Acta Materialia 99 (2015) 273–280

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Brittle film-induced cracking of ductile substrates

Tao Guo [a], Lijie Qiao [a,*], Xiaolu Pang [b,*], Alex A. Volinsky [c]

[a] Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, Beijing 100083, China
[b] Department of Materials Physics and Chemistry, University of Science and Technology Beijing, Beijing 100083, China
[c] Department of Mechanical Engineering, University of South Florida, Tampa, FL 33620, USA

A R T I C L E I N F O

Article history:
Received 29 May 2015
Revised 22 July 2015
Accepted 23 July 2015
Available online 14 August 2015

Keywords:
Brittle film
Ductile substrate
Film-induced cracking
Dislocations
Crack velocity

A B S T R A C T

Film and substrate mechanical integrity is essential for the whole system's performance. In the present study, cracking of brass ductile substrate induced by brittle TiN film fracture was observed. Counter-intuitively, instead of protecting the ductile substrate, a brittle film can cause its premature fracture, as demonstrated here experimentally. Brittle film fracture could induce cracking of ductile substrate at considerably low strain level. Analytical calculation based on energy conservation during crack propagation is presented to explain this phenomenon of film-induced cracking. It is shown that crack depth penetrated into the substrate is a function of both crack velocity and the number of dislocations emitted from the crack tip. Relatively thick brittle films and fast propagating cracks favor fracture of the ductile substrates. The critical crack velocity, which can induce the cracking of brass substrate, is 61 m/s. The presence of brittle film could not only prevent dislocations escaping from the surface of the crystal and inhibit dislocations emitting from surface dislocation sources, but also initiate a channel crack with high velocity due to brittle fracture. Both of them contribute to crack propagation in soft brass substrate. This study provides an alternative view to the notion that a brittle film can protect the ductile substrate from damage.

1. Introduction

Excellent film performance depends on and requires mechanical integrity of the film-substrate system [1–3]. For better film-substrate system designs, thin film failure mechanisms and parameters controlling these processes have been widely studied, including cracking [4], buckling [5], bubble formation [6], debonding [7] and delamination [8]. Up to now, these studies focused on failure mechanisms of the film itself, along with the interfacial properties. However, if a micro-crack can be initiated in the ductile substrate due to the film cracking, then the whole system would be much easier to fail because of the stress concentration in front of the crack tip under tensile stress [9]. Previously this film-induced ductile substrate cracking has been only addressed by modeling, but without experimental efforts. While it is normally believed that the brittle film protects the ductile substrate from damage, the current study shows otherwise.

Substrate damage is induced by brittle film channel cracking under tensile stress. Affected by preparation technology and service environment (humidity, temperature, frictional wear, etc.), brittle films are exposed to a combination of residual and external stresses [10–13]. These stresses could cause brittle films to crack at low strain due to the films' extremely low fracture toughness [13]. Generally, channel cracks nucleate from the top surface of the film under normal tensile stress [4]. Once the channel crack initiates in a brittle film, there are three possible ways for the crack to extend [14]. The crack may stop at the interface, propagate along the interface, or propagate toward the substrate. Modeling results of crack propagation have illustrated that the cracks will penetrate along the interface and propagate within the substrate if a stiff film is supported by a compliant substrate [15,16]. The depth of penetration into the substrate depends on the difference in elastic modulus and toughness between the film and the substrate. Experimentally observing the cross-section of the brittle film-ductile substrate interface under uniaxial tension shows that after the formation of parallel channel film cracks, substrate localized elastic–plastic deformation will occur at the crack tip (diamond on Ti [4], CrN or Cr_2N on brass [11]). In lithium batteries, the cracking of Si film electrode, caused by lithiation and delithiation, could lead to increase of hardness and elastic modulus of the Ti current collector substrate underneath the film [3]. However, films on brittle substrates, such as NiAl on Si, can form channel cracks through both the film and the substrate because of the residual stress change caused by annealing [17]. The crack

* Corresponding authors.
E-mail addresses: lqiao@ustb.edu.cn (L. Qiao), pangxl@mater.ustb.edu.cn (X. Pang), volinsky@usf.edu (A.A. Volinsky).

http://dx.doi.org/10.1016/j.actamat.2015.07.059
1359-6454/

penetration into the Si substrate was explained by the Ye's theory [14]. Moreover, environmentally degraded embrittled polymer surfaces could serve as a site for brittle crack initiation, causing the underlying polymer substrate to fail in a brittle fashion [18]. All of these phenomena are the results of film crack propagation to the substrate. Brittle film tensile fracture strain, ε_F, is much lower than the ductile substrate tensile fracture strain. Examples of such systems include diamond-like carbon on stainless steel ($\varepsilon_F = 1.2\%$) [19], Al_2O_3 on Al–5%Mg ($\varepsilon_F = 2\%$) [20] and diamond on Ti ($\varepsilon_F = 1\%$) [4]. Nevertheless, brass fracture strain is about 30% (tested by stretching), since large plastic deformation occurs before rupture. Therefore, the original motivation for this paper is to experimentally investigate if cracking of the brittle film could induce ductile brass substrate fracture at relatively low strain levels.

