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ENHANCED INTERFACE TOUGHNESS IN BI-MODAL NANO-ALUMINA-TITANIA COATINGS

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Abstract: Two different modes of delamination in nano-alumina-titania coatings on steel substrates, which are attributed to the conventional fully-melted (FM) and the bi-modal fully-melted and partially-melted (FM-PM) coating, are discussed. Using simple theoretical models of the coating/substrate interfaces, typical for these coatings, we analyze the profits of the bi-modal FM-PM coatings over the conventional FM coatings in terms of effective specific energy of adhesion, critical strain of delamination, and critical thickness of the coating. It is shown that use of the bi-modal FM-PM coatings can lead to doubling the interface toughness and increasing the critical strain by 50% and the critical thickness by more than 130%.

1 INTRODUCTION

The structure and mechanical properties of nanocrystalline bulk materials, films and coatings represent the subject of intensive research efforts involving experimental analysis, computer simulations and theoretical modeling; see, e.g., [1-21]. In recent years, a particular attention has been paid to nanocrystalline ceramic films and coatings [12-21] whose best samples exhibit superstrength, superhardness and good wear resistance. However, in the case of coatings, these outstanding properties can be used in practical applications if the toughness of the coatings and coating/substrate interface is also high enough. One of the ways to enhance the toughness is the fabrication of so-called bi-modal nanostructures in the coatings.

For example, the creation of bi-modal nanostructure in nano-alumina-titania (Al_2O_3-13wt.% TiO_2) plasma-sprayed ceramic coatings on steel substrates resulted in an increase in the interface toughness from 22 to 45 J × m^{-2} [22-24]. The first value was attributed to "conventional" coatings, which had a microstructure consisting primarily of fully-molten (FM) and solidified "splats" of nanocrystalline γ-Al_2O_3 [24]. The second value was characteristic for the "nano" coatings containing regions of FM "splats" interspersed with partially-molten (PM) rounded microstructural features [24]. The substructure in these PM features (20–50 μm diameter) consisted of α-Al_2O_3 grains (0.5–1 μm) surrounded by a TiO_2-rich amorphous phase. Scanning and transmission electron microscopy observations demonstrated that the FM/steel interfaces in both the "conventional" and the "nano" coatings were cracked (before mechanical testing), whereas the PM/steel interfaces in the "nano" coating were adherent.

The failure modes in the two types of coatings were found rather different [22-24]: long, wide separate cracks leading to extended delamination were typical for "conventional" coatings, while short, narrow multiple cracks and suppressed delamination were characteristic for "nano" coatings. In fact, the PM regions being enriched by TiO_2 amorphous phase served as obstacles for crack propagation in "nano" coatings and along the coating/substrate interface. The main possible reasons are that (i) the

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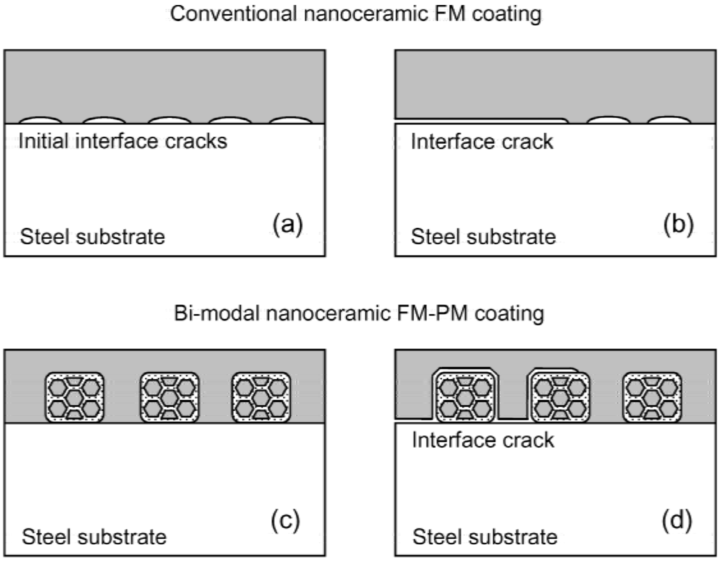

Fig. 1. Different modes of delamination of (a, b) the conventional FM coatings and (c, d) the bi-modal FM-PM coatings from the steel substrate. Parts (a) and (c) image the initial states of the coating/substrate interfaces before external loading; parts (b) and (c) show the propagation of a large interface crack through (b) joining the initial interface cracks or (c) bypassing the PM regions.

free surface energy of the amorphous phase is larger than that of the FM “splat”, (ii) the misfit strain due to the contact of the steel substrate with the amorphous phase is lower than that for the contact with a FM “splat”.

