

# Brittle film-induced cracking of ductile substrates



Tao Guo<sup>a</sup>, Lijie Qiao<sup>a,\*</sup>, Xiaolu Pang<sup>b,\*</sup>, Alex A. Volinsky<sup>c</sup>

<sup>a</sup> Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, Beijing 100083, China

<sup>b</sup> Department of Materials Physics and Chemistry, University of Science and Technology Beijing, Beijing 100083, China

<sup>c</sup> Department of Mechanical Engineering, University of South Florida, Tampa, FL 33620, USA

## ARTICLE INFO

### Article history:

Received 29 May 2015

Revised 22 July 2015

Accepted 23 July 2015

### Keywords:

Brittle film  
Ductile substrate  
Film-induced cracking  
Dislocations  
Crack velocity

## ABSTRACT

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.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

## 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<sub>2</sub>N 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](mailto:lqiao@ustb.edu.cn) (L. Qiao), [pangxl@mater.ustb.edu.cn](mailto:pangxl@mater.ustb.edu.cn) (X. Pang), [volinsky@usf.edu](mailto:volinsky@usf.edu) (A.A. Volinsky).

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,  $\varepsilon_F$ , 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],  $\text{Al}_2\text{O}_3$  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  $\times$  6 mm  $\times$  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  $\mu\text{m}$  was deposited on the front 15.5 mm  $\times$  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  $\times$  1.5 mm) were loaded under three-point bending along the bottom 15.5 mm  $\times$  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:  $\varepsilon_x(y) = \varepsilon_{\text{top}} \cdot 2y/h$ , where  $h$  is the substrate thickness and  $y$  is the distance from the neutral axis. Normal strain,  $\varepsilon_x$ , 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  $2 \cdot 10^{-2} \text{ s}^{-1}$  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  $\times$  6 mm). The

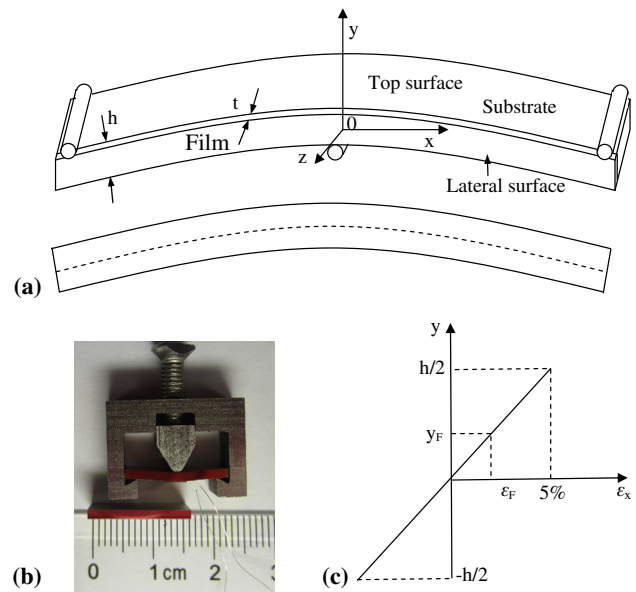


Fig. 1. (a) Schematics of the substrate with the film on the lateral surface under three-point bending; (b) Image of samples before and after bending; (c) Strain along the vertical section at  $x = \text{constant}$ , shown schematically in (a).

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 ( $\sigma_s$ ) and fracture strength ( $\sigma_f$ ) of brass substrate was tested by stretching, using a loading rate of  $10^{-4} \text{ s}^{-1}$ .

## 3. Experimental results

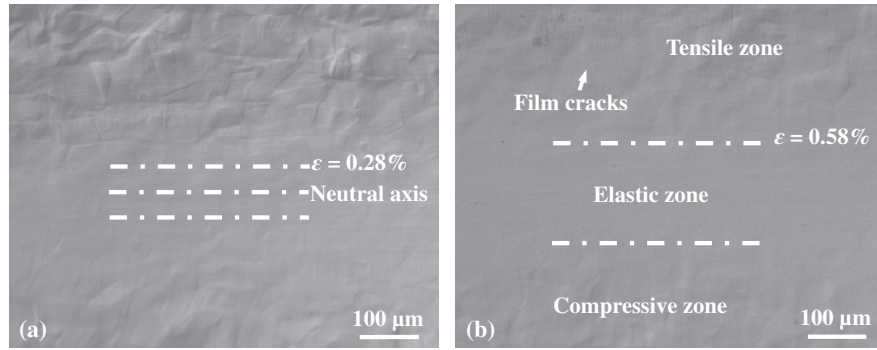
### 3.1. Plastic deformation of substrate with and without film under tensile stress

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.

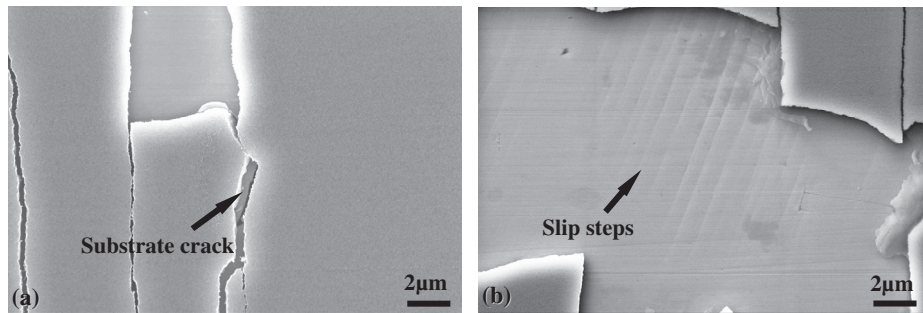
### 3.2. Film-induced substrate cracking

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.

