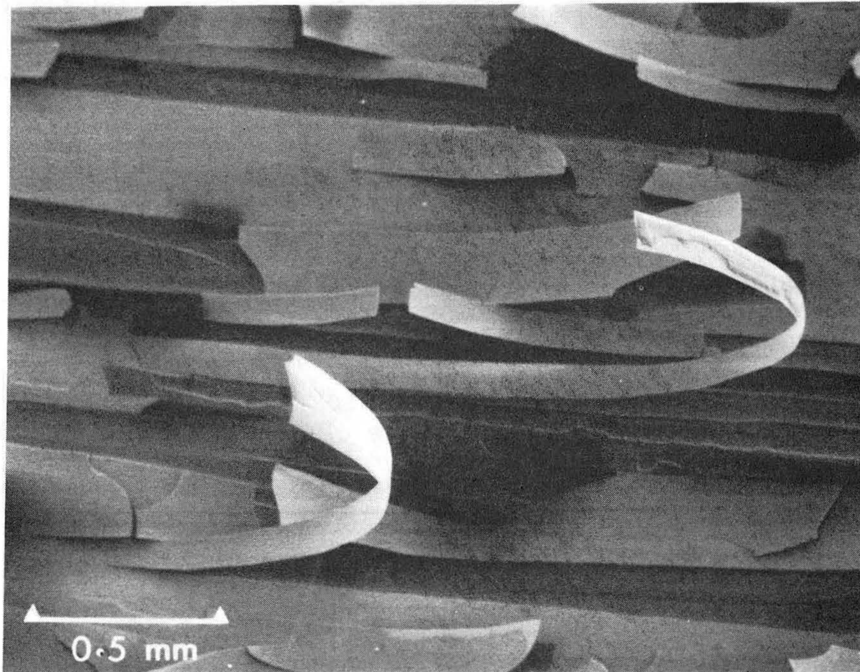


Fig. 3. Spontaneous cracking of residually stressed films.

For in-plane compression, film delamination with buckling can initiate at flaws far from the edge. The driving force for extension only develops for a cracked region exceeding a critical buckling size; it rapidly approaches an asymptote as C increases further [5]. This limiting G is a factor (1-a) smaller than that for edge delamination and occurs at larger C/t than for edge cracking without crack closure. For round delaminations, a ≃ 0.4 [5], giving a larger critical thickness. In practice complex buckling often obtains involving intergrowth of "wormy" buckles which sometimes coalesce, as observed for microbuckling of oxide scale at a critical thickness, and reported for deposited films [6 and refs. cited].

The effects of large tensile stresses are illustrated, Fig. 4, by Cr films on glass or Si. Films were electron beam evaporated (EBE) onto sputter etched substrates at an oblique angle. These films first split along lines radiating from the evaporation source. Subsequently, the long ribbons crack across, delaminate, and curl significantly owing, in part, to a stress gradient within the film. Calculations based upon the curvature of delaminated ribbons suggest the maximum tensile stresses were about 4-8 GPa (0.01E-0.02E) and had a 20:1 anisotropy [7]. The splitting and delamination occur slowly (over weeks) at room temperature and faster after annealling between 200 - 330°C; this is believed to reflect an increase in stresses caused by local atom rearrangement near poorly equilibriated grain boundaries.

Delamination from glass initially occurs at or very near the interface as cracks extend from splits in the Cr film; however, final delamination often involves fracture several film thicknesses within the substrate. For films on Si most of the delamination cracks are 1 to 3 film thicknesses deep within the substrate, as seen in Fig. 4. Apparently, the interfacial G_c are comparable to or exceed those for the substrates. It is of interest that G_c is lower for (111) cleavage of Si than for glass, and the fraction of substrate fracture was higher for Si.



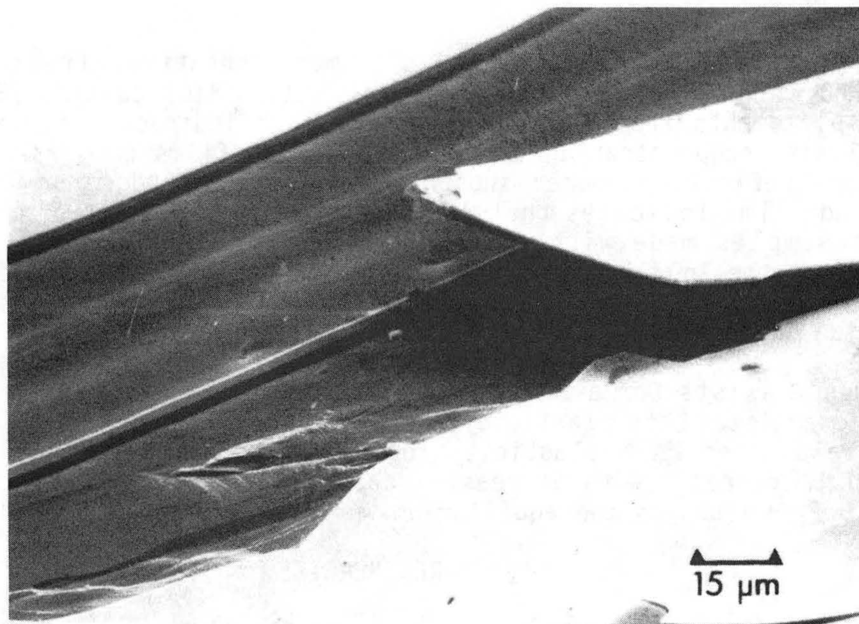


Fig. 4. Spontaneous splitting, delamination and curling of evaporated 1.2 μm Cr films from glass (a) and Si (b) substrates. (XBB 850-9586 and XBB 850-10254)