In the present paper, we consider the difference between the two modes of failure at the nano-alumina-titania coating/substrate interface in terms of effective specific energy of adhesion, critical strain of delamination [25], and critical thickness of the coatings [18].

2. MODEL

Consider a model crack which propagates along the coating/substrate interface in two different cases of conventional FM (Fig. 1a,b) and bi-modal FM-PM (Fig. 1c,d) nanoceramic coatings. Before external loading, the conventional FM coating/substrate interface contains many initial interface cracks (Fig. 1a), while the bi-modal FM-PM coating/substrate interface (Fig. 1c) is free of the initial cracks. Under external loading, the process of delamination proceeds through the propagation of a large interface crack, joining the initial cracks in the first case (Fig. 1b) or bypassing the PM regions in the second case (Fig. 1d).

Let the thickness h of the coating be much larger than the characteristic size d of a PM region. Then in both the cases, at the scale of h, the interface crack looks planar, and the critical condition of its propagation can be described as

$$G_d = \gamma_{cs}, \tag{1}$$

where G_d is the energy release rate which is characteristic for the delamination process and γ_{cs} is the effective specific energy of adhesion of the coating and substrate. Following Cherepanov [25], G_d is given by

$$G_d = \frac{h\left(\varepsilon+\varepsilon_0\right)^2 E_c}{2\left(1-\nu_c^2\right)}, \tag{2}$$

where ε is the tensile strain in the coating, ε_0 is the elastic strain due to the misfits in interatomic spacings and thermal expansion coefficients of the coating and the substrate, E_c is the Young modulus of the coating and ν_c is its Poisson ratio. From (1) and (2) yields that the critical strain is

$$\varepsilon_{crit} = \sqrt{\frac{2\gamma_{cs}\left(1-\nu_c^2\right)}{hE_c}} - \varepsilon_0. \tag{3}$$

Following Cherepanov [25], the delamination proceeds if ε reaches ε_{crit}.

Let us consider what happens with terms entering formula (3) when the conventional FM coating is replaced by the bi-modal FM-PM coating. First, the absolute value of ε_0 diminishes due to lower temperatures of the system fabrication [24]. Since ε_0 is negative (it is estimated as about of –0.001 for the conventional FM coating [24]), a decrease in its modulus seems to lead to a decrease in the critical strain ε_{crit}. On the other hand, Bansal et al. [24] noticed that a decrease in the modulus of ε_0 can enhance the adhesion between the bi-modal FM-PM coating and the steel substrate and result in elimination of initial interface cracks. This contribution can be taken into account by means of appropriate modification of the effective specific energy of adhesion γ_{cs}. Therefore, second, one should consider the changes in this latter term.

A model of the interface between the conventional FM coating and the steel substrate is shown in Fig. 2a. Before external loading, the model interface area of square S is composed of the bonded region (shown white in Fig. 2a) and the initial interface cracks (shown black in Fig. 2a) of sum square S_{cr}. Therefore the effective square of the bonded region is $S_{eff}^{FM} = S - S_{cr}$. If under external loading this bonded region is transformed to a crack (delamination), the corresponding increase in the surface energy can be written as follows

$$\Gamma_{eff}^{FM} = S_{eff}^{FM}\left(\gamma_{cer}^{FM} + \gamma_{st} - \gamma_{int}^{FM\text{-}st}\right), \tag{4}$$

where γ_{cer}^{FM} and γ_{st} are the specific surface energies of the conventional FM coating and the steel substrate, respectively, and $\gamma_{int}^{FM\text{-}st}$ is the specific energy of the FM coating/steel interface before external loading. With the surface fraction of initial interface cracks $s_{cr} = S_{cr}/S$, the effective specific adhesion energy γ_{cs}^{FM} reads

$$\gamma_{cs}^{FM} = \frac{\Gamma_{eff}^{FM}}{S} = \left(1 - s_{cr}\right)\left(\gamma_{cer}^{FM} + \gamma_{st} - \gamma_{int}^{FM\text{-}st}\right). \tag{5}$$

Therefore, the critical strain of delamination in the case of the conventional FM coating is

$$\varepsilon_{crit}^{FM} = \sqrt{\frac{2\left(1 - s_{cr}\right)\left(\gamma_{cer}^{FM} + \gamma_{st} - \gamma_{int}^{FM\text{-}st}\right)\left(1 - \nu_c^2\right)}{hE_c}} - \varepsilon_0^{FM}. \tag{6}$$