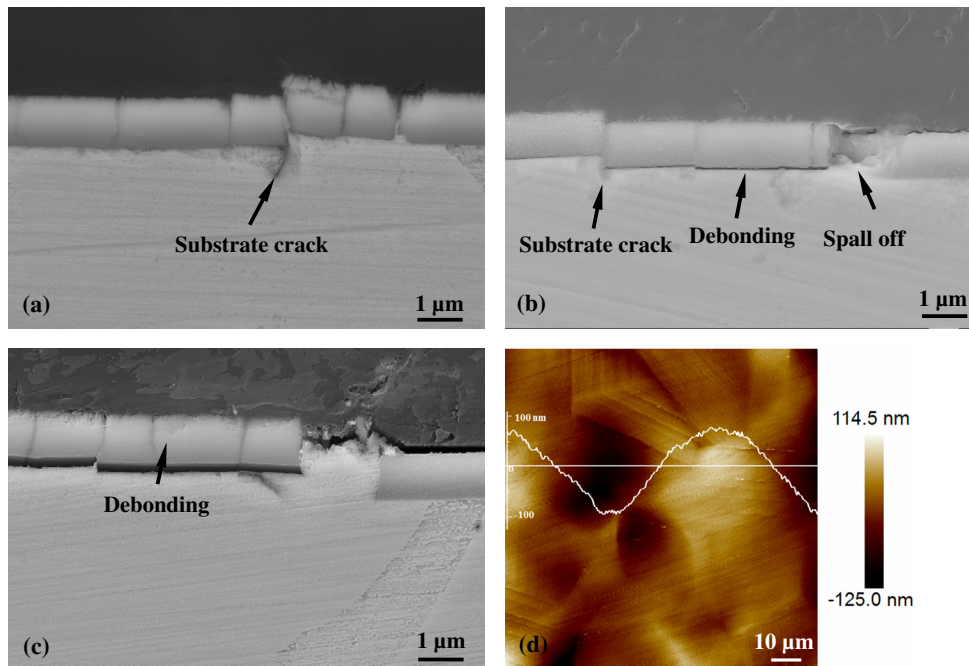
To study the crack depth penetrated into the substrate, cross-sections of the interface were observed with SEM. As seen in Fig. 4a, the film had good adhesion with the substrate, and no decohesion occurred. The depth of the channel film crack penetrated into the substrate was about 1  $\mu\text{m}$ .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



**Fig. 2.** Polarized light optical microscope images of the brass samples without and with TiN film bending to the 5% strain on the top surface: (a) Without the film the plastic deformation occurs at  $\epsilon = 0.28\%$ ; (b) With the film the plastic deformation occurs at  $0.58\%$  and the presence of TiN film delays the plastic deformation of the brass substrate.



**Fig. 3.** SEM images of the TiN film/brass substrate surface after bending test: (a) Film crack penetrates into the brass substrate and no slip steps occur near the crack; (b) No cracking occurs in the brass substrate with lots of parallel slip steps.



**Fig. 4.** Cross-section of the interface: (a) The film has good adhesion with the substrate, the depth the channel crack in the film penetrates into the substrate is about  $1\ \mu\text{m}$ ; (b) Slight debonding along the interface accompanied by small size crack of the substrate and decohesion of the film; (c) Obvious debonding and no cracking of the substrate; (d) The AFM image of the lateral surface of brass without the film after bending to 5% strain. Here, the height changes continuously and the maximum height difference is about  $200\ \text{nm}$ .

of weaker interfacial strength, part of the crack energy was released by propagating along the interface. As a consequence, the film crack could induce a small size crack in a ductile substrate and debond along the surface, as seen in Fig. 4b. When the channel

crack met a very weak interface, the crack would propagate along the interface because of the high toughness of the substrate. This caused serious decohesion of the film along the interface with no tendency of the crack to extend into the substrate, as seen in

Fig. 4c. The steps in Fig. 4a and b were the result of plastic deformation and cracking of the substrate. The height of the lateral surface of brass without the film after bending to 5% changed continuously, and the maximum height difference was about 200 nm, as seen in Fig. 4d. Once the cracking of the substrate occurred at a low strain, the plastic deformation near the crack couldn't keep in a continuous mode. Instead, a step formed where the crack existed, as seen in Fig. 4a and b.

Fig. 5 shows the substrate surface morphology after removing part of the film. As previously described, the substrate crack was right underneath the cracked film. The width of the crack opening close to the substrate surface was about 0.8  $\mu\text{m}$ , which was much larger than the crack width presented in Fig. 4a. When the substrate cracked, induced by a film channel crack, the crack opening displacement of both cracks was small. As the applied strain increased, both cracks could be opened. After unloading, the crack in the elastic brittle film could recover. However, the crack can't recover in the elastic–plastic substrate. This resulted in the crack opening displacement of the substrate being larger than the film.

#### 4. Discussion

Most brittle materials, such as TiN film, fracture in a brittle fashion under tensile stress. As a result, the crack velocity in such brittle materials is very high, tremendously affecting the underlying substrate. To study the mechanism of brittle film-induced cracking of ductile substrates, the effect of brittle films on dislocation emission in ductile substrates and the effect of crack velocity on the deformation in front of the crack tip should be taken into account.

