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Experimental observations on the mechanical properties of nanoscale ceramic/Teflon multilayers

J.L. He [a,b,*], L.D. Wang [a,b], W.Z. Li [a,b], H.D. Li [a,b]

[a] *Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*

[b] *Laboratory of Advanced Materials, Tsinghua University, Beijing 100084, China*

Abstract

Inspired by the ingenious architecture of nacre and its outstanding mechanical properties, we prepared nanoscale ceramic (TiC, Si_3N_4, B_4C)/Teflon multilayers by ion beam sputtering deposition at room temperature. The toughness, hardness and tribological properties were systematically investigated as well as the multilayer structures. It was found that the toughness of ceramic/Teflon multilayers were all significantly improved in comparison with the corresponding monolithic ceramic material, but the hardness was decreased. However, there were optimized layer thickness arrangements with which the multilayer toughness and hardness can be favorably combined to obtain better comprehensive properties. It was found by this study that ceramic/polymer multilayers with the optimized layer thickness arrangement had good performance in wear resistance.

Keywords: Multilayers; Hardness; Toughness; Tribology; Nanoscale; Simulation

1. Introduction

Nanocomposites have been widely recognized as a new generation of materials with many unique properties. The micro-design and precise control of the microstructures in these composites are regarded as the cruxes of the nanocomposite development. In this respect, nature is indeed a great source of inspiration. Living organisms excel at design and processing. Excellent properties can usually be developed with very common base materials. As for mechanical properties, nacre is a typical model. Composed of alternating layers of proteins and $CaCO_3$ platelets, nacre possesses considerably high mechanical properties such as fracture toughness and strength [1]. The main cause is its unique 'brick and mortar' structure which can efficiently integrate the stiffness of aragonite crystals and the plasticity of biopolymetrics.

Many researches were thus agitated in the field of biomimetics. The laminated structure of nacre was thoroughly studied and many attempts were made to try to realize it with artificial multilayers [2–6]. Despite the fact that considerable enhancement in strength or toughness were obtained, the influences of layer thickness arrangement are still not very clear. In natural nacre, the thickness of organic or inorganic layers is almost identical for a certain species [1]. This phenomenon is interesting. It can only be comprehended as that such a layer arrangement is the best optimized arrangement, for it is the result of millions of years of evolution. For artificial multilayers there should also be some optimized layer arrangements with which the multilayer can exhibit the best comprehensive properties. However, studies in this respect are very rare.

In this work, we prepared ceramic/polymer multilayers with a polymeric material, Teflon, and several ceramic materials, including TiC, Si_3N_4, B_4C. The multilayers were designed to simulate the nacre not only in the respect of laminated structure but also with the most approximate layer thickness arrangement. The hardness, toughness and tribological properties were studied together with the multilayer structures.

2. Experimental

Ceramic/Teflon multilayers were prepared in an ion beam sputtering system which was described elsewhere [7]. Individual layers were deposited by sputtering the corresponding targets with an Ar^+ ion beam. Multilayers were obtained by alternative deposition. The typical film growth rates were 0.5, 1.3, 0.8 and 2 Å s^{-1} respectively for TiC, Si_3N_4, B_4C and Teflon. All multilayers were deposited to about 0.5 μm thick.

* Corresponding author. Fax: +86-10-62771160; E-mail: zjz-dms@mail.tsinghua.edu.cn

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Silicon wafers were used as substrates. During deposition, the substrates were water cooled and their temperature was kept below 60°C.

The composition and structure of the ceramic and Teflon layers were examined by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and infrared (IR) analysis. The laminated structures in the multilayers were directly examined by field-electron scanning electron microscopy (FESEM) observation on the cross-section. Multilayer hardness was tested by an HXD-1000 microhardness tester under a load of 5 g force.

The toughness of ceramic/Teflon multilayers was comparatively evaluated by Vicker's indentation method. At first, films were deposited on silicon wafer to the same thickness. Vickers indentation was then carried out at raising loads to find the critical load under which cracks happened around the impression. This critical load was taken as the 'toughness' of the film. Since the substrates were all the same and the films had the same thickness, such a critical 'cracking' load should be an indication of the multilayer's cracking resistance. This means the 'toughness' data can be used for comparison between samples, even when the cracks were initiated by the substrate first. This method proved to be quite accurate and repeatable. The scatter of the critical load was within ± 2 g for all the multilayers in this work.