In the case of the bi-modal FM-PM coating, the coating/substrate interface practically does not contain initial interface cracks and is composed of the FM region (shown planar white in Fig. 2b) and the PM inclusions (shown as white boxes of characteristic dimensions $d \times d \times \alpha d$ in Fig. 2b, where α is a dimensionless parameter) [22-24]. Let under external loading the delamination occur through opening interface cracks between the FM region and the steel substrate, and between the FM region and the PM inclusions (see Fig. 1b), as it was observed in experiments [22-24]. Therefore, the corresponding increase in the surface energy is given by

$$\Gamma_{eff}^{FM\text{-}PM} = \left(S - Nd^2\right)\left(\gamma_{cer}^{FM} + \gamma_{st} - \gamma_{int}^{FM\text{-}st}\right) + Nd^2\left(1 + 4\alpha\right)\left(\gamma_{cer}^{FM} + \gamma_{cer}^{PM} - \gamma_{int}^{FM\text{-}PM}\right), \tag{7}$$

where N is the number of the PM inclusions per the coating/substrate interface square S, γ_{cer}^{PM} is the specific surface energy of a PM inclusion, and $\gamma_{int}^{FM\text{-}PM}$ is the specific energy of the FM/PM interface before external loading. With the surface fraction of PM inclusions $s_{PM} = Nd^2/S$, the effective specific adhesion energy $\gamma_{cs}^{FM\text{-}PM}$ takes the form

$$\gamma_{cs}^{FM\text{-}PM} = \frac{\Gamma_{eff}^{FM\text{-}PM}}{S} = \left(1 - s_{PM}\right)\left(\gamma_{cer}^{FM} + \gamma_{st} - \gamma_{int}^{FM\text{-}st}\right) + s_{PM}\left(1 + 4\alpha\right)\left(\gamma_{cer}^{FM} + \gamma_{cer}^{PM} - \gamma_{int}^{FM\text{-}PM}\right), \tag{8}$$

from which the critical strain of delamination in the case of the bi-modal FM-PM coating yields:

$$\varepsilon_{crit}^{FM\text{-}PM} = \sqrt{\frac{2\left[\left(1 - s_{PM}\right)\left(\gamma_{cer}^{FM} + \gamma_{st} - \gamma_{int}^{FM\text{-}st}\right) + s_{PM}\left(1 + 4\alpha\right)\left(\gamma_{cer}^{FM} + \gamma_{cer}^{PM} - \gamma_{int}^{FM\text{-}PM}\right)\right]\left(1 - \nu_c^2\right)}{hE_c}} - \varepsilon_0^{FM\text{-}PM}. \tag{9}$$

3. RESULTS

Let us make the numerical estimates of the quantities entering formulas (5) and (8). For definiteness, we take $\gamma_{cer}^{FM} \approx \gamma_{cer}^{PM} \approx \gamma_{cer}^{Al_2O_3}$ and $\gamma_{int}^{FM\text{-}PM} \approx \gamma_{cer}^{Al_2O_3}/2$ with $\gamma_{cer}^{Al_2O_3} \approx 30\ \mathrm{J} \times \mathrm{m}^{-2}$ [26]; $\gamma_{st} \approx 2\gamma_{int}^{FM\text{-}st} \approx \mu_{st} b_{st}/8 \approx 2.4\ \mathrm{J} \times \mathrm{m}^{-2}$, where $\mu_{st} \approx 77$ GPa and $b_{st} \approx 2.5$ Å are the shear modulus and the interatomic distance, respectively, of the steel substrate, and usual approximation $\gamma \approx \mu b/8$ between the specific surface energy γ and the shear modulus μ of a metal is used. Then, for rather realistic values $s_{cr} \approx s_{PM} \approx 0.3$ and $\alpha \approx 0.2$, we obtain $\gamma_{cs}^{FM} \approx 22$ J × m^{-2} and $\gamma_{cs}^{FM\text{-}PM} \approx 46$ J × m^{-2}. Therefore, according to formula (1), $G_d^{FM} \approx \gamma_{cs}^{FM} \approx 22$ J × m^{-2} and $G_d^{FM\text{-}PM} \approx \gamma_{cs}^{FM\text{-}PM} \approx 46$ J × m^{-2}, which correspond well to the experimentally measured values 22 J × m^{-2} and 45 J × m^{-2} [22-24], respectively. Using the quantities G_d^{FM} and $G_d^{FM\text{-}PM}$ as measures of the interface toughness, we can conclude that use of the bi-modal FM-PM coatings can result in doubling this very important characteristic of the coating/substrate system.