##### 4.1. The effect of thin films on dislocation emission in ductile substrates

Dislocations can be emitted in polycrystalline metals under applied load. If a hard film is present on a metal surface, the process of dislocation nucleation near the surface will be altered. In the past few decades researchers have found that thin films can affect the plastic deformation of the bulk metal, for example, by increasing the resolved shear stress [25]. This phenomenon can be interpreted in terms of the film preventing the exit of dislocations from the surface of the crystal or inhibiting dislocation emission from the surface dislocation sources. This hypothesis was proven to be correct both experimentally and theoretically. Martin and McGee [26] showed that if the film was harder than the substrate, the image force induced by the thin film repulsed dislocations near the interface in the substrate. This is because the strain energy of dislocations in hard films is larger than in

ductile substrates. The effect of a hard film would be more significant if the distance of the dislocation to the interface was similar to the film thickness. Therefore, it was difficult for dislocations produced near the surface in the ductile substrate to move under external stress toward the interface because of the repulsive image force. In later research, based on the calculations of the I, II and III crack modes, Zhang et al. pointed out that the critical stress intensity factor for dislocation emission from the crack tip was greatly influenced by the film stiffness as well as the film thickness [27,28]. When the film thickness is larger than the critical value, it is difficult for dislocations to be emitted from the crack tip if the film is harder than the substrate, while a softer film makes the dislocation emission easier. There is also good evidence to support the hypothesis that films can be effective in inhibiting dislocation escape from the surface of a crystal. Brame and Evans [29] investigated the deformation of thin films on solid substrates and came to a conclusion that the mode of deformation was determined by the ease with which dislocations could move through the film from the underlying substrate. They found that the main influence is the nature of the film–metal interface, characterized by the difference between them.

The effect of brittle TiN film on brass substrate deformation under tensile stress can be clearly seen in Fig. 2. It indicates that the presence of film can be effective in both inhibiting the operation of surface dislocation sources and limiting the egress of dislocations produced at sources near the surface. As these dislocations pile up against the film in the substrate, some internal sources would eventually be shut off by the back stress. In this manner the film could have a dual effect of restricting substrate deformation. It is worth mentioning that the effect of brittle film on dislocation emission and motion near the surface is based on strong film adhesion, otherwise, it couldn't act as a barrier layer.

##### 4.2. Crack velocity effect on the ductile substrate fracture mode

When a crack initiates in the brittle TiN film under a fast loading rate, the crack velocity is very high as it leaves the film. If it continues to propagate, there is a significant effect on the cracking mode of the substrate. Cracks can spread either in a brittle or a ductile manner in metals, depending on how rapidly plastic flow occurs. The crack velocity determines the local plastic dissipation rate in front of the crack tip, i.e. the number of dislocations emitted per unit crack area [30]. In simulations described by Zhao and Li [31], the number of dislocations emitted from a moving crack is much smaller than the saturated number, which could be emitted from a stationary crack. This steady state number decreases as crack velocity increases. According to Freund [32], for a straight moving crack under mode I loading, the dynamic fracture energy and the energy release rate depend only on the crack velocity:

$$\Gamma(v) = (1 - v_c/v_R)G(l, \sigma) \quad (1)$$

Here,  $v_R$  is the Rayleigh wave velocity,  $G(l, \sigma)$  is the energy release rate, which can be expressed as  $G(l, \sigma) = K^2(l, 0)(1 - v^2)/E$ . In Eq. (1), an increasing crack velocity decreases dynamic fracture energy. This indicates that plastic energy dissipation, induced by dislocations produced at the advancing crack surface, decreases. On the other hand, for dislocations located in front of the crack, if the crack tip moves fast enough, the motion of dislocations may be slower than the crack and some of them are annihilated at the crack surface [23]. This is similar to the studies of brittle-to-ductile transition (BDT) behaviour in single phase (usually single crystal) materials, such as silicon [33]. It has been established that the process controlling the BDT is the motion of dislocations in the region near the crack tip, rather than dislocation nucleation at or near the crack tip. Therefore, a fast-running crack could not only inhibit

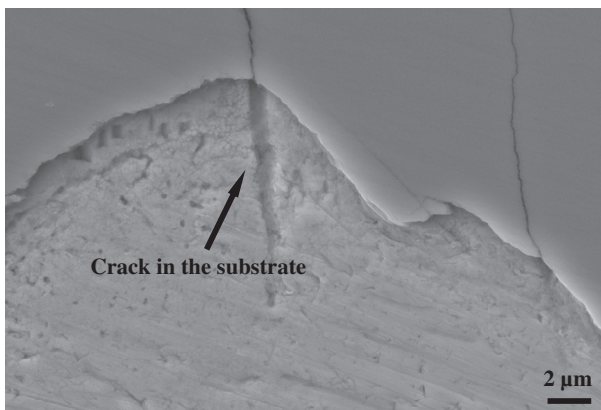


Fig. 5. Surface of the sample after removing part of the film. The crack opening displacement of the substrate crack near the surface is about 0.8  $\mu\text{m}$ , larger than the crack in TiN film.

dislocation emission in front of it, but also lead some existing dislocations to be annihilated at the crack surface. Both of them contribute to the propagation of a crack in a ductile substrate.

