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Zr−N surface alloying layers fabricated in pure titanium substrates by plasma surface alloying

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Abstract: The Zr−N alloying layers were prepared on the surface of pure titanium substrates by plasma surface alloying technique to improve the surface properties. The microstructure, chemical composition, and hardness of Zr−N surface alloying layers were analyzed to understand the mechanisms of surface alloying and hardness improvement. The tribological performance of Zr−N surface alloying layers was studied by ball-on-disc wear machine. The results show that Zr−N alloying layers formed are homogeneous and compact. The Zr−N surface alloying layer consists of an outer nitride layer and an inner diffusion zone of zirconium and nitrogen. The surface treatment enhances the hardness of the surface layers of pure titanium substrates greatly and a surfaces hardness of HK1870 is obtained. Though Zr−N surface alloying layer does not show friction-reducing effect, it improves the wear resistance of pure titanium obviously.

Key words: pure titanium; plasma surface alloying; Zr−N surface alloying layer; hardness; tribological properties

1 Introduction

Titanium and titanium alloys are widely used in aerospace, chemical and biomedical industries, because of their extraordinary corrosion resistance, high mechanical strength and low density. However, titanium and its alloys have low hardness and poor wear resistance [1−3]. The problem can be overcome by changing the nature of the surfaces of titanium and its alloys using different surface engineering techniques and many studies have been done in this field [4−10]. Plasma surface alloying technique is one of the effective surface treatment techniques, which can be employed to fabricate surface alloying layers having metallurgical binding with the metallic substrates, and it has been successfully used to improve wear resistance, corrosion resistance, anti-oxidation performance, and antibacterial property of metal materials [11−15].

Transition metal nitrides have charming properties, such as high melting point, high hardness, chemical stability and corrosion resistance. Among them, zirconium nitride has attracted much attention in surface modification of the materials [16−18]. While for plasma surface alloying technique, seldom work is done in the formation and properties of zirconium nitride surface layers. The present work is concerned with the fabrication of Zr−N alloying layers on the surface of commercially pure titanium substrates by plasma surface alloying technique and the components, structure, and tribological properties of the Zr−N alloyed layers were studied.

2 Experimental

The Zr−N alloying layers were fabricated using plasma surface alloying technique. In the experiments, substrate samples were made of commercially pure titanium with 99.9% purity and were polished to a roughness of about 0.1 μm before surface treatment. The sputtering target was zirconium with 99.9% purity. The pure titanium samples were cleaned by argon ion bombardment prior to surface alloying. Argon gas and Ar−N_2 mixture gas were controlled using mass flow controllers. The chamber pressure was kept at 40 Pa, the distance between the sputtering target and substrate

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sample was 18 mm, the substrate temperature was 960 °C, and the processing time was 3 h. The target voltage was controlled at −760 to −820 V, the substrate voltage was −450 to −500 V, and the flux mixing ratio of Ar to N_2 was 1:1.

The microstructure and the wear scars of the samples were examined with NEOPHOT 21 optical microscope. To observe the microstructure, cross-sectioned samples were polished to a roughness of R_a<0.1 μm, and etched in a HF−HNO_3−H_2O etching solution. The surface roughness of the samples was measured using a TR240 surface roughness meter. Element distribution of the surface alloying layers was analyzed using Spectro GDA750 discharge optical emission spectrometer. Phases formed in the surface alloying layers were analyzed using D/Max 2500 X-ray diffractometer with Cu K_α radiation. Microhardness across the cross sections of the sample and the surface hardness of the sample were investigated by a Knoop indenter under a load of 0.1 N for 10 s holding.

The tribological tests were performed on a WM−2004 ball-on-disk tribometer. The counter body was Al_2O_3 ceramic ball with a diameter of 4.8 mm, a hardness of HV2000, and a surface roughness of 0.20 μm. The tests were performed at a sliding speed of 150 r/min and a normal force for 5 N. The diameter of the sliding track was 12 mm. The tests were performed at atmospheric pressure with an ambient temperature (25±2) °C and a relative humidity of (60±5)%. The tracks of the wear scars were measured using white light interference.