Taking these values on mind, it is easy to estimate the gain in the critical strain of delamination due to replacement of the conventional FM coating by the bi-modal FM-PM coating. Using formulas (5), (6), (8) and (9), and the well known relationship $E = 2\mu(1 + \nu)$, we found

$$\varepsilon_{crit}^{FM\text{-}PM} - \varepsilon_{crit}^{FM} = \sqrt{\frac{\gamma_{cs}^{FM\text{-}PM}\left(1-\nu_{FM\text{-}PM}\right)}{h\mu_{FM\text{-}PM}}} - \sqrt{\frac{\gamma_{cs}^{FM}\left(1-\nu_{FM}\right)}{h\mu_{FM}}} + \Delta\varepsilon_0. \qquad (10)$$

where $\Delta\varepsilon_0 = \varepsilon_0^{FM} - \varepsilon_0^{FM\text{-}PM} < 0$. For $\nu_{FM\text{-}PM} = \nu_{FM} = 0.22$, $\mu_{FM\text{-}PM} = 154$ GPa, $\mu_{FM} = 168$ GPa, and $h = 100 - 300$ μm [24], formula (10) gives a value from $\approx(1.53\text{-}1.01)10^{-3} + \Delta\varepsilon_0 = 0.52 \times 10^{-3} + \Delta\varepsilon_0$ (for $h = 100$ μm) to $\approx(0.88\text{-}0.58)10^{-3} + \Delta\varepsilon_0 = 0.3 \times 10^{-3} + \Delta\varepsilon_0$ (for $h = 300$ μm). Thus, the first term of the critical strain of delamination increases by ≈ 50% due to the replacement of the conventional FM coating by the bi-modal FM-PM coating. This gain is diminished, however, by the second negative term which is hard to estimate based on available data.

It is worth noting that in the practice of fabricating the nanoceramic coatings, the situation is possible when the coating starts to delaminate after its thickness has reached a critical value [18]. Assuming $\varepsilon = 0$ in this case, from formulas (1) and (2) we obtain this critical value as

$$h_{crit} = \frac{\gamma_{cs}\left(1-\nu_c\right)}{\mu\varepsilon_0^2}. \qquad (11)$$

Comparing the cases of the conventional FM coating and the bi-modal FM-PM coating, one can estimate the ratio $h_{crit}^{FM\text{-}PM}/h_{crit}^{FM}$ as follows

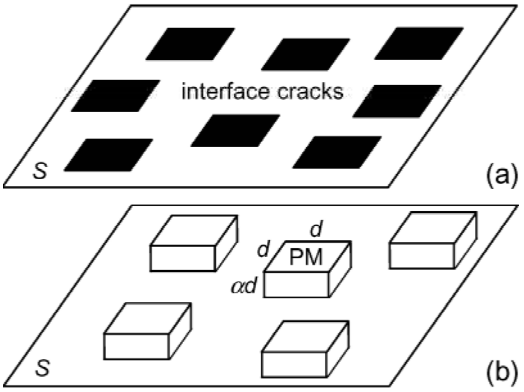

Fig. 2. Models of (a) conventional FM coating/steel and (b) bi-modal FM-PM coating/steel interface areas of square *S* before external loading. Black features in (a) denote the interface cracks (delaminations). White boxes in (b) image the PM regions of dimensions *d* × *d* × α*d*.

$$\frac{h_{crit}^{FM\text{-}PM}}{h_{crit}^{FM}} = \frac{\gamma_{cs}^{FM\text{-}PM}}{\gamma_{cs}^{FM}} \frac{\mu_{FM}\left(1-\nu_{FM\text{-}PM}\right)}{\mu_{FM\text{-}PM}\left(1-\nu_{FM}\right)} \frac{\left(\varepsilon_0^{FM}\right)^2}{\left(\varepsilon_0^{FM\text{-}PM}\right)^2}. \qquad (12)$$

With the aforementioned numerical values for the system parameters, formula (12) gives

$$\frac{h_{crit}^{FM\text{-}PM}}{h_{crit}^{FM}} \approx 2.3 \frac{\left(\varepsilon_0^{FM}\right)^2}{\left(\varepsilon_0^{FM\text{-}PM}\right)^2}. \qquad (13)$$

Taking into account that $\varepsilon_0^{FM}/\varepsilon_0^{FM\text{-}PM} > 1$ [24], we can conclude that $h_{crit}^{FM\text{-}PM}/h_{crit}^{FM} > 2.3$.

4. SUMMARY

We have discussed two different modes of delamination in nano-alumina-titania coatings on steel substrates, which are attributed to different microstructures of the coating. The first mode, which is the propagation of a large crack along a relatively planar interface containing many small initial cracks, has been observed earlier in the conventional FM coating/steel interface. The second mode is the growth of a large curvilinear crack which has to bypass the PM regions dispersed along the interface. This situation is typical for the bi-modal FM-PM coatings. Using simple theoretical models of these interfaces, we have estimated the profits of the bi-modal FM-PM coatings over the conventional FM coatings in terms of effective specific energy of adhesion, critical strain of delamination, and critical thickness of the coating. It has been shown that use of the bi-modal FM-PM coatings can lead to doubling the interface toughness and increasing the critical strain by 50% and the critical thickness by more than 130%. Our estimate for the interface toughness is in a good accordance with earlier experimental measurements.

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