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MEASUREMENT OF THE ULTIMATE SHEAR STRENGTH OF A METAL–CERAMIC INTERFACE

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Abstract—The ultimate shear strength of a metal–ceramic interface has been measured by depositing a thin film of the ceramic on a ductile, metal substrate. As the metal is plastically stretched the ceramic film develops cracks that are oriented transverse to the pulling direction. The density of the cracks (the number per unit length) increases as more and more plastic strain is applied to the metal substrate. Eventually the crack density reaches a constant value and is not influenced by further plastic deformation of the metal. Theoretical analysis of the problem prescribes that the minimum and the maximum spacing between the cracks should differ by a factor of two. Also, the ultimate shear strength of the metal–ceramic interface is related to the tensile fracture strength of the ceramic film and the *largest* spacing between the cracks; both of these quantities are measured in this simple technique. Experiments performed with 60 nm thick films of silica bonded to pure copper substrates show the tensile fracture strength of the film to be in the range 3.4–6.7 GPa, and the ultimate shear strength of the interface to lie in the range 0.56–1.67 GPa.

Résumé—La résistance au vieillissement d'une interface métal–céramique a été mesurée en déposant un film mince de céramique sur un substrat métallique ductile. Quand le métal est étiré plastiquement des fissures, orientées transversalement à la direction de tirage, se développent dans le film de céramique. La densité de fissures (leur nombre par unité de longueur) augmente au fur et à mesure que la déformation plastique est appliquée au substrat de métal. Finalement, la densité de fissures atteint une valeur constante et n'est pas influencée par une déformation supplémentaire du métal. Une analyse théorique du problème prédit que les espacements minimal et maximal entre les fissures diffèrent d'un facteur deux. Aussi, la résistance à la rupture par cisaillement de l'interface métal–céramique est liée à la résistance de la rupture en traction du film de céramique et au plus grand espacement entre les fissures; ces deux quantités sont mesurées avec cette technique simple. Les expériences réalisées avec des films de silice de 60 nm d'épaisseur liés à des substrats de cuivre pur montrent que la force de rupture en traction du film se situe dans le domaine 3,4–6,7 GPa, et que la résistance en cisaillement de l'interface se situe dans l'intervalle 0,56–1,67 GPa.

Zusammenfassung—Die äußerste Scherfestigkeit einer metall-keramischen Grenzfläche wurde an einem dünnen Keramikfilm, der auf einem duktilen metallischen Substrat abgeschieden worden war, gemessen. Wird das Metall plastisch gedehnt, dann bilden sich in der keramischen Schicht Risse, die quer zu der Zugrichtung liegen. Die Dichte dieser Risse (Anzahl pro Einheitslänge) nimmt mit der plastischen Dehnung des Metallsubstrates und erreicht schließlich einen konstanten Wert, der durch weitere plastische Dehnung nicht mehr beeinflußt werden kann. Die theoretische Analyse dieses Falles ergibt, daß sich minimaler und maximaler Abstand zwischen den Rissen um den Faktor Zwei unterscheiden sollten. Außerdem hängt die äußerste Scherspannung der metall–keramischen Grenfläche mit der Bruchfestigkeit im Zugversuch des keramischen Filmes und dem *größten* Abstand zwischen den Rissen zusammen. Beide Größen können mit diesem einfachen Versuch gemessen werden. Experimente an 60 nm dicken Siliziumdioxidfilmen auf reinem Kupfer zeigen eine Bruchfestigkeit im Zugversuch zwischen 3, 4 und 6, 7 GPa, die äußerste Scherfestigkeit der Grenzfläche liegt zwischen 0,56 und 1,67 GPa.

INTRODUCTION

The ultimate shear strength of metal–ceramic interfaces is an important fundamental parameter when considering failure mechanisms in metal matrix/ceramic fiber composites. In the case of ceramic–ceramic composites, an indentation technique has been used successfully to measure the shear strength of the interface [1]. A microhardness indentor is pushed on one fiber and the load at which the fiber debonds from the ceramic matrix is measured and related to the shear strength. This method may not be suitable for the metal–ceramic composites because of the relatively low yield stress of the metal; the indentation technique can be expected to work well only when the shear strength of the interface is less than yield strength of the matrix.

