Rare Metal Materials and Engineering
Volume 47, Issue 11, November 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com

Cite this article as: Rare Metal Materials and Engineering, 2018, 47(11): 3295-3300.

ARTICLE

Effect of Substrate Pre-carburizing on Properties of TiN (Ti) Hard Coatings Deposited on Ti-6Al-4V Alloy

Wang Yanfeng[1,2], Li Zhengxian[2], Li Wei[3], Du Jihong[2], Ji Shouchang[2], Zhang Changwei[2]

[1] Xi'an University of Architecture & Technology, Xi'an 710055, China; [2]Northwest Institute for Nonferrous Metal Research, Xi'an 710016, China; [3] Science and Technology on Reactor System Design Technology Laboratory, Nuclear Power Institute of China, Chengdu 610213, China

Abstract: Interface fracture often occurs in systems of soft substrate and hard coatings during the service process, which is related to the weak interface strength and the unstable expansion of cracks along the interface induced by the residual thermal stress. The residual thermal stress mainly comes from the mismatch of thermal physical properties between matrix and hard coatings. In this study, a gradient carburized layer was prepared on TC4 substrate before the deposition of TiN(Ti) coatings using double glow plasma carburization. And then the mono- and multilayer TiN(Ti) coatings were synthesized on the carburized layer, forming composite hard coatings. The effect of substrate carburizing on properties of coatings was studied. The results show that the composite coatings' hardness can be increased nearly 2 times and the bonding strength is enhanced to over 80 N, compared with that of mono-and multilayer TiN(Ti) coatings. Also the interface brittle fracture tendency is restrained obviously by the hardened substrate, and the coordinative deformation ability of the coating at extra load is optimized. The composite coating composed of pre-carburized layer and TiN hard coating shows a higher strength and toughness.

Key words: carburized layer; TiN/TiN coating; interface fracture; micro hardness; bonding strength

Hard coatings by physical vapor deposition, such as TiN, TiAlN and C/TiAlSiN, which have higher hardness, better wear and oxidation resistance, could improve the surface performance of components in high-speed manufacturing[1-6]. However, these coatings often exhibit a higher level residual stress and brittleness which result in fracture and flaking [7,8]. Many efforts on the control of residual stress and toughness enhancement have been made [9-11].

Based on architectural approaches, some researchers have investigated that multilayer coatings of ductile metallic and brittle ceramic-like layers possess better toughness and adhesion strength due to their low and constant level of residual stress [12-16]. R. Ali et al. formulated a numerical mode of Ti/TiN multilayer by multi-physics and found an optimal thickness of each individual layer in a multilayer causing a significant decrease in residual stress and improvement in adhesion [17]. M. Azadi et al studied the TiN/TiC multilayer coatings on hot work tool steel and that the increase in the number of interlayers could result in an enhancement in microhardness and fracture toughness compared to monolayer coatings[18]. J. Li et al researched the multiple TiN/Ti coating, and found that multilayer structure could offer a greater resistance to cracking and delamination [19].

Despite a lot of achievements on the multilayer coatings' design and properties, less effort is focused on the interface between coating and substrate, and also limited researches have been reported about the effect of substrate pre-strengthening on coatings properties. In this paper the TC4 substrate was pre-strengthened by a carburized layer using double glow plasma carburization before deposition of the TiN(Ti) coatings. And the effects of substrate pre-carburization on properties of mono- and multilayered TiN (Ti) hard coatings were studied in detail.