3 Results and discussion

3.1 Structure and mechanical properties of Zr−N surface alloying layers

The surface roughness of Zr−N surface alloyed samples is about 0.9 μm which is larger than that of the untreated pure titanium sample. The micrograph of the cross-section of Zr−N surface alloyed pure titanium sample is shown in Fig. 1. A homogeneous and compact surface alloying layer is formed on the pure titanium substrate.

The distribution of the major elements and the typical X-ray diffraction pattern of Zr–N surface alloying layer are shown in Figs. 2 and 3, respectively. In the outer layer of the surface alloying layer the content of Zr is much higher than N content, while the contrary case happens in the inner layer. For instance, on the outmost surface of the surface alloying layer, Zr and N contents are about 24.9% and 2.7%, respectively. At the depth of 10 μm, they are about 0.8% and 5.7%, respectively. The phases in the out surface layer of the sample after Zr−N surface alloying include Zr_3N_4, Ti_4N_3, Ti_2N and

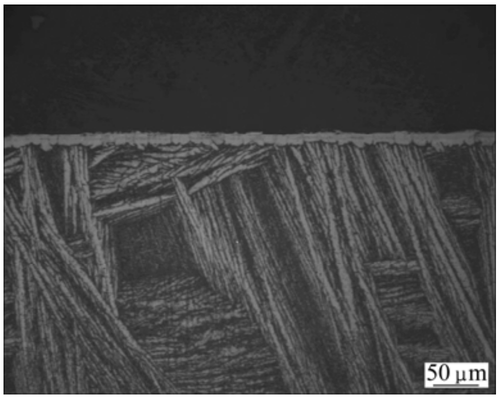

Fig. 1 Optical micrograph of cross-section of Zr−N surface alloyed pure titanium sample

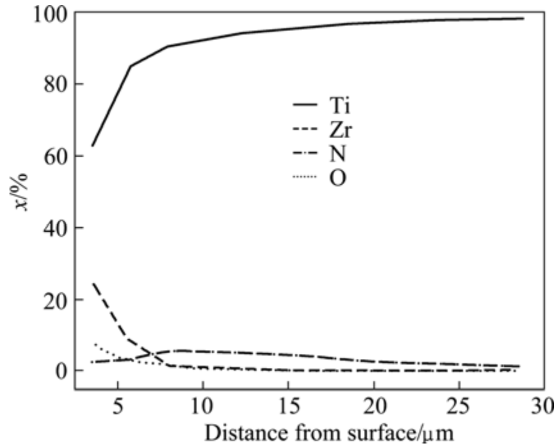

Fig. 2 Element distribution of Zr−N surface alloyed pure titanium sample

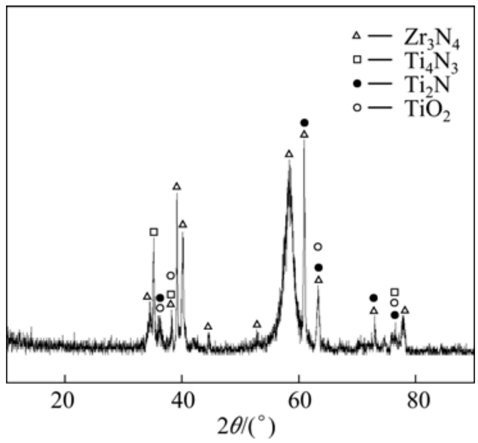

Fig. 3 XRD pattern of Zr−N surface alloying layer

TiO_2. The formation of a small quantity of TiO_2 is because oxygen also exists in the surface alloying layer induced by the gas pollution in the process of Zr−N surface alloying. Combining the analytical results of Figs. 2 and 3, the Zr−N surface alloying layer is composed of the outer compound layer and the inner diffusing layer. In the diffusing layer, interstitial N atoms and institutional Zr atoms are in pure titanium substrate and N content is much higher than Zr content mainly due to the diffusion rate of N with a smaller atomic size across the surface compound layer.