In the case of fiber reinforced polymers and fiber reinforced metals, the interface shear strength has been measured by pulling the unidirectional fiber composites in tension. This causes the fiber to fragment into several pieces and the size of these fragments can be related to the interface strength [2–4]. The technique presented here is a variation of this method. Rather than studying the composite we study only the interface by depositing a thin film, with a large surface area, on a substrate of the metal. The metal is then

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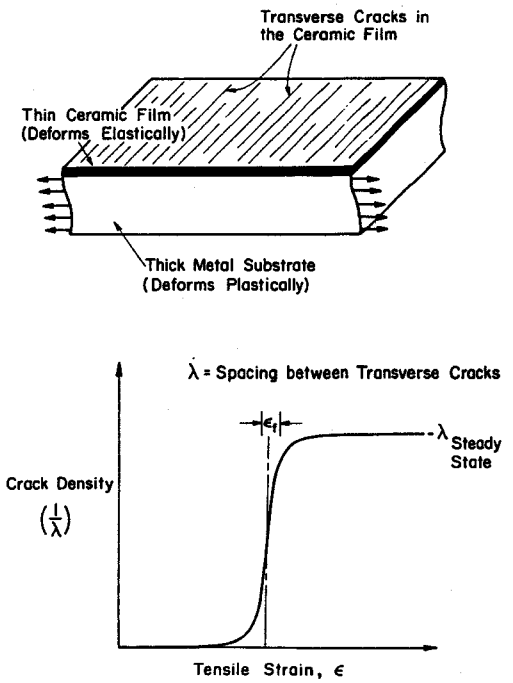

Fig. 1. Illustration of the experimental technique (top). A schematic of the increase in crack density in the silica film with the strain applied to the copper substrate (bottom).

deformed plastically in tension while the crack on the surface of the ceramic film is observed. The strain at which the cracks begin to appear gives a measure of the tensile fracture strength of the ceramic film. The steady state spacing between the cracks can be analyzed to yield the ultimate shear strength of the interface.

First, the theoretical analysis of the problem is presented. That is followed by presentation of results from very thin films of silica that are deposited on copper substrates.

THEORY

The procedure of the experiment and a schematic of the results is explained in Fig. 1. A thin ceramic film is deposited on an "infinitely" thick metal substrate and the composite is deformed uniaxially. The same strain is applied to the metal and the ceramic, except that the metal deforms by plastic deformation and the ceramic by elastic deformation. The development of transverse cracks with increasing strain is expected to show sigmoidal behavior. The tensile strength of the film, $\hat{\sigma}$, is related to the fracture strain, ϵ_f, by the equation

$$\hat{\sigma} = \epsilon_f E \tag{1}$$

where E is the Young's modulus of the ceramic film. As illustrated in Fig. 1, ϵ_f will be determined by the change in crack density with applied strain.

We now analyze the ultimate shear strength of the interface in terms of the crack spacing λ. Consider first the case where two cracks a distance L apart, at positions A and B, have formed in the film as shown in Fig. 2(i). The film cross-section is now stress free at surfaces A and B. Yet the film is stretched and is held in place by the strength of the shear bond along the interface. The distribution of the shear stress is likely to be as illustrated in Fig. 2(ii). Free body equilibrium condition, applied to the section of the film AB, requires that the shear stress integrated over the distance $x = 0 \rightarrow L$ must be equal to zero. The shear stress, therefore, must be antisymmetric as shown in Fig. 2(ii). As a reasonable approximation we assume that it has a sinusoidal form, that is

$$\tau = \hat{\tau} \sin \frac{2\pi x}{\hat{\lambda}}, \quad 0 \leqslant x \leqslant \frac{\hat{\lambda}}{2} \tag{2a}$$

$$\tau = 0, \quad \frac{\hat{\lambda}}{2} < x < \left(L - \frac{\hat{\lambda}}{2}\right) \tag{2b}$$