1 Experiment

Received date: November 25, 2017
Foundation item: National International Science and Technology Corporation (2014DFR50450)
Corresponding author: Wang Yanfeng, Senior Engineer, Northwest Institute for Nonferrous Metal Research, Xi'an 710016, P. R. China, Tel: 0086-29-86231077, E-mail: yfwang420@163.com

In this work, the Ti/TiN multilayer coatings as well as corresponding TiN monolayer coatings were synthesized on TC4 alloys by plasma enhanced ion plating system. Before deposition, the TC4 substrate was strengthened firstly by forming a diffused carburized layer on the surface using double glow plasma carburization. This diffused carburized layer could form an increasing hardness gradient on TC4 substrate and also induce compressive stress which is good for the interface bonding strength. Fig.1 shows the schematic of the double glow plasma carburization system. The sample was fixed on the work electrode and the source electrode was made of high purity graphite. In Ar plasma atmosphere, the carbon atoms and ions were sputtered by the glow discharge between anode and source electrode, and enhanced further by the second glow discharge between anode and work electrode; the second glow discharge could heat the sample to supply more energy for the carbon diffusion. So the carburized layer could be formed quickly on the sample surface and TC4 substrate's hardness was enhanced. After that, the monolayer TiN and 6 periods of multilayer Ti/TiN coatings were deposited. Also the TC4 alloys without pre-carburization were used as substrates for comparison. Deposition parameters are presented in Table 1.

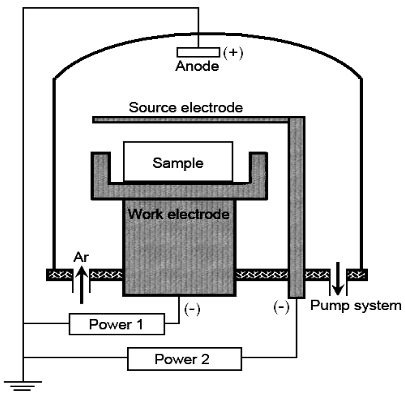

Fig.1 Schematics of the double glow plasma carburization system

Cross-sectional morphology of the mono- and multilayer TiN(Ti) coatings were characterized by the scanning electron microscopy operated at 20 kV (JSM-6460F, SEM). And a MH-5 digital Vickers micro hardness test instrument was used to determine coating's hardness with the test load of 0.24 N and dwell time of 10 s. The coating's adhesion and interface fracture mechanism were evaluated by a scratch tester (Rockwell HRC penetrator). The scratch was 4 mm in length on which the load was increased linearly from 0 N up to 100 N. After the test, the fracture morphology of coating, especially the crack initiation and propagation were observed by SEM.

2 Results and Discussion

2.1 Structural characterization

Fig.2 shows the cross-sectional SEM images of mono- and multilayer TiN(Ti) coatings deposited on TC4 substrates with and without pre-carburization. All the coatings exhibit a dense columnar morphology, with tight bonding with substrate. No obvious defects could be observed, even at regions close to the substrate. The monolayer TiN coating as shown in Fig.2a and Fig.2b have a thickness over 5 μm. In the images of multilayer Ti/TiN coatings (corroded by acid solutions of HNO_3 and HF) as shown in Fig.2c and Fig.2d, the multilayer architecture, composed of ～0.32 μm thick Ti layer (dark contrast) and ～1.5 μm thick TiN layer (light contrast) is clearly observed. The modulated period is precisely controlled to be 6 and the modulate ratio of Ti to TiN is about 0.2. The coating's thickness can reach over 10 μm with no adhesion. In addition it can be found that the mono- and multilayer TiN(Ti) are bonded tightly with the TC4 of pre-carburization, as shown in Fig.2b and Fig.2d.

Table 1 Summary of deposition of mono- and multilayer TiN(Ti) hard coatings

No.	Type of layers	Type of substrates	Time of deposition/min	Thickness/μm
1	TiN	TC4	90' TiN	7.2
2	6 periods Ti/TiN	TC4	6 periods (3'Ti+17'TiN)	11.2
3	TiN	TC4 with pre-carburization	90'TiN	6.1
4	6 periods Ti/TiN	TC4 with pre-carburization	6 periods (3'Ti+17'TiN)	10.6

Note: " ' " is time (min)