#### 4.3. Crack propagation and arrest in the substrate

The cracking behavior of thin brittle films on ductile substrates under tensile stress can generally be comprehended by the shear lag model, where the normal stress in the substrate is transferred to the coating due to the shear stress at the interface [34–36]. When the stress reaches the fracture stress of the brittle film, cracks nucleate from the surface and then propagate toward the interface. As the film crack arrives at the interface, the emission of dislocations in front of the crack tip can be significantly altered by the presence of brittle film, which is clearly demonstrated in Appendix A. In addition, the stress intensity at the crack tip can be affected enormously by the dislocations in front of it. The local crack tip stress intensity is lower than the applied stress intensity because of the shielding effect [37]. It can be written as

$$K_{\text{tip}}(t) = K_{\text{app}}(t) - K_{\text{dis}}(t) = \dot{K}_{\text{app}} t - \frac{Gb}{2\pi(1-\nu)} \sum_{i=1}^{N(t)} r_i(t)^{-1/2} \quad (2)$$

where  $\dot{K}_{\text{app}}$  is the applied stress intensity factor rate,  $G$  is the shear modulus,  $b$  is the Burgers vector,  $r_i(t)$  is the distance of each dislocation to the crack tip, and  $N(t)$  is the number of dislocations. It is clearly demonstrated that the shielding effect of dislocations in the near tip region is greatly reduced because of the presence of film and fast-running crack. Then it becomes possible for the channel film crack to propagate in the ductile brass substrate.

It is assumed that the interfacial strength is high and the crack passes through the interface with almost no energy loss. Based on the crack energy consumption during propagation, the expression for the change in the crack velocity,  $\delta v_c$ , per characteristic crack advance distance,  $\delta l$ , can be obtained, as demonstrated by Eq. (B4) in the Appendix B. The crack initiates in the TiN film, and then extends into the brass substrate, thus the crack propagates in two different materials. To describe the crack propagation in the brass substrate, kinetic energy of the crack in the TiN film is transformed into the kinetic energy in brass with the same velocity. For brass,  $E = 150$  GPa,  $\rho = 8.93$  g/cm<sup>3</sup> [38],  $\sigma_G = 300$  MPa and for TiN film,  $E = 220$  GPa,  $\rho = 5.22$  g/cm<sup>3</sup> [38],  $\sigma_G = 4600$  MPa [39]. Substituting these parameters into Eq. (B2), the equivalent crack length in brass is about 20  $\mu\text{m}$  when the TiN film thickness is 1.3  $\mu\text{m}$ . The crack depth vs crack velocity can be obtained by using Eq. (B4) with  $\nu = 0.34$ ,  $\rho = 8.93$  g/cm<sup>3</sup>,  $v_R = 2100$  m/s [38],  $l_0 = 2 \times 10^{-5}$  m,  $E = 150$  GPa,  $\sigma_G = 300$  MPa,  $\delta l = b = 2.5 \times 10^{-10}$  m,  $r = 10^{-6}$  m,  $r_0 = 2.5 \times 10^{-10}$  m and  $\gamma = 1.6$  J/m<sup>2</sup> [40]. For simplicity it is assumed that the incremental crack advance,  $\delta l$ , is equal to the Burgers vector,  $b$ . Eq. (B4) indicates that the substrate crack depth will increase with the characteristic crack advance distance,  $\delta l$ . The ductility of the system could be reduced simply by increasing the characteristic distance  $b$ . That is to say, if one assumes that  $\delta l = 10b$  or larger, the number of dislocations emitted in front of the moving crack decreases compared to  $\delta l = b$ . Therefore, one can adjust the number of dislocations,  $N$ , to reflect different scenarios, including the effect of crack velocity on dislocation emission in front of the crack and the effect of the characteristic crack advance distance on the crack depth propagated in the substrate. Calculation results for ten dislocations emitted per characteristic crack depth are shown in Fig. 6a, and for one emitted dislocation in Fig. 6b. The more dislocations emitted in front of the crack tip, the shorter the depth the crack propagated into the substrate. The crack depth in the substrate is sensitive to the initial crack velocity when it just crosses the interface and the number of dislocations emitted at the crack tip. The crack velocity slowly decreased during the initial propagation

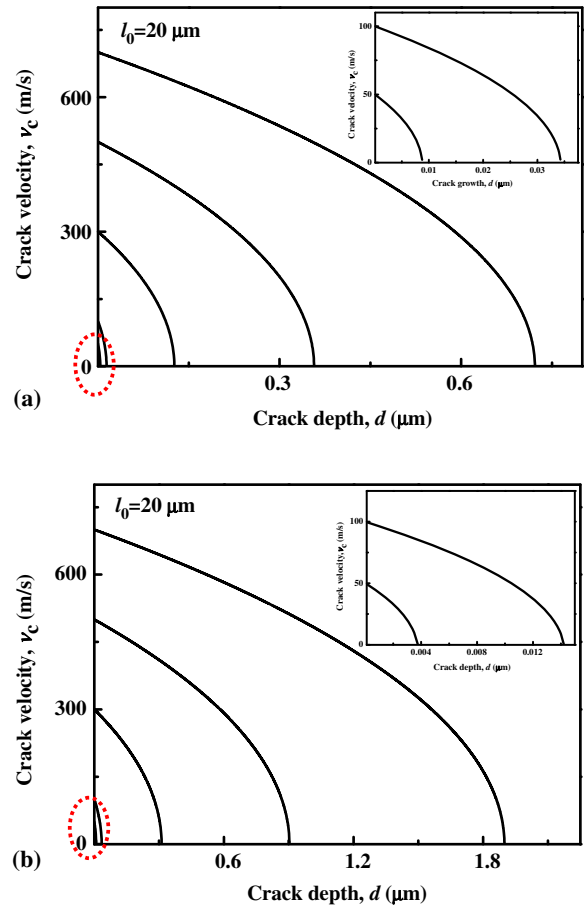


Fig. 6. The crack jump distance as a function of the velocity of the channel crack as it leaves the film with different number of dislocations emitted per characteristic crack advance distance using Eq. (B4): (a) Ten dislocations and (b) One dislocation.

stage and then rapidly decreased until total arrest. For the initial velocity of 50 m/s, the crack depth in the substrate is about several nm, which can be ignored compared with the film thickness. However, for a high crack velocity of 700 m/s, the penetration depth is noticeable, as shown in Fig. 6. As a consequence, if the film is ductile, the crack velocity in it would be much smaller than in brittle film, then the cracking of ductile substrate would be absent.