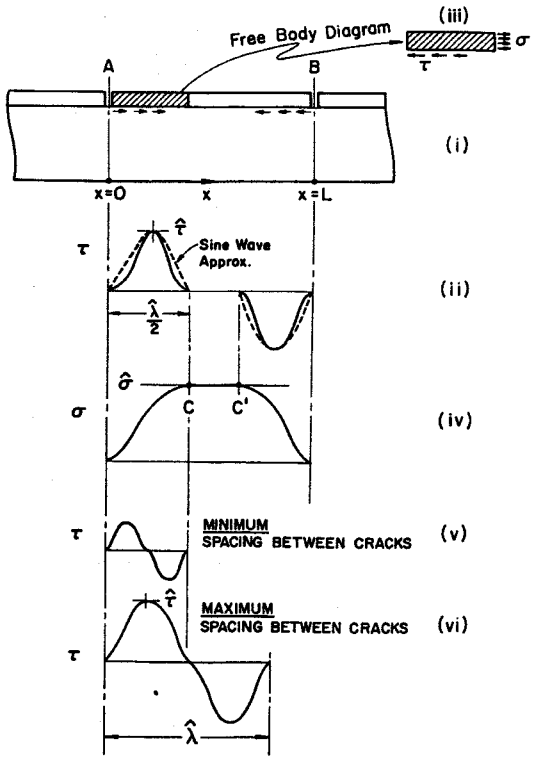

Fig. 2. Stress distributions at the metal ceramic interface, and through the thickness of the film when transverse cracks are formed in the silica film. τ is the shear stress supported at the interface, and σ is the in-plane stress in the film. The shear stress is assumed to have a sinusoidal shape (ii). The form of σ in (iv) is defined by the free body diagram (iii). The minimum and the maximum crack spacing is uniquely related to $\hat{\lambda}$, which is the wavelength of the sine function used to define $\hat{\tau}$ in (ii); this is because new cracks can form only in the region CC′ where the tensile stress is maximum. The nearest new crack can form at position C. Ultimately the large spacing between the cracks can be $\hat{\lambda}$. Thus the minimum and the maximum crack spacings are separated by a factor of two (if the fracture strength of the films as well as the ideal shear strength of the interface are assumed to be single valued).

and

$$\tau = -\hat{\tau}\sin\frac{2\pi}{\hat{\lambda}}\left[x-\left(L-\frac{\hat{\lambda}}{2}\right)\right],$$

$$\left(L-\frac{\hat{\lambda}}{2}\right)\leqslant x\leqslant L. \tag{2c}$$

We assume the in-plane stress in the film, σ, to be uniform through the cross-section of the film. It will be a function of x; this relationship is calculated by considering a series of free body diagrams for the film, for different values of x; an example is illustrated in Fig. 2(iii). That leads to the following equation for σ

$$\sigma(x)=\frac{1}{\delta}\int_0^x \tau\,\mathrm{d}x. \tag{3}$$

Equation (3) gives the following result for $\sigma(x)$

$$\sigma(x)=\frac{\hat{\lambda}\hat{\tau}}{\pi\delta}\sin^2\left(\frac{2\pi x}{\hat{\lambda}}\right),\quad 0\leqslant x\leqslant\frac{\hat{\lambda}}{2} \tag{4a}$$

$$\sigma(x)=\hat{\sigma}=\frac{\hat{\lambda}\hat{\tau}}{\pi\delta},\quad \frac{\hat{\lambda}}{2}<x<\left(L-\frac{\hat{\lambda}}{2}\right) \tag{4b}$$

and

$$\sigma(x)=\frac{\hat{\lambda}\hat{\tau}}{\pi\delta}\sin^2\frac{\pi}{\hat{\lambda}}(L-x),\left(L-\frac{\hat{\lambda}}{2}\right)\leqslant x\leqslant L. \tag{4c}$$

Consider now the spatial distribution of new additional cracks. They can form anywhere in the region of maximum stress, that is in the region CC′. Each new crack will change the stress distribution. Cracks will continue to form as long as the space between adjacent cracks includes a region where $\sigma\geqslant\hat{\sigma}$. This concept immediately leads to bounds on the minimum and the maximum crack spacing.

The minimum crack spacing, which we call λ_0, obtains if a new crack forms at position C in Fig. 2(iv). That would produce the stress distribution illustrated in Fig. 2(v). In this case the shear stress from the adjacent cracks will overlap so that the maximum value of the shear stress will become less than $\hat{\tau}$. This case is not of interest since our objective is to measure the maximum value of τ that can be supported by the interface.

The maximum crack spacing will occur when adjacent cracks are a distance $\hat{\lambda}$ apart. If the spacing is greater, then the situation equivalent to Fig. 2(iv) will obtain, raising the possibility of forming another crack, which will decrease the spacing to less than $\hat{\lambda}$.

The stress distribution for the maximum crack spacing is illustrated in Fig. 2(vi). In this case the stress distribution is given by the equation

$$\sigma(x)=\hat{\sigma}\sin^2\frac{\pi x}{\hat{\lambda}} \tag{5a}$$

and

$$\hat{\tau}=\frac{\pi\delta}{\hat{\lambda}}\hat{\sigma}. \tag{5b}$$

†Talysurf 5-120, Taylor-Hobson, England.
‡Randolph Research Ellipsometer, Model 43603.