Microhardness distribution with the depth of Zr−N surface alloying layer is shown in Fig. 4. From surface to about 40 μm in depth, the hardness decreases drastically, and then decreases slowly and approximately linearly with the increase of the depth. The surface hardness of HK 1870 is obtained for Zr−N surface modified sample, which is much higher than that of pure titanium substrate. Apparently, the Zr−N surface alloying layer significantly enhances the surface hardness of pure titanium substrate. The very high hardness at the subsurface is due to the formation of the nitrides. The hardness decreases through the diffusion zone to approach the base microhardness of the substrate.

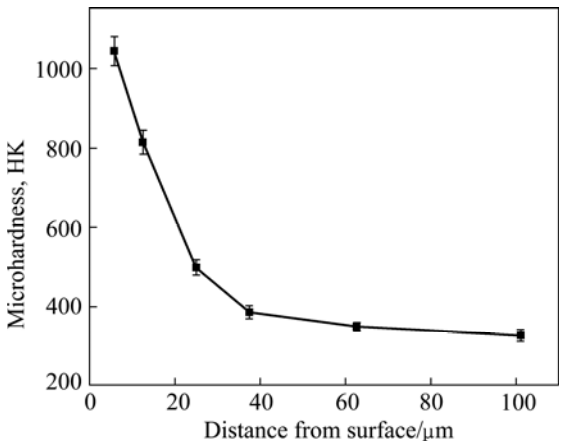

Fig. 4 Microhardness vs distance from surface of Zr−N surface alloying layer

3.2 Tribological properties of Zr−N surface alloying layers

The wear experiments were carried out both to untreated and Zr−N surface alloyed pure titanium samples. The curves of the friction coefficient vs sliding distance of the samples are shown in Fig. 5. The two curves can be characterized by the initial transient state followed by a relatively steady state. At the steady state, the friction coefficient of Zr−N surface alloyed sample is much more unstable than that of the untreated pure titanium sample. The friction coefficients changed around 0.45 and 0.52 for untreated and Zr−N surface alloyed pure titanium samples, respectively. The Zr−N surface alloyed pure titanium did not show friction-reducing effect. The increase of the surface roughness after Zr−N surface alloying treatment is a key factor to the increase of the friction coefficient.

The wear scars of untreated and Zr−N surface alloyed pure titanium samples after sliding for 100 m are shown in Fig. 6 (For untreated sample, only a part of the wear scar is shown). The widths of the wear tracks of untreated and surface alloyed pure titanium samples are 1541.2 μm and 542.6 μm, respectively. A much narrower and shallower track is shown for the surface alloyed pure titanium sample which shows the improved wear resistance property compared with the pure titanium sample. Table 1 lists the wear volume and wear rate of the untreated and Zr−N surface alloyed pure titanium samples. The wear rate of the Zr−N surface alloyed pure titanium is about 1/13 of that for untreated pure titanium.

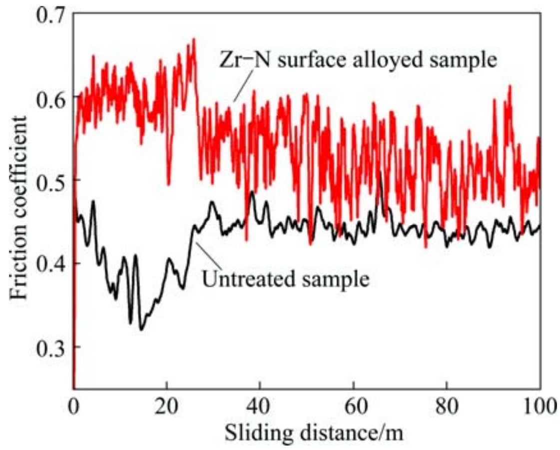

Fig. 5 Friction coefficient vs sliding distance of Zr−N surface alloyed and untreated pure titanium samples