In this study, kinetic energy is the driving force for the crack propagation into the substrate, which depends on the initial crack velocity and length. The effect of crack velocity has been discussed above. Fig. 7 shows the influence of the initial crack length (film thickness) on the depth that the crack extends into the substrate under the same conditions of crack velocity and ten dislocations emitted per characteristic crack advance distance, equal to the Burgers vector. According to Zhang et al. [27,28], when the film is thinner than the critical thickness, a harder film makes the dislocation emission easier, and so it couldn't act as a barrier layer to inhibit dislocation emission, which will make the substrate hard to crack. In Fig. 7, the depth of crack propagated in the substrate increases with the initial crack length (film thickness). However, as discussed above, the cracking of ductile substrate induced by brittle film cracking is based on the strong interfacial strength. Generally, the adhesion strength increases with film thickness at small thickness, then decreases as the film becomes thicker [41]. Therefore, a relatively thick brittle film contributes to the cracking of ductile substrate.

In the present analysis, to simplify the model it is assumed that the number of dislocations emitted from the crack tip is constant

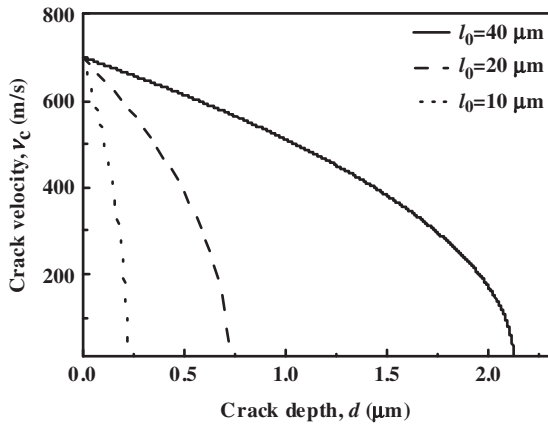


Fig. 7. The influence of initial crack length (film thickness) on the crack growth at the same initial crack velocity of 700 m/s.

and doesn't depend on the crack velocity in the above discussion. This assumption is not rigorous, and in fact, the faster the crack, the smaller the number of dislocations emitted in front of the advancing crack [31]. Thus, as the crack velocity decreases, the number of dislocations emitted from the crack tip increases, and the shielding effect is enhanced, as described by Eq. (2), until crack blunting. On the other hand, as shown by the model results in Fig. 6, the film crack will induce cracking of the substrate, even at very low velocity. However, this is not consistent with the experimental observation. According to Hirth and Lothe [42], the stress concentration will be induced by dislocations if they are piled up in front of a barrier, and when the stress achieves the atomic bonding force, a microcrack is formed. The critical number of dislocations to form a microcrack can be written as:

$$n = \frac{3\pi^2\gamma}{4b(\tau_c - \tau_f)} \quad (3)$$

Here,  $\gamma$  is the surface energy, and  $\tau_c$  and  $\tau_f$  are the critical shear stresses for a cleavage crack to nucleate and the lattice friction for the dislocation to move. If the microcrack nucleates when the material yields,  $\tau_c - \tau_f = \tau_s = \sigma_s/2$ . Here  $\tau_s$  is the critical shear stress for plastic deformation and  $\sigma_s$  is the yield stress. Using  $\sigma_s = 190$  MPa, obtained by a tensile test, and  $b = 2.5 \times 10^{-10}$  m, and  $\gamma = 1.6$  J/m<sup>2</sup> [40], the critical number of dislocations is about 498 for the brass substrate to form a microcrack. Combining Eqs. (B2) and (B3) subject to the condition that  $n = 498$ , the critical crack velocity of 61 m/s can be obtained. When the crack velocity exceeds this critical value, the substrate cracks, otherwise, the substrate cracking will be absent. Therefore, the developed model could semi-quantitatively explain the film-induced brittle cracking of the substrate for high crack velocities. More work is needed to improve the model by quantitatively describing relationships between the crack velocity and the number of dislocations.

## 5. Conclusions

Cracking of the ductile substrates induced by film cracking was successfully observed in three-point bending both from the surface of the film and cross-sections of the interface. The plastic deformation at the surface of the sample without TiN film occurred at 0.28% strain. However, plastic deformation at the surface of the sample with TiN film was delayed and occurred at 0.58% strain. The presence of film can be effective in both inhibiting the operation of surface dislocation sources and limiting the egress of dislocations produced at sources near the surface. It is the fast-running film crack which causes the ductile substrate to crack. The analytical

calculation based on energy conservation shows that the depth of the crack penetrating into the substrate is a function of the crack velocity when it leaves the film and the number of dislocations emitting from the crack tip. The critical crack velocity, which can induce brass substrate cracking, is 61 m/s, and below this crack velocity, the cracking of the substrate will be absent. Furthermore, for a relatively thick film, strong interfacial strength and a brittle substrate favor substrate cracking. Brittle film on a ductile substrate, thicker than the critical thickness, can act as a barrier layer to inhibit dislocation emission from the metal substrate close to the interface because of the image forces. Brittle films also contribute to initiate channel cracks with high velocity due to the brittle cracking of the film, which eventually leads to cracking of the substrate.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (51271022, 51431004), Beijing Higher Education Young Elite Teacher Project (YETP0353), National Basic Research Program of China (Grant No. 2012CB937502).