Furthermore the maximum and the minimum crack spacing are linked by the equation

$$\lambda_0=\frac{\hat{\lambda}}{2} \tag{6a}$$

where

$$\lambda_0\leqslant\lambda\leqslant\hat{\lambda}. \tag{6b}$$

The objective of the experiments is to measure the ultimate shear strength of the interface, $\hat{\tau}$. It is most simply obtained through equation (5b). That requires two measurements: $\hat{\sigma}$, that is the fracture stress of the ceramic film, and $\hat{\lambda}$ which is the *maximum* spacing of the cracks when the crack density becomes constant. The fracture stress is obtained by measuring the strain, ϵ_f, when the cracks begin to form; its value may have a range since the fracture strength may have some variability, as illustrated schematically in Fig. 1. The quantity $\hat{\lambda}$ can be measured accurately by studying a large number of cracks in a single specimen. The validity of the theory can be addressed by checking the distribution in the crack spacing; according to equation (6b) the minimum and maximum crack spacings should differ by a factor of two.

EXPERIMENTAL

Preparation and characterization of films

Silica films were deposited on the copper substrate by the sol-gel process [5, 6].

Strips of pure (99.9%) copper, approximately 3 mm wide × 25 mm long × 0.3 mm thick were chemically polished in a mixture consisting of equal parts by volume of nitric acid, phosphoric acid and glacial acetic acid at 60°C for 2 min. After rinsing with water and ethyl alcohol, the strips were dip coated in a sol consisting of tetraethylorthosilicate (TEOS), ethyl alcohol, water and conc. HCl in the molar 0.8:15.0:5.8:0.02. The sol was prepared by mixing the ingredients and stirring the mixture for 1 h. The coated strips were dried in an oven at 40°C for 8 h. Hydrolysis and condensation reactions take place during the drying of the liquid remaining on the substrate surface, leading to the formation of a silica gel film. The films were subsequently heated at 2°C min^{-1} in a vacuum of 1×10^{-6} torr to 600°C, held at that temperature for 0.1 h and cooled by switching the furnace off; this procedure was used to sinter and densify the films.

The thickness of the silica film after the treatment at 600°C was measured with a profilometer† and its refractive index was measured using an ellipsometer.‡ These measurements were used to obtain an estimate of the relative density of the film.

Thickness of the silica film and its refractive index were found to be 63 ± 2 nm and 1.428 respectively. Taking the refractive index of fused silica [7] to be 1.45845, the relative density, ρ, of the film is obtained using the relation [8]

$$\rho=\frac{n_p^2-1}{n^2-1} \tag{7}$$

where n and n_p are the indices of refraction of fused silica (100% dense) and the porous film respectively. The density of the film estimated by this method is 0.922 relative to the fused silica.

The Young's modulus of fully dense silica film is 73 GPa [9]. Assuming that the elastic properties scale as the rule-of-mixtures when the film is slightly porous, we estimate the Young's modulus of our films to be $E = 67.3$ GPa.

Mechanical measurements

The copper substrates were pulled uniaxially in a straining stage equipped with a micrometer. The straining stage was calibrated by measuring the actual change in length of the plastically deformed copper strips. The substrates were intermittently removed from the straining stage and examined in a scanning-electron-microscope in order to study the development of cracks in the silica film.

The SEM analysis showed that *all* cracks in the silica film formed normal to the tensile axis irrespective of the orientations and the grain boundaries of the underlying grains in the copper substrate. Heavy deformed bands, in the form of shear slip traces, were visible through the film—an example is shown in Fig. 3—but the primary fractures in the film remained aligned normal to the strain axis.

The density of cracks in the film developed rapidly at a strain of 10%. At a strain of less than 5%, practically no cracks could be seen. A few formed at 5% strain, their number grew rapidly at 10%, and when the strain was greater than 25% the number of cracks became constant. The number density of the cracks are quoted in Table 1. Typical photographs of the cracks in the silica film at 5 and 10% strain are shown in Fig. 5.