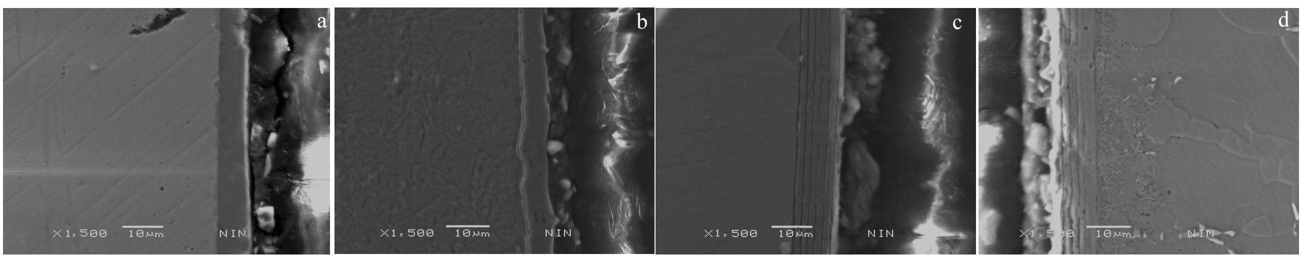

Fig.2 Cross-sectional SEM images of mono- and multilayer TiN(Ti) coatings on TC4 substrates with and without pre-carburization: (a) monolayer TiN coating; (b) monolayer TiN coating with pre-carburization; (c) multilayer Ti/TiN coating; (d) multilayer Ti/TiN coating with pre-carburization

2.2 Effect of pre-carburization on coatings' hardness and bonding strength

The microhardness test was carried out on the TiN monolayer and Ti/TiN multilayer on TC4 substrate with and without pre-carburization. As shown in Fig.3, the sample with 6 periods of Ti/TiN coatings has a higher hardness (HV), about 13 000 MPa, than the monolayer TiN coating. The higher hardness of the multilayer system can be attributed to the increase in the number of interfaces, acting as barriers to dislocation movement, so the plastic deformation is restrained[20,21]. After pre-carburization, the TC4 substrate was hardened and the coating's hardness was improved further. As shown in Fig.3, the hardness (HV) of monolayer TiN deposited on TC4 with pre-carburization is about 20 000 MPa and that of multilayer Ti/TiN coating is higher, about 23 000 MPa. The mechanism can be explained by the TC4 substrate strengthening. The carburized layer makes the substrate harder and gains a higher plastic deformation resistance. At the interface of the coating and substrate, the coating's plastic deformation is restricted by the hard substrate and the dislocation movement is restrained. So the hardness is improved.

Fig.4 shows the bonding strength of the mono- and multilayer TiN (Ti) deposited on TC4 substrates with and without pre-carburization. In this work, the monolayer TiN coating with a thickness over 5 μm has the lowest bonding strength, about 25 N with TC4 substrate (Fig.4a), but it is enhanced remarkably when the substrate is strengthened in advance. The bonding strength can reach above 75 N as shown in Fig.4c. Similarly, the bonding strength of the multilayer Ti/TiN coating with 6 periods shows the same current. Even though the thickness exceeds 10 μm, coating's bonding strength is increased from 55 to 80 N due to the function of carburized layer (compared with Fig.4b and Fig.4d).

In fact, the higher bonding strength of composite coating systems can be attributed to the optimization of microstructure. Firstly, it has been explained in the literature that a lower residual stress could be obtained in multilayer Ti/TiN coating which is good for restraining the crack expansion, and the crack-tip was blunted by plastic deformation of the ductile Ti interlayer[22,23]. Secondly, a compress stress was induced at the interface of the coating and substrate

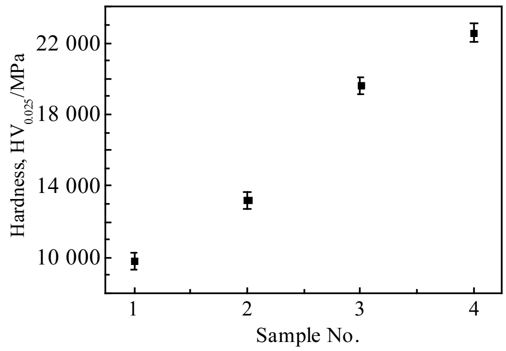

Fig.3 Hardness characterization of mono- and multilayer TiN(Ti) coatings with and without pre-carburization