## Appendix A

When the channel crack arrived at the film-substrate interface under tensile stress, it extended into the brass substrate, as shown in Fig. A1a. The influence of TiN film on dislocation emission in the substrate near the interface can be described by using the concepts developed by Rice et al. [43]. A semi-infinite crack with mode I applied stress is shown in Fig. A1b. The crack-tip plastic zone is modeled as a single slip plane inclined at an angle  $\theta$  to the crack plane, with a dislocation source close to the crack tip lying on each slip plane. Dislocations will be produced at the dislocation source if the total stress is positive, and move away along the slip plane to form a one-dimensional array on each slip plane. The shear stress,  $\tau_i$  on the  $i^{\text{th}}$  dislocation in such an array of dislocations is given by [43]:

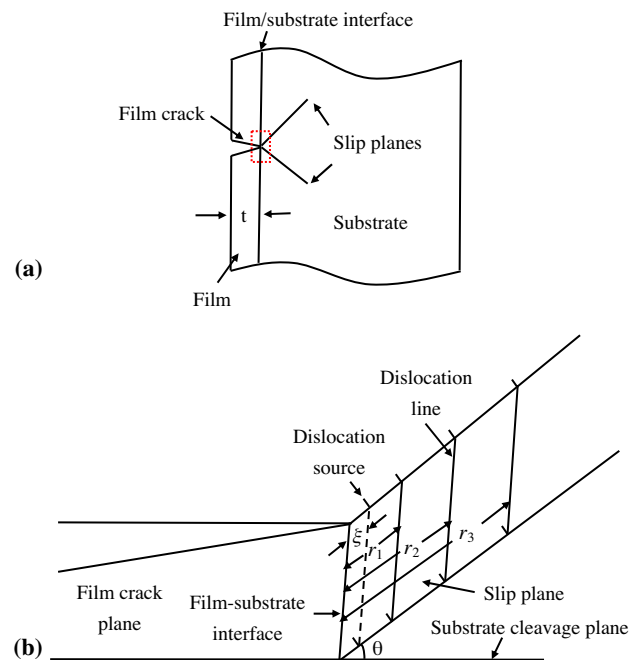


Fig. A1. (a) The schematic of the film and substrate when a crack arrives at the interface; (b) The geometry of dislocation, crack and film-substrate interface. Edge dislocations pile up in the slip plane at  $r_i > t$  because of the film presence.

$$\tau_i = \frac{K_{\text{app}}}{r_i^{1/2}} f(\theta) - \frac{Gb}{4\pi r_i} - \tau_f b + \frac{Gb}{2\pi} \sum_{j=1}^N \frac{\sqrt{r_i/r_j}}{r_i - r_j} \quad (\text{A1})$$

where  $K_{\text{app}}$  is the applied stress intensity factor,  $r_i$  is the distance to the dislocation from the tip of the crack,  $\theta$  is the angle between the slip plane and the crack plane,  $G$  is the shear modulus,  $\tau_f$  is lattice friction for dislocation to move,  $b$  is the Burgers vector, and  $N$  is the number of dislocations in front of the crack tip. The first term is related to the crack-tip stress field, the second term is the image force induced by the brittle film and crack on the dislocation at distance  $r_i$ . The third term is the friction force for the dislocation to move and the fourth term describes the image force of all other dislocations on the one dislocation,  $i \neq j$ . If a dislocation is inclined to be nucleated at the location  $r_i = \xi$ , the forces acting on it should be positive. Without the TiN film, the repulsive image force on the dislocation in front of the crack would be much smaller, and dislocations may be emitted in front of the crack.

## Appendix B

When the film crack propagates into the substrate, the decrease of the crack kinetic energy ( $E_K$ ) and the work done during the crack extension by the applied stress ( $W$ ) contribute to the crack propagation. However, the surface energy induced by forming new surfaces ( $E_S$ ), the plastic energy induced by emitting dislocations ( $E_D$ ) and the increase of the strain energy stored in the system ( $U$ ) provide resistance to crack propagation. Thus, based on the conservation of energy [23]:

$$\Delta(W - E_K) = \Delta(E_S + E_D + U) \quad (\text{B1})$$

Here, the heat dissipation effects have not been taken into account. According to the study by Mott of steel brittle fracture [44], kinetic energy of a moving crack of unit width when it leaves the film and crosses through the interface can be expressed as:

$$E_K = \left( \frac{k\rho\sigma_G^2}{2E^2} \right) l^2 v_c^2 \quad (\text{B2})$$

where  $l$  is the crack length,  $E$  is the Young's modulus,  $v_c$  is the crack velocity,  $\rho$  is the density and  $k$  is a dimensionless constant, determined from  $\sqrt{2\pi/k} = 0.38$  [38].  $\sigma_G$  is the nominal Griffith stress for the initial crack length. In the brass substrate, as the crack velocity decreases, the emission of dislocations in front of the crack tip would increase, leading to the  $\sigma_G$  changed between  $\sigma_e$  (elastic limit strength at a loading rate of  $10^{-4} \text{ s}^{-1}$ ) and  $\sigma_0$  (theoretical fracture strength, about  $E/10$ ), during the propagation of a crack in brass. Here, for simplification, it is assumed that for ductile brass  $\sigma_G = \sigma_f$ , and  $\sigma_f$  is the fracture strength, for brittle TiN film,  $\sigma_G = \sigma_f$ .