INDENTATION-INDUCED DELAMINATION

Indentation induces delamination of films, driven by misfit from material displaced from the impression. Thus, indentation methods are applicable for estimating G_c and modeling contact damage to films. The relationship between delamination size and G_c depends upon whether the film buckles or splits, and if it does, on the residual film stress. The available analysis assumes that the film is softer than the substrate, that indentation does not penetrate through the film, and that residual stresses are compressive [8].

Indentation tests on 8 μm sputtered ZnO and 0.5-1 μm evaporated Cr films on glass demonstrate that delamination increases with load even when the penetration depth, d, far exceeds the film thickness. However, film buckling and cracking can reduce delamination. When d/t exceeded 4-10, delamination was nonuniform and smaller [9]. Interfacial delamination of similar 1 μm Cr films on glass was very sensitive to interfacial chemistry as affected by differences in substrate cleaning, use of an ultrathin Cu underlayer, or exposure to moisture which enhanced delamination. The EBE Cr films on glass or Si exhibit much greater delamination sizes, extensive splitting, and spalling at higher loads, owing to the higher residual tension. These results suggest indentation can be extended to a wider thickness range than expected.

DISCUSSION

Variously deduced interfacial fracture energies, G_c, are summarized in the Table. The DCB results are the most reliable mechanical data, as analysis is straightforward and crack loading is tensile. Variability in G_c may reflect differences in Cu thickness and yield stress, but substrate cleanliness causes the major effect.

Interpretation of indentation tests is more tentative. Previous work used 5-10 μm ZnO films sputtered onto Si with an 0.1 μm SiO_2 coating [8]. Concerns about displacements from the indenter led to an indirect calibration. Using this analysis, nonpenetrating indentations in ZnO films on glass give a lower G_c, perhaps reflecting poorer substrate cleaning. Preliminary analysis for penetrated films indicates that G_c varied by 1 to 2 orders of magnitude for Cr/glass samples made with different cleaning methods [9]. The high G_c suggested for the ZnO/Si system may reflect effects of shear loading since G_c exceeds those for the SiO_2 interlayer and the Si substrate in tension although calibration uncertainties preclude a conclusion.

Evidence exists for a plasticity contribution to Cu/glass interfacial fracture energies. Less plasticity would be expected in Cr films owing to the higher yield stress. A plasticity contribution for the Nb/Al_2O_3 system was suggested to decrease with increasing crack velocity [10]. Interpreting the available G_c values as the equilibrium work of adhesion would imply negative

FRACTURE ENERGIES

FILM/SUBSTRATE	G_c, J/m^2	H_2O INDUCED GROWTH	COMMENT
Cu/Glass	0.14 - 8	YES	DCB
ZnO/Glass	∿ 4	?	Indent.
$ZnO/SiO_2/Si$	14	?	Indent.(8)
Cr/Glass	∿ 8	YES	Crack often in glass
Cr/Si	> 4	LITTLE	Delam. largely in Si
Comparisons (Mode I loading)			
Glass	8	YES	
ZnO	18	PROBL.	Polycryst.
Si	4	LITTLE	Sing. cryst.

interfacial energies, whereas appreciable positive values are expected. Thus, interpretation awaits quantification of all irreversible contributions.

CONCLUDING REMARKS

Thin film delamination has been examined using fracture mechanics. Direct measurements, and cracking within substrates, show that for clean, well bonded systems interfacial fracture energies are similar to those for the substrate. They exceed the work of adhesion owing to irreversible behavior, including plasticity. However, fracture energies can be far lower evidently owing to poor bonding from adsorbed layers of hydroxyl, water, alkoxides, or organics.

Simple analyses show that spontaneous delamination can be driven by high residual stresses in films exceeding a critical thickness. Although edge delamination is easiest, more complex delamination originates in the center for well bonded but highly stressed films. The additional difficulties attending such delamination, i.e. buckling for compressive films or splitting for tensile films forestall delamination to a degree.

Although these evaluations provide important insights, several features require further study. The subsurface delamination for tensile stressed Cr films on glass and Si reveals that extension at a unique strain energy release rate, G_c, is an insufficient criterion for predicting crack path or for describing fracture resistance under combined tensile and shear loading; criteria reflecting a preference for paths with minimal shear may provide insights. Assessment is also required on the effect of splitting resistance for delamination of tensile films and on termination of delamination by spalling. Identification of initiating flaws awaits investigation although contact damage and inclusions appear to be important.

Indentation has potential for assessing fracture energies and delamination resistance, but study is required evaluating effects of buckling, tensile residual stresses and the extent of penetration of very thin films.

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