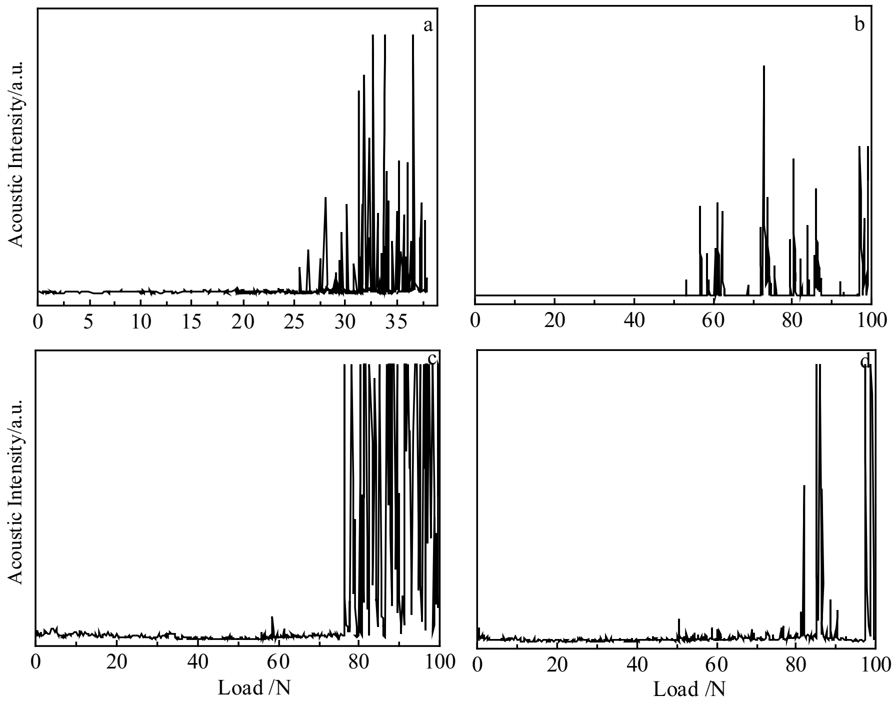

Fig.4 Bonding strength of mono- and multilayer TiN(Ti) coatings on TC4 substrates without and with pre-carburization: (a) monolayer TiN coating, (b) monolayer TiN coating with pre-carburization, (c) multilayer Ti/TiN coating, and (d) multilayer Ti/TiN coating with pre-carburization

by the carburized layer which can also improve adhesion and toughness. Thirdly, the system with hard substrate and coating shows a higher coordinated deformation ability at extra test load in a micro area, avoiding the brittle crack initiation and expansion along the interface, so the fracture of the coating from substrate can be blocked, compared with the system of soft substrate and hard coating. When a higher scratch test load (>85 N in this work) was applied on the coating, this coordinated deformation was broken and adhesive failure occurred.

2.3 Effect of pre-carburization on coating's interface fracture mechanism

Based on the interface fracture morphologies, the effect of pre-carburization on coating's interface mechanism was studied.

As shown in Fig.5a, the monolayer TiN coating cracked at initial scratch stage and then fractured continuously along the scratch. From Fig.5b which is the magnified area of Fig.5a, it can be seen that the coating shows a brittle and fatal fracture with crack initiation and expansion. The fracture mode can be attributed to the interface stress and the coating itself. As we all know, the system of soft substrate and hard coating often has higher residual stress, because of their mismatch of physical properties, which accumulates at the interface. The ceramic-like TiN coating possesses higher brittleness. So the interface brittle fracture occurs at the function of extra scratch load.

After pre-carburization, the coating fracture is restrained. From Fig.6a, the coating cracked until the second half of the scratch, meaning an improvement in fracture resistance, which is consistent with the test result in Fig.4b.