When a moving crack of unit width emits a dislocation, it loses a certain amount of energy equal to the energy of unit length of the moving dislocation [45]:

$$E_D = \frac{Eb^2}{8\pi(1+\nu)} \frac{1}{(1 - v_d^2/v_R^2)^{1/2}} \ln \frac{r}{r_0} \quad (\text{B3})$$

Here,  $v_d$  is the dislocation velocity, which is assumed to be equal to the crack velocity,  $v_c$ . When a crack moves with velocity  $v$  through a population of dislocations, the dislocations must move with comparable velocity to affect the crack motion.  $v_R$  is the Rayleigh wave velocity and  $b$  is the Burgers vectors, while  $r$  is the distance to the dislocation core and  $r_0$  is the core cut-off radius and  $\nu$  is the Poisson's ratio. The strain energy stored in the system of unit width can be expressed as  $U = \pi\sigma_G^2 l^2 / E$ . Here,  $\sigma_G$  is the fracture stress and  $l$  is the crack length. When a moving crack propagates over the length  $\delta l$  in the brass substrate, the surface energy of unit width induced by forming new surfaces can be expressed as  $E_S = 2\gamma\delta l$ . In this paper, since the work done by the external stress cannot

respond fast enough to contribute to the crack growth [23], a microscopically significant crack depth in the substrate is caused by the extremely high film crack velocity, then  $W = 0$ . Based on Eq. (B1), the following expression for the change in the crack velocity,  $\delta v_c$ , per characteristic crack advance distance,  $\delta l$ , can be obtained:

$$\delta v_c = N \frac{E^3 b^2}{8\pi(1+\nu)k\rho\sigma_G^2 l^2 v_c} \frac{1}{(1 - v_d^2/v_R^2)^{1/2}} \ln \frac{r}{r_0} - \frac{v_c}{l} \delta l + \frac{2\pi E}{k\rho l v_c} \delta l + \frac{2E^2 \gamma}{k\rho\sigma_G^2 l^2 v_c} \delta l \quad (\text{B4})$$

Here,  $N$  is the number of dislocations emitted from the moving crack tip.  $E$ ,  $b$ ,  $\rho$ ,  $\sigma_G$ ,  $\nu$ ,  $\gamma$  are the Young's modulus, Burgers vector, density, Griffith stress, Poisson's ratio and surface energy of the brass substrate, respectively.  $r$  is the distance to the dislocation core and  $r_0$  is the core cut-off radius of dislocation in the brass substrate.  $k$  is a dimensionless constant.

## References

- [1] J. Andersons, S. Tarasovs, Y. Leterrier, Evaluation of thin film adhesion to a compliant substrate by the analysis of progressive buckling in the fragmentation test, *Thin Solid Films* 517 (2009) 2007–2011.
- [2] Z. Chen, L.Y.L. Wu, E. Chwa, O. Tham, Scratch resistance of brittle thin films on compliant substrates, *Mater. Sci. Eng. A* 493 (2008) 292–298.
- [3] X. Xiao, P. Liu, M.W. Verbrugge, H. Haftbaradaran, H. Gao, Improved cycling stability of silicon thin film electrodes through patterning for high energy density lithium batteries, *J. Power Sources* 196 (2011) 1409–1416.
- [4] F. Ahmed, K. Bayerlein, S.M. Rosiwal, M. Göken, K. Durst, Stress evolution and cracking of crystalline diamond thin films on ductile titanium substrate: analysis by micro-Raman spectroscopy and analytical modelling, *Acta Mater.* 59 (2011) 5422–5433.
- [5] M.J. Cordill, F.D. Fischer, F.G. Rammerstorfer, G. Dehm, Adhesion energies of Cr thin films on polyimide determined from buckling: experiment and model, *Acta Mater.* 58 (2010) 5520–5531.
- [6] X.J. Lou, M. Zhang, S.A.T. Redfern, J.F. Scott, Local phase decomposition as a cause of polarization fatigue in ferroelectric thin films, *Phys. Rev. Lett.* 97 (2006) 177601.
- [7] N. Lu, Z. Suo, J.J. Vlassak, The effect of film thickness on the failure strain of polymer-supported metal films, *Acta Mater.* 58 (2010) 1679–1687.
- [8] K.B. Yeap, K. Zeng, D. Chi, Determining the interfacial toughness of low- $k$  films on Si substrate by wedge indentation: further studies, *Acta Mater.* 56 (2008) 977–984.
- [9] J. García, J. Fernández, J. Cuetos, F. Costales, Fatigue effect of WC coatings thermal sprayed by HVOF and laser treated, on medium carbon steel, *Eng. Fail. Anal.* 18 (2011) 1750–1760.
- [10] H. Köstenbauer, G.A. Fontalvo, M. Kapp, J. Keckes, C. Mitterer, Annealing of intrinsic stresses in sputtered TiN films: The role of thickness-dependent gradients of point defect density, *Surf. Coat. Technol.* 201 (2007) 4777–4780.
- [11] S. Krishnamurthy, I. Reimanis, Multiple cracking in CrN and Cr<sub>2</sub>N films on brass, *Surf. Coat. Technol.* 192 (2005) 291–298.
- [12] K.W. McElhane, Q. Ma, Investigation of moisture-assisted fracture in SiO<sub>2</sub> films using a channel cracking technique, *Acta Mater.* 52 (2004) 3621–3629.
- [13] L. Zhang, H. Yang, X. Pang, K. Gao, A.A. Volinsky, Microstructure, residual stress, and fracture of sputtered TiN films, *Surf. Coat. Technol.* 224 (2013) 120–125.
- [14] T. Ye, Z. Suo, A.G. Evans, Thin film cracking and the roles of substrate and interface, *Int. J. Solids Struct.* 29 (1992) 2639–2648.
- [15] J. Beuth, Cracking of thin bonded films in residual tension, *Int. J. Solids Struct.* 29 (1992) 1657–1675.
- [16] M. Thouless, Z. Li, N. Douville, S. Takayama, Periodic cracking of films supported on compliant substrates, *J. Mech. Phys. Solids* 59 (2011) 1927–1937.
- [17] P. Wellner, O. Kraft, G. Dehm, J. Andersons, E. Arzt, Channel cracking of  $\beta$ -NiAl thin films on Si substrates, *Acta Mater.* 52 (2004) 2325–2336.
- [18] P. So, L.J. Broutman, The effect of surface embrittlement on the mechanical behavior of rubber-modified polymers, *Polym. Eng. Sci.* 22 (1982) 888–894.
- [19] H.J. Kim, M.W. Moon, D.I. Kim, K.R. Lee, K.H. Oh, Observation of the failure mechanism for diamond-like carbon film on stainless steel under tensile loading, *Scr. Mater.* 57 (2007) 1016–1019.
- [20] C. Xie, W. Tong, Cracking and decohesion of a thin Al<sub>2</sub>O<sub>3</sub> film on a ductile Al–5%Mg substrate, *Acta Mater.* 53 (2005) 477–485.
- [21] R.C. Newman, T. Shahrabi, K. Sieradzki, Film-induced cleavage of alpha-brass, *Scr. Metall.* 23 (1989) 71–74.
- [22] K. Sieradzki, R.C. Newman, Stress-corrosion cracking, *J. Phys. Chem. Solids* 48 (1987) 1101–1113.
- [23] K. Sieradzki, R.C. Newman, Brittle behavior of ductile metals during stress-corrosion cracking, *Philos. Mag. A* 51 (1985) 95–132.
- [24] R. Kelly, A. Frost, T. Shahrabi, R.C. Newman, Brittle fracture of an Au/Ag alloy induced by a surface film, *Metall. Trans. A* 22 (1991) 531–541.