Table 1. The number of cracks per unit length forming at various applied tensile strain

Strain (%)	Crack density (mm^{-1})
5	654
10	1550
25	1587

The distributions of the crack spacing, at different strains, are given in Fig. 4. At 25% strain, the minimum and the maximum crack spacing spans from 0.3 to 1.1 μm which is greater than the ratio of a factor of two that is expected in the ideal case where all the cracks form at once, at a single value of the applied strain. We believe that statistical techniques can be developed to relate the distribution in the values of the tensile fracture strength of the film to the distribution in the crack spacing. For the present we assume the following values for $\hat{\sigma}$, λ_0 and $\hat{\lambda}$ from the current data:

$$\hat{\sigma} = 0.10\,E$$
$$\lambda_0 = 0.4\,\mu\text{m}$$
$$\hat{\lambda} = 0.8\,\mu\text{m} \qquad (8)$$

where $\hat{\sigma}$ is obtained from equation (1) by substituting $\epsilon_f = 0.10$.

The ultimate shear strength of the interface, $\hat{\tau}$, is estimated by substituting for $\hat{\sigma}$, δ and $\hat{\lambda}$ in equation (4b). We have that $\delta = 63$ nm, and $E = 67.3$ GPa. This gives $\hat{\sigma} = 6.73$ GPa, and substituting $\hat{\lambda} = 0.8\,\mu$m

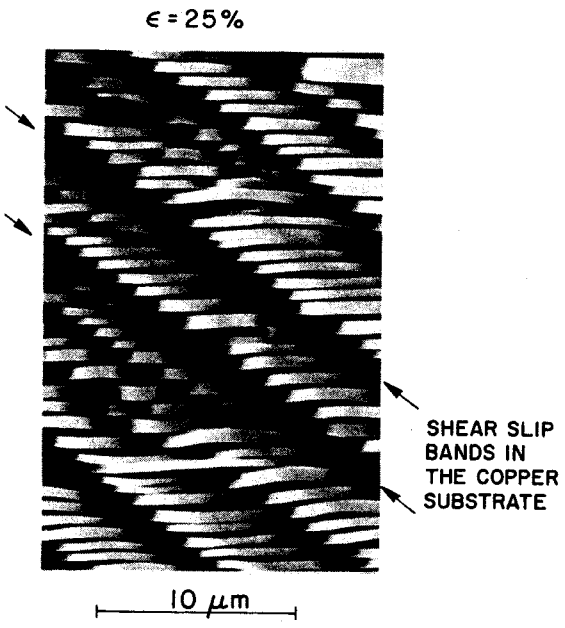

Fig. 3. The shear slip bands in the copper appear as relief in the silica film. However, the crack spacing is not influenced by the orientation and the localization of the slip bands. $\epsilon = 25\%$.

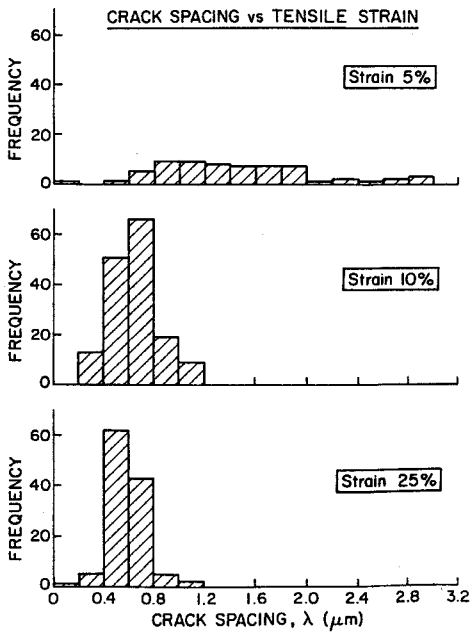

Fig. 4. The distribution of crack spacing, λ, obtained at applied tensile strain of 5, 10 and 25%.