Tribological test was carried out by a ball-on-disk tribometer. The sliding ball was 10 mm in diameter and was made of hardened AISI 52100 steel. Sliding speed was 40 mm s^{-1} and the load was 5N. The tribological properties were also studied by a nanotribology test that was conducted with a CSPM-930 atomic force microscope.

3. Results and discussion

3.1. Structural analysis

In this study, both the TEM diffraction pattern and XRD analysis showed that the Si_3N_4 and B_4C layers were amorphous and the TiC was polycrystalline. The present paper emphasizes on TiC/Teflon system.

The structures of sputtering deposited Teflon films were characterized by XPS and IR. Fig. 1(b) shows the XPS C1s spectrum of the Teflon films prepared in this study. It can be seen that the proportion of CF_2 is dominant in comparison with other CF_x groups [8,9]. The XPS C1s spectrum of the original Teflon material is also shown (Fig. 1(a)). Comparison between the two spectra indicates that the sputtering deposited Teflon films had chemical bonds very similar to those of original Teflon.

The laminated structure of ceramic/Teflon multilayers was directly confirmed by FESEM observation on the multilayer cross-section. It was found that for all the samples in this study the multilayered structure was clear but the interfaces were very rough. This indicates that the multilayer structure

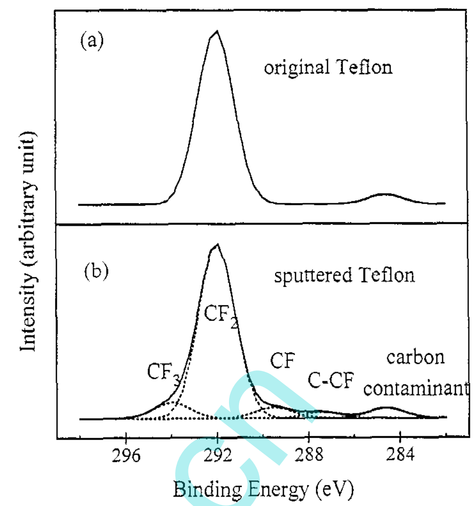

Fig. 1. XPS C1s of (a) original Teflon material and (b) the sputtered Teflon film.

in ceramic/polymer systems was not so well formed as in ceramic/metal systems [10–12].

3.2. Mechanical properties

For all the ceramic/Teflon multilayers in this study, the toughness was found to be considerably improved in comparison with the corresponding monolithic ceramic material. For example, the toughness of Si_3N_4/Teflon multilayer with individual layer thickness $t_{Si3N4} = 78$ nm and $t_{Teflon} = 69$ nm was 30 g, which was almost three times greater than that of pure Si_3N_4 (7 g). The B_4C/Teflon multilayer with $t_{B4C} =$ 60 nm and $t_{Teflon} = 20$ nm had a toughness of 92 g; also much higher than that of pure B_4C (26 g). The toughness improvement in ceramic/Teflon multilayers can be attributed to the soft and ductile Teflon layers. The main mechanisms are bridging of advancing cracks and plastic deformation during crack propagation [13]. This was proved by the fracture morphology of TiC/Teflon multilayers. As shown in Fig. 2, clear evidence for bridging and plastic deformation of Teflon layers can be observed.

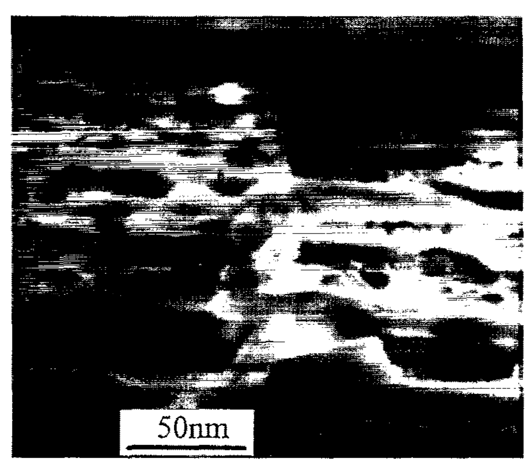

Fig. 2. Fracture surface of TiC/Teflon multilayer with $t_{TiC} = 120$ nm and $t_{Teflon} = 40$ nm.