Besides, the fracture of the composite coating is discontinuous and is restrained in a smaller area, comparing with that of monolayer TiN in Fig.5. So it can be believed that the monolayer TiN coating's fracture resistance is improved by the pre-carburization of substrate.

The study of multilayer Ti/TiN coating shows that a significant improvement in properties, especially in bonding strength can be achieved[12]. Correspondingly, the effect of pre-carburization on fracture of multilayer Ti/TiN coating is also positive. Before pre-carburization, the multilayer Ti/TiN coating with 6 periods only shows a crack initiation and propagation mode, as shown in Fig.7a. With increasing the scratch load, more and more micro cracks can be seen at the edge of scratch track, and the crack propagation direction is deflected. From the magnified area of Fig.7a, the fracture morphology in a smaller area along the crack can be seen in Fig.7b and that fracture only occurs at several periods of multilayer, suggesting the Ti/TiN coating is not totally destroyed.

Further, the composite coating with pre-carburized layer and multilayer Ti/TiN coating has a higher interface fracture resistance. As shown in Fig.8a, no obvious crack or fracture can be seen, and only a smaller fracture is found at the end of scratch track, at about 80 N of scratch load. Fig.8b presents the fracture morphology of white area in Fig.8a. A gradual peeling with a layer-by-layer mode can be seen clearly, which is consistent with that of Ti/TiN multilayer coating, as shown in Fig.7b. The peeling mode can be explained as follows: the first TiN interlayer of composite coating fractured firstly at higher contact stress induced by

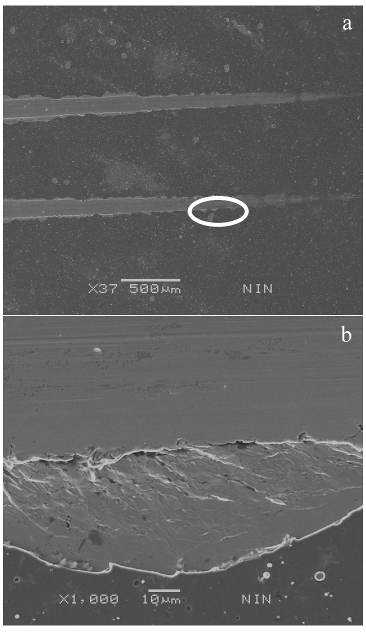

Fig.5 Fracture morphologies of monolayer TiN coating: (a) macro scratch track and (b) local magnified area

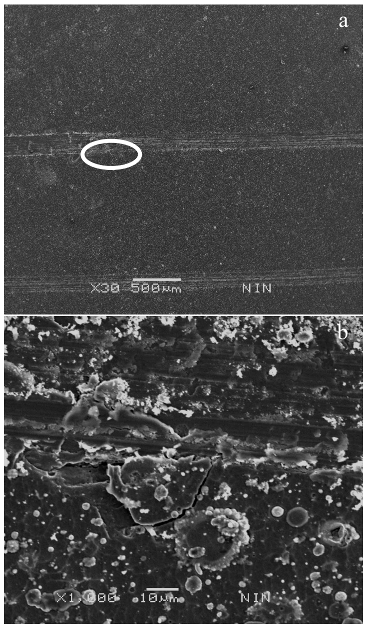

Fig.6 Fracture morphologies of composite coating with carburized layer and monolayer TiN coating: (a) macro scratch track and (b) local magnified area

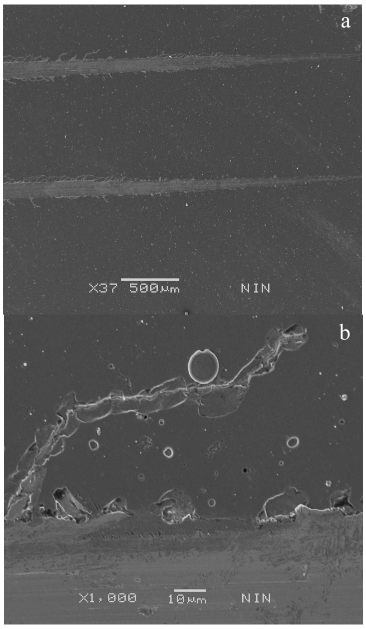

Fig.7 Fracture morphologies of Ti/TiN coating with 6 periods: (a) macro scratch track and (b) local magnified area