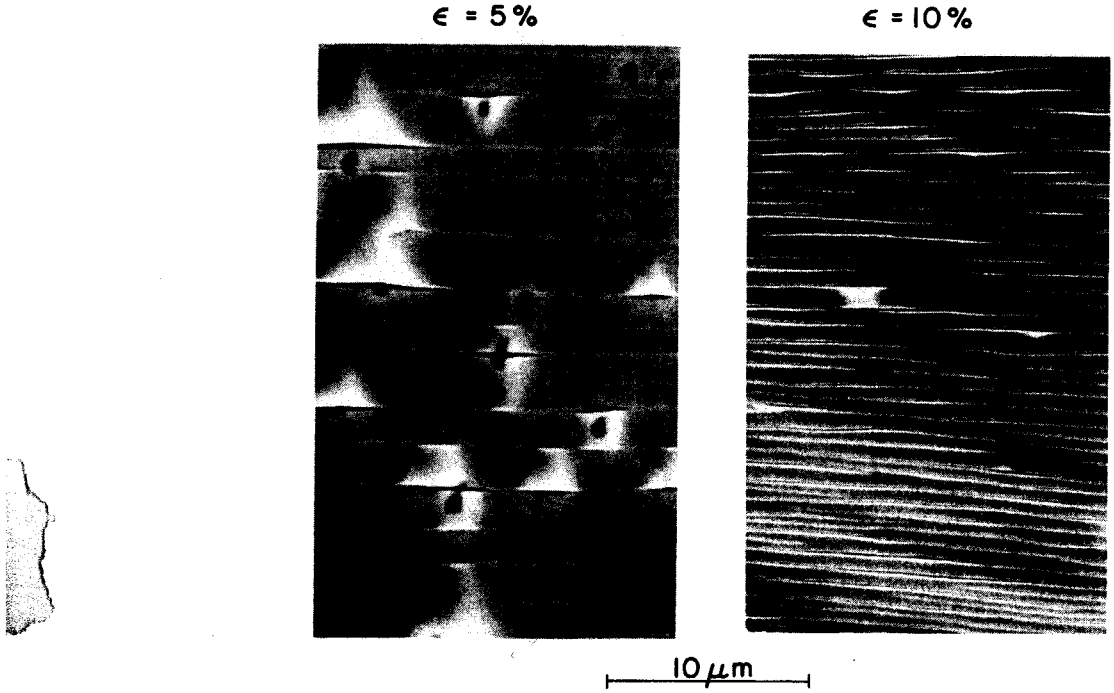

Fig. 5. Typical SEM micrographs of cracks in the silica film at 5 and 10% tensile strain. The tensile axis was normal to the crack profiles.

we obtain the following value for $\hat{\tau}$

$$\hat{\tau} = 1.67\ \text{GPa}. \tag{9}$$

The value presented in equation (9) is an average number. We are hesitant to prescribe a variation in $\hat{\tau}$ at the present time since that requires a correlation between the statistical distributions for $\hat{\sigma}$ and $\hat{\lambda}$. However, it would be useful to estimate what may be the lowest possible estimate of $\hat{\tau}$ on the basis of the current data. The measurement of δ is quite precise and its variation is negligible. That means that the error arises from $\hat{\sigma}$ and $\hat{\lambda}$; where $\hat{\tau} \propto (\hat{\sigma}/\hat{\lambda})$. The lowest possible value for $\hat{\tau}$ obtains for the smallest possible $\hat{\sigma}$ and largest possible $\hat{\lambda}$. Since we found that the cracks appeared only when the strain was greater than 5%, the smallest possible value for ϵ_f is 5%, that is, $\hat{\sigma}$ could be a factor of two smaller than assumed for equation (9). Similarly, from the results presented in Fig. 5, we estimate the maximum possible value of $\hat{\lambda}$ to be 1.2 μm, which is a factor of 1.5 greater than assumed in equation (9). Thus the minimum possible value for $\hat{\tau}$ could be a factor of 3 smaller than equation (9), that is, 560 MPa.

If $\hat{\tau}$ for the silica–copper interface lies in the range 0.56–1.67 GPa, it means that the yield strength of the interface is approximately one fifth of the ideal shear strength of crystal copper. (The shear modulus of copper at room temperature is 74 GPa and its ideal shear strength may be estimated at 5% of the shear modulus.) The results suggest that the strength of the copper–silicon–oxygen bonds is nearly the same as the strength of the copper–copper bonds. The finding is not altogether surprising since the enthalpy of formation of metal oxides is often greater than the heat of evaporation of pure metals.

We must also consider the mechanism of yielding at the interface as well as the role of strain concentrations caused by the obstruction of slip bands at the silica–copper interface. This factor is probably not very important in our measurements because the crack spacing and orientation are not influenced by the details of the plastic strain in the copper substrate. The fact that slip steps by themselves do not cause the silica film to spall suggests a strong bond between the oxide and the metal.

The fracture strengths of the silica films we have measured—about 5–10% of the Young's modulus—are high but still more than a factor of two smaller than strengths of optical quality, highly polished, silica fibers. In these fibers fracture strengths as high as 22% of the Young's modulus, for fiber diameter of 30 μm, have been reported [9].

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