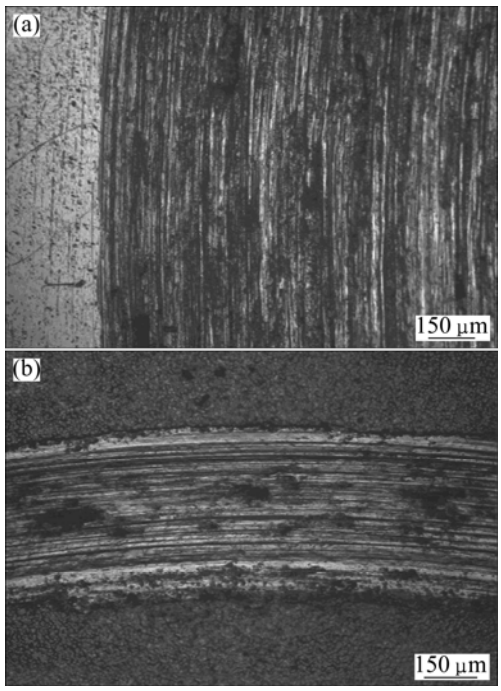

Fig. 6 Wear scars of untreated sample (a) and Zr−N surface alloyed sample (b)

The structure and hardness of the Zr−N surface modification layer play an important role in the wear behavior of Zr−N surface modified pure titanium. As shown in section 3.1, the surface hardness of Zr−N surface modified pure titanium is HK1870, which is much higher than that of the pure titanium substrate. Moreover, by plasma surface alloying technique, the Zr−N surface alloying layer is composed of the outer hard nitride layer and the inner diffusing layer. The diffusing layer results in the gradient distribution of components along the depth from the surface to the substrate and the interface between the Zr−N surface layer and the substrate disappears. So the stress can be greatly relaxed and the adhesion is highly improved. The hardness of the Zr−N surface alloying layer also displays gradient distribution which can greatly improve the load-bearing capacity of the pure titanium substrate. The improvement of wear resistance of the Zr−N surface alloyed pure titanium is believed to be contributed to the gradient structure and hardness characteristics of the Zr−N surface alloying layer.

Table 1 Wear volume and wear rate of untreated and Zr−N surface alloyed pure titanium samples

Material	Wear volume/ mm^3	Wear rate/ $(mm^3 \cdot N^{-1} \cdot m^{-1})$
Untreated sample	4.728	9.46×10^{-3}
Zr-N surface alloyed sample	0.353	7.06×10^{-4}

4 Conclusions

1) A uniform and compact Zr−N surface alloying layer can be formed on pure titanium substrates by plasma surface alloying technique. The Zr−N surface alloying layer consists of an outer nitride layer and an inner diffusion zone.

2) Zr−N surface alloying layer enhances the surface hardness of pure titanium substrate greatly. The diffusing layer results in the gradient distribution of hardness in Zr−N surface alloying layer which improves the load-bearing capacity of the pure titanium substrate. With Al_2O_3 sliding ball the friction coefficient of Zr−N surface alloying layer is around 0.52 at the steady state which does not show the friction-reducing effect. However, the Zr–N surface alloying layer improves the wear resistance of pure titanium substrate obviously.

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纯钛表面 Zr−N 等离子合金化

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摘 要：为了改善纯钛的表面性能，利用等离子表面合金化技术在纯钛表面形成 Zr−N 改性层。对 Zr−N 改性层的微结构、成分及硬度进行测试，并对改性层形成及表面硬度提高的机理进行分析。利用球−盘磨损试验对表面改性纯钛的摩擦学性能进行研究。结果表明，在纯钛表面形成了均匀致密的 Zr−N 改性层，改性层由表面 Zr−N 化合物层和基体内 Zr、N 的扩散层构成。Zr−N 表面改性层显著提高了纯钛的表面硬度，表层的最高硬度约为 HK1040。Zr−N 表面改性层没有减摩效果，但明显改善了纯钛的磨损性能。

关键词：纯钛；等离子表面合金化；Zr−N 表面合金层；硬度；摩擦学性能

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