- [25] S. Harper, A. Cottrell, Surface effects and the plasticity of zinc crystals, *Proc. Phys. Soc. London. Sect. B* 63 (1950) 331–336.
- [26] D.M. Martin, T.D. McGee, The interaction of dislocations and boundaries, *Acta Metall.* 17 (1969) 929–932.
- [27] T.Y. Zhang, C.F. Qian, Interaction of a screw dislocation with a thin-film-covered mode III crack, *Acta Mater.* 44 (1996) 4513–4520.
- [28] T.Y. Zhang, C.F. Qian, T. Wang, P. Tong, Interaction of an edge dislocation with a thin-film-covered crack, *Int. J. Solids Struct.* 37 (2000) 5465–5492.
- [29] D. Brame, T. Evans, Deformation of thin films on solid substrates, *Philos. Mag.* 3 (1958) 971–986.
- [30] A. Stroh, A simple model of a propagating crack, *J. Mech. Phys. Solids* 8 (1960) 119–122.
- [31] R.H. Zhao, J. Li, Dynamic emission of dislocations from a moving crack, *J. Eng. Mater. Technol.* 107 (1985) 277–281.
- [32] L. Freund, Crack propagation in an elastic solid subjected to general loading—II. Non-uniform rate of extension, *J. Mech. Phys. Solids* 20 (1972) 141–152.
- [33] J. Samuels, S. Roberts, The brittle-ductile transition in silicon. I. Experiments, *Proc. R. Soc. Lond. A* 421 (1989) 1–23.
- [34] D.C. Agrawal, R. Raj, Measurement of the ultimate shear strength of a metal-ceramic interface, *Acta Metall.* 37 (1989) 1265–1270.
- [35] S. Frank, U.A. Handge, S. Olliges, R. Spolenak, The relationship between thin film fragmentation and buckle formation: synchrotron-based in situ studies and two-dimensional stress analysis, *Acta Mater.* 57 (2009) 1442–1453.
- [36] U.A. Handge, Analysis of a shear-lag model with nonlinear elastic stress transfer for sequential cracking of polymer coatings, *J. Mater. Sci.* 37 (2002) 4775–4782.
- [37] V. Lakshmanan, J. Li, Edge dislocations emitted along inclined planes from a mode I crack, *Mater. Sci. Eng. A* 104 (1988) 95–104.
- [38] T.Y. Fan, *Dynamic Fracture: Principle and Application*, Beijing Institute of Technology Press, 2005, p. 111.
- [39] S. Massl, W. Thomma, J. Keckes, R. Pippan, Investigation of fracture properties of magnetron-sputtered TiN films by means of a FIB-based cantilever bending technique, *Acta Mater.* 57 (2009) 1768–1776.
- [40] J. Meakin, H. Wilsdorf, Dislocations in deformed single crystals of alpha brass, *Trans. AIME* 218 (1960) 737–745.
- [41] D. Sheeja, B.K. Tay, K.W. Leong, C.H. Lee, Effect of film thickness on the stress and adhesion of diamond-like carbon coatings, *Diam. Relat. Mater.* 11 (2002) 1643–1647.
- [42] J.P. Hirth, J. Lothe, *Theory of Dislocations*, 2nd ed., John Wiley and Sons Inc., New York, 1982.
- [43] J. Rice, M. Johnson, M. Kanninen, *Inelastic Behavior of Solids*, McGraw-Hill, New York, NY, 1970, pp. 641–670.
- [44] N. Mott, *Fracture of metals: theoretical considerations*, *Engineering* 165 (1948) 16–18.
- [45] F.R. Nabarro, *Theory of Crystal Dislocations*, Oxford University Press, 1967, pp. 483–484.