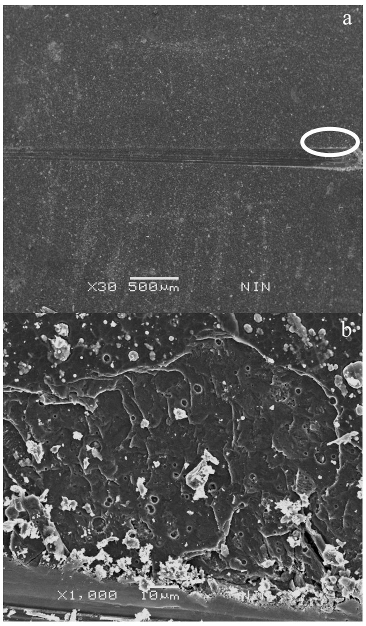

Fig.8 Fracture morphologies of composite coating with carburized layer and 6 periods of Ti/TiN coating: (a) macro scratch track and (b) local magnified area

scratch load, and the micro cracks continue to expand, causing the second TiN layer fracture. Along this process, the energy of crack tip is absorbed by the tougher Ti interlayer and decreases gradually. When the energy loss exceeds the power of crack propagation, the cracks would stop expanding and the coating would not be fractured any more.

The positive effect of pre-carburization on coating fracture mechanism can be explained in three aspects. Firstly, a gradient hardening layer formed by carbon diffusion which is good for improving the physical matching of substrate and coating, so the interface bonding strength is enhanced, avoiding the interface fracture. Secondly, a compressive stress gradient is also induced before deposition of TiN coating. Then the tensile stress, accumulating at the interface during the process of coating deposition, was offset by that stress gradient, forming a lower residual stress. The reduction of residual stress in the coating could inhibit the micro crack propagation during the scratch, unless increasing the scratch load. Thirdly, the carrying capacity of composite coating is improved by the hardened substrate, which means the strengthening of coordinative deformation at extra load. As a result, the crack initiation resistance is enhanced.

In summary, the internal factors of crack initiation and propagation, such as residual stress and coating brittleness are significantly suppressed. And large areas of interface fracture are prevented due to the lower interface stress and higher bonding strength. Even an instantaneous breaking occurs, the influenced area is limited, without affecting the integrity of the coating. In other words, the toughness of composite coating is improved.

3 Conclusions

1) The positive effect of substrate carburizing on properties of mono- and multilayer TiN(Ti) coatings was studied. A harder substrate makes the coating has a higher plastic deformation resistance, possessing a higher hardness. Also the bonding strength is improved by forming a lower stress gradient at the function of carbon diffusion.

2) The composite coating's carrying capacity is enhanced, which means a better coordinative deformation ability, and the crack initiation and propagation are significantly suppressed. So the interface brittle fracture is inhibited.