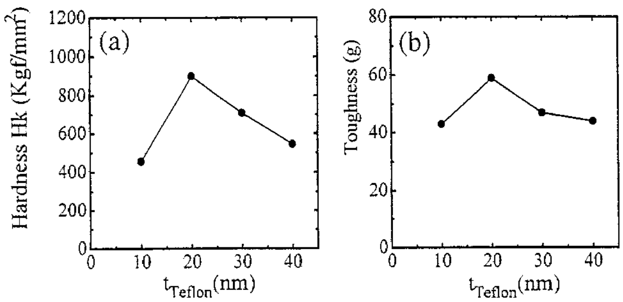

Fig. 3. (a) Hardness and (b) toughness of TiC/Teflon multilayers as a function of the thickness of Teflon layers. (Thickness of TiC layers are constant at 60 nm.)

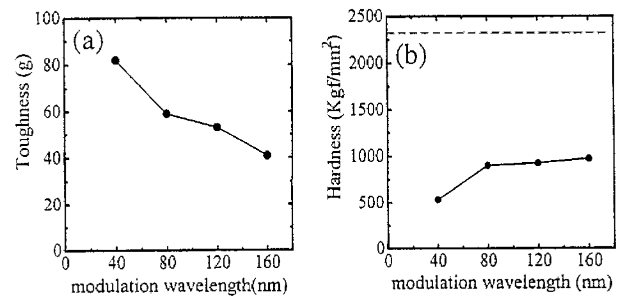

Fig. 4. (a) Hardness and (b) toughness of TiC/Teflon multilayers as a function of the the modulation wavelength when the component fraction is the same (75 vol.% TiC).

While the toughness was improved in comparison with corresponding monolithic ceramics, the multilayer hardness was decreased. For the two B_4C/Teflon and Si_3N_4/Teflon multilayers mentioned above, the hardness was 1578 and 1704 Kgf mm^{-2}, respectively. Both were smaller than the hardness of corresponding ceramics, i.e. $Hk_{Si3\ N4}$ = 2016 Kgf mm^{-2} and Hk_{B4C} = 2115 Kgf mm^{-2}. In TiC/Teflon systems, similar results were obtained.

In this study, it was also found that both multilayer hardness and toughness showed dependence on the specific layer thickness arrangement. These relations were thoroughly studied in the TiC/Teflon system.

The first factor to be considered is the component fraction. Intuitively, a greater fraction of Teflon in the multilayer can be supposed to result in a higher toughness and a smaller hardness and vice versa. Unfortunately, this was not the exact case in ceramic/Teflon multilayer toughness and hardness behavior. In Fig. 3(a), the hardness of TiC/Teflon multilayers was plotted as a function of the thickness of Teflon layers, t_{Teflon}, while the thickness of TiC layers, t_{TiC}, was kept constant at 60 nm. It can be seen that the multilayer hardness steadily increases when t_{Teflon} is reduced from 40 to 20 nm. Then the multilayer hardness reaches a maximum at about t_{Teflon} = 20 nm. Further decrease of t_{Teflon} can only result in a hardness decrease.

The multilayer toughness is shown in Fig. 3(b). As can be seen, the multilayer toughness first increases with increasing t_{Teflon} then decreases with it. A toughness maximum happened around t_{Teflon} = 20 nm. This is because the 'toughness' is influenced by both strength and plasticity. Introduction of a suitable amount of Teflon into the multilayer can improve the plasticity. Thus, the toughness can be increased. However, too much Teflon can greatly lower the strength. As a result, multilayer 'toughness' can also be decreased. This suggests that in order to get a good toughness the component fraction should be properly adjusted.