Many studies have shown that surface films, such as de-alloyed layers or passive films, formed in corrosive environments, could cause brittle fracture of many normally ductile metals and thus induce stress-corrosion cracking [21–23]. The concept of film-induced cracking was first proposed by Newman and Sieradzki to explain both transgranular and intergranular stress-corrosion cracking resulting from surface films [22,23]. The model was based on the idea that a crack, originating in a surface layer, can obtain high enough velocity to penetrate into the underlying substrate, even if the substrate is a face centered cubic (fcc) metal. However, there are several mechanisms to control the brittle fracture of metals during stress-corrosion cracking. It is hard to distinguish whether the crack is initiated by the surface film fracture or some other corrosion cracking mechanisms, such as slip dissolution or adsorption-induced brittle fracture [24]. Thus, the second aim of this paper is to verify the validity of the film-induced cracking model by depositing a brittle film on a ductile substrate, and thus eliminating environmental effects.

2. Experimental procedure

The dimensions of the brass substrates were 15.5 mm × 6 mm × 1.5 mm. The chemical composition of the brass alloy was 62 wt.% Cu and 38 wt.% Zn. TiN film with a thickness of about 1.3 µm was deposited on the front 15.5 mm × 1.5 mm surface. The TiN films were deposited by reactive RF-pulsed magnetron sputtering in an industrial physical vapor deposition system. Young's modulus of the film and substrate were measured by nanoindentation (TI900, Hysitron, USA). The brass samples with TiN film on the front lateral surface (15.5 mm × 1.5 mm) were loaded under three-point bending along the bottom 15.5 mm × 6 mm surface, as shown schematically in Fig. 1a. Fig. 1b shows the samples before and after bending, along with the three-point bending device. Direct observation of the lateral surface using scanning electron microscope (SEM, Supra™ 55) allowed for measuring the crack spacing at different normal strain levels. Assuming that the externally applied moment is constant along the same longitude, the strain can be calculated, as: $\varepsilon_x(y) = \varepsilon_{top} \cdot 2y/h$, where h is the substrate thickness and y is the distance from the neutral axis. Normal strain, ε_x, variations along the y axis are shown schematically in Fig. 1c. The maximum strain on the top sample surface was measured during the three-point bending by using a strain gauge. The height difference induced by plastic deformation of the substrate after bending was observed by polarized light optical microscope (Olympus, Japan). When the maximum strain on the top surface increased with a strain rate of $2 \cdot 10^{-2}\ s^{-1}$ to the $\varepsilon = 5\%$ strain, the sample was unloaded and examined with the SEM. After observing the surface topography of the lateral surface after bending, the sample was embedded into epoxy resin and its top surface was polished (15.5 mm × 6 mm). The cross-section of the interface was then observed. After that, the epoxy resin was dissolved by industrial epoxy remover. Then the lateral surface with film was slightly polished using a polishing cloth. Because of the weak adhesion strength between the film and substrate after the crack density reached a saturated value at large strain, some areas of the film were removed by slight polishing. The yield strength (σ_s) and fracture strength (σ_f) of brass substrate was tested by stretching, using a loading rate of $10^{-4}\ s^{-1}$.

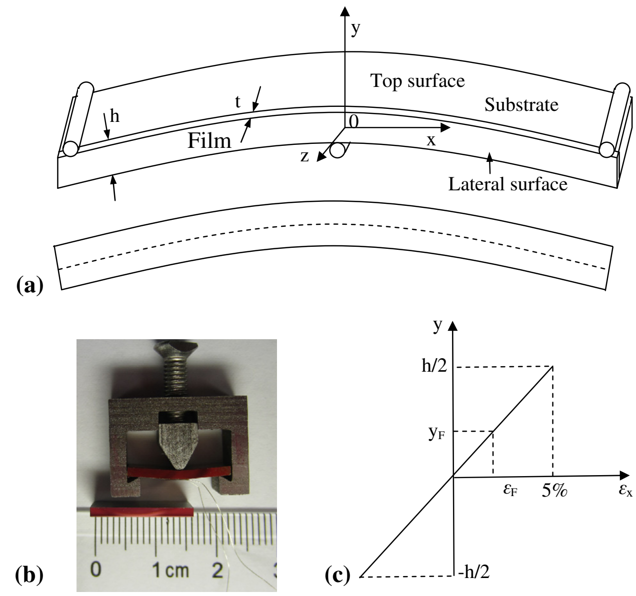

Fig. 1. (a) Schematics of the substrate with the film on the lateral surface under three-point bending; (b) Image of samples before and after bending; (c) Strain along the vertical section at x = constant, shown schematically in (a).

3. Experimental results

3.1. Plastic deformation of substrate with and without film under tensile stress

Brass substrates with and without TiN films on the front lateral surface were bent to the maximum strain of 5%. The height difference induced by plastic deformation of the substrate can be observed by a polarized light optical microscope. The plastic deformation of the sample without TiN film occurred at 0.28%, as shown in Fig. 2a. However, plastic deformation of the sample with TiN film was delayed and occurred at 0.58%, as shown in Fig. 2b. In addition, near the elastic zone, the degree of plastic deformation of the brass without the film was much larger than in brass with the film. It indicates that the TiN film has a significant effect on plastic deformation of the brass substrate.

3.2. Film-induced substrate cracking

As seen in Fig. 3a, the location where the brass substrate cracked was exactly below the cracked film, which indicated that the film crack induced cracking of the substrate. However, in some other places where the film spalled off, no crack in the substrate was observed, and instead, many parallel slip steps occurred, as seen in Fig. 3b.

To study the crack depth penetrated into the substrate, cross-sections of the interface were observed with SEM. As seen in Fig. 4a, the film had good adhesion with the substrate, and no decohesion occurred. The depth of the channel film crack penetrated into the substrate was about 1 µm. However, for the case