References

1 Bartosik M, Holec D, Apel D *et al*. *Scripta Materialia*[J], 2017, 127: 182

2 Arulkirubakaran D, Senthilkumar V. *International Journal of Refractory Metals and Hard Materials*[J], 2017, 62(A): 47

3 Tang Y, Ma B, Liu B *et al. Rare Metal Materials and Engineering*[J], 2016, 45(12): 3057

4 Danek M, Fernandes F, Cavaleiro A *et al. Surface and Coatings Technology*[J], 2017, 313: 158

5 Wang Y F, Li Z X, Du J H *et al. Applied Surface Science*[J], 2011, 258(1): 456

6 Shypylenko A, Pshyk A V, Grześkowiak B *et al. Materials & Design*[J], 2016, 110: 821

7 Wang L, Zhong X, Zhao Y *et al. Journal of Asian Ceramic Societies*[J], 2014, 2(2): 102

8 Vaz F, Rebouta L, Goudeau P *et al. Thin Solid Films*[J], 2002, 402(1-2): 195

9 Voglia E, Tillmann W, Selvadurai-Lass U. *Applied Surface Science*[J], 2011, 257(20): 8550

10 Evans A G, Hutchinson J W. *Acta Metallurgica et Materialia*[J],1995, 43(7): 2507

11 Tillmann W, Vogli E. *Advanced Engineering Materials*[J], 2008, 10(1-2): 79

12 Mori T, Fukuda S, Takemura Y. *Surface and Coatings Technology*[J], 2001, 140(2): 122

13 Bouaouina B, Besnard A, Abaidiaa S E *et al. Applied Surface Science*[J], 2017, 395: 117

14 Dang C, Li J, Wang Y *et al. Applied Surface Science*[J], 2016, 386: 224

15 Wang Y F, Li Z X, Wang H N *et al. Rare Metal Materials and Engineering*[J], 2017, 46(5): 1219

16 Song G H, Luo Z H, Li F *et al. Transactions of Nonferrous Metals Society of China*[J], 2015, 25(3): 811

17 Ali R, Sebastiani M, Bemporad E. *Materials and Design*[J], 2015, 75: 47

18 Azadi M, Rouhaghdama A S, Ahangarani S *et al. Surface & Coatings Technology*[J], 2014, 245: 156

19 Li J, Zheng H, Sinkovits T. *Applied Surface Science*[J], 2015, 352: 502

20 Abadias G, Michel A, Tromas C *et al. Surface & Coatings Technology*[J], 2007, 202(4-7): 844

21 Stueber M, Holleck H, Leiste H *et al. Journal of Alloys and Compounds*[J], 2009, 483(1-2): 321

22 Voevodin A A. *Surface & Coatings Technology*[J], 2001, 148 (1): 38

23 Subramanian C, Cavallaro G, Winkelman G. *Wear*[J], 2000, 241(2): 228

基体预渗碳对 Ti-6Al-4V 合金表面 TiN(Ti)硬质膜层性能的影响

王彦峰[1,2]，李争显[2]，李 维[3]，杜继红[2]，姬寿长[2]，张长伟[2]

(1. 西安建筑科技大学，陕西 西安 710055)

(2. 西北有色金属研究院，陕西 西安 710016)

(3. 中国核动力研究设计院 核反应堆系统设计技术重点实验室，四川 成都 610213)

摘 要：硬质膜层在服役过程中，往往由于膜基界面强度的不足导致膜层过早的发生界面的剥落失效，这种剥落失效主要是由界面残余热应力诱导的显微裂纹的失稳扩展引发的。残余热应力主要来源于基体与膜层材料在热膨胀系数、弹性模量等物理性能的不匹配。为了降低这种不匹配性，在制备 TiN 硬质膜层之前，通过辉光离子扩渗技术在 TC4 基体表面形成具有一定深度、梯度结构的渗碳硬化层，然后利用等离子增强离子镀技术制备了单层及多层复合 Ti/TiN 膜层，研究基体预渗碳层对其表面不同结构 TiN(Ti)硬质膜层性能的影响。结果表明，基体经过预渗碳强化处理后，相比于单一 TiN 或多层复合 Ti/TiN 硬质膜层，复合渗镀层的表面硬度能提高近 2 倍，膜基结合强度可达 80 N 以上。同时，经过硬化后的基体显著抑制了其表面复合硬质膜层的界面脆性断裂倾向，复合膜层在外加载荷作用下的与基体的协同变形能力得到加强，强韧性显著提高。

关键词：渗碳层；TiN/TiN 膜层；界面断裂；显微硬度；结合强度

作者简介：王彦峰，男，1983 年生，高级工程师，西北有色金属研究院腐蚀与防护研究所，陕西 西安 710016，电话：029-86283410，E-mail: yfwang420@163.com