Modulation wavelength, an important parameter for nanoscale multilayers, is another factor influencing the multilayer hardness and toughness. Fig. 4 illustrates its effects when the component fraction is the same (75 vol.% TiC). As can be seen, the multilayer toughness decreases with modulation wavelength and the hardness increases with it. This is different from ceramic/metal systems where hardness usually increased when the modulation wavelength was reduced [10–13].

If comprehensively evaluated concerning both hardness and toughness, TiC/Teflon multilayers should have some favorable layer thickness arrangements with which the multilayer hardness and toughness can be so properly combined that its performance is improved as a whole. This is because, in general, multilayer toughness and hardness are contrary to each other. A higher hardness usually means a smaller toughness, as demonstrated in Fig. 4. So, in order to obtain good comprehensive properties, a trade-off has to be made between the hardness and toughness. For TiC/Teflon multilayers, hardness and toughness can be favorably combined to achieve better performance in some applications such as wear resistance. According to this study, multilayers with t_{TiC} = 90 nm and t_{Teflon} = 30 nm should be more promising in wear applications because its toughness and hardness were both moderate.

Fig. 5(b) shows the tribological behavior of this TiC/Teflon multilayer in ball-on-disk test. It can be seen that the multilayer friction coefficient is smaller than that of pure TiC (Fig. 5(a)). It should also be noted that there is no obvious periodic variation in the friction coefficient. The wear procedure steadily went on. Friction coefficient was maintained at about 0.35. This indicates that this multilayer had good performance in the wear test. It is consistent with the above analysis.

For Si_3N_4/Teflon multilayers, the friction coefficients were also smaller than that of pure Si_3N_4. This was confirmed

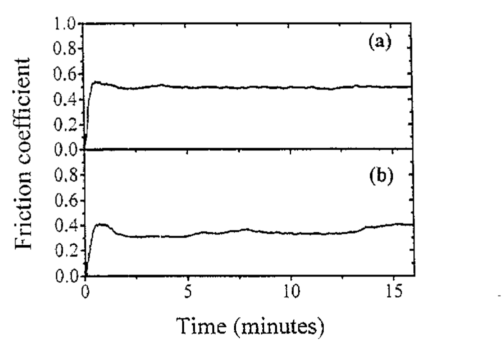

Fig. 5. Friction coefficient of (a) pure TiC and (b) TiC/Teflon multilayer with t_{TiC} = 90 nm and t_{Teflon} = 30 nm.

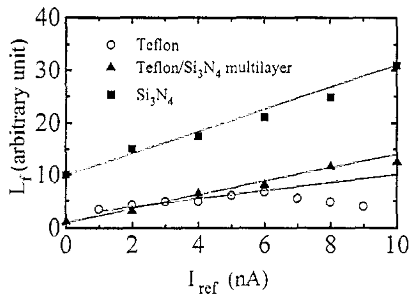

Fig. 6. Friction coefficients of Teflon, Si_3N_4 and Si_3N_4/Teflon multilayer in nanotribology test.

by the nano-tribology test. As shown in Fig. 6, the slope of the line is an indication of the friction coefficient. It can be seen that the Si_3N_4/Teflon multilayer has a friction coefficient very close to that of Teflon; much smaller than that of Si_3N_4.

4. Conclusions

The present work confirmed that it is possible to experimentally prepare Teflon nanolayers by ion beam sputtering. Nanoscale ceramic (TiC, Si_3N_4 and B_4C)/Teflon multilayers were thus prepared. Multilayer hardness, toughness and tribological properties were studied. It was found that the toughness of ceramic/Teflon multilayers was generally improved in comparison with the corresponding monolithic ceramic materials. However, the multilayer hardness was decreased. Both toughness and hardness showed dependence on the individual layer thickness arrangement. A favorable combination of multilayer toughness and hardness could be achieved by optimizing the layer thickness arrangement. Ball-on-disk tribological test showed that the multilayers with optimized layer thickness arrangement had good performance in wear resistance. For all the ceramic/Teflon multilayers, the friction coefficient was found to be reduced in comparison with the corresponding monolithic ceramic material.

Acknowledgements

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