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ARTICLE

Microstructure and Wear Resistance of Intermittent Vacuum Gas Nitriding Layer on TB8 Titanium Alloy

Yang Chuang, Ma Yaqin, Liu Jing

Guizhou Normal University, Guiyang 550025, China

Abstract: The intermittent vacuum gas nitriding (IVGN) process was introduced to improve the wear resistance of TB8 titanium alloy. The phase constitution and microstructure of the surface-modified layer were measured by XRD and SEM, and the surface hardness and wear resistance of the treated samples were analyzed. The results indicate that the surface-modified layer composed of TiN, $TiN_{0.3}$, Ti_2AlN and α-Ti is formed after IVPN treatment at 800 °C for 4 h. The microstructure of modified layer is dense and has good bonding with its substrate. The surface HV hardness of the treated samples can reach up to 8.5~9.0 GPa, which is three times as much as that of the untreated samples. The thickness of the hardened layer is 100~120 μm. The wear resistance is greatly improved due to the formation of a thick hardened layer.

Key words: TB8 titanium alloy; intermittent vacuum; gas nitriding; microstructure; wear resistance

TB8 titanium alloy is a new type of metastable β titanium alloy developed in China. Its corrosion resistance and antioxidant activity are greatly improved due to an increased Mo-content. Compared with other titanium alloys, TB8 titanium alloy has higher strength above 1300 MPa. Owing to its high specific strength, low elastic modulus, and excellent cold formability, TB8 titanium alloy is an ideal structural material in the aeronautical and astronautical fields. However, like other titanium alloys, TB8 titanium alloys also have low surface hardness and poor wear resistance, all of which will lead to a low service life and restrict their applications in engineering fields.

Titanium nitrides possess excellent properties including high hardness, a low friction coefficient, good chemical stability, excellent biological compatibility, and high electrical conductivity[1-3]. The preparation of a titanium nitride modified layer on the titanium alloy surface is an effective way to improve its surface hardness and wear resistance. The preparation of titanium nitrides layer may be achieved by many methods including plasma nitriding[4,5], laser gas nitriding[6,7], and gas nitriding[8,9]. These methods have succeeded in improving surface hardness and wear resistance, but problems persist. Plasma nitriding has a high manufacturing cost, a complex operation process and depends on the geometry of the materials, so complex-shaped parts cannot be processed[10]. Laser nitriding induces significant thermal stress which often leads to the formation of cracks and pores, which results in surface roughness. However, traditional gas nitriding has many advantages, such as being a simple, low cost process which results in a high matrix bond strength and no sample geometric requirements. Li et al[11] improved the surface hardness and corrosion resistance of commercial pure titanium using gas nitriding, and they obtained a nitride layer of 8 μm on the surface of the pure titanium after nitriding at 850 °C for 16 h. Titanium has a strong affinity with nitrogen and titanium nitrides have high stability. When traditional gas nitriding is used for titanium alloys, the nitrogen is difficult to diffuse to the inner matrix resulting in the nitride layer that is formed by traditional gas nitriding being thin and a long treatment time.

The surface activity of the samples can be increased greatly under vacuum conditions, which helps to promote the absorption and diffusion of the surface nitrogen atoms. This was shown in our previous studies where the surface hardness

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Corresponding author: Yang Chuang, Ph. D., Professor, School of Materials and Architecture Engineering, Guizhou Normal University, Guiyang 550025, P. R. China, Tel: 0086-851-83227436, E-mail: 276905017@qq.co.com

and wear resistance of TC4 titanium alloy improved greatly using vacuum nitriding with a short processing time[12]. In the present study, the modified layer with a continuous hardness gradient was formed on the surface of TB8 titanium alloy by intermittent vacuum gas nitriding (IVGN). By applying this method, it is expected that the high hardness and wear resistance of TB8 titanium will be quickly improved. The microstructure and mechanical properties of nitrided samples are further discussed.

1 Experiment

In this study, the sample for applying the IVGN process was TB8 titanium alloy with a surface HV hardness of 2.8~3.0 GPa. The chemical composition of TB8 alloy is given in Table 1.

TB8 titanium samples (Φ15 mm×10 mm) were prepared by wire cutting. Before IVGN treatment, the samples were mechanically ground using metallographic sandpaper and polished to a smooth surface. Then all samples were cleaned with an ultrasonic cleaner in acetone for 10 min, rinsed in distilled water, and air dried.

The IVGN process was implemented using a SKGLG tube furnace. The nitriding treatment process is shown in Fig.1. High purity nitrogen (99.99%) was used as a reactive gas and the following IVGN process was applied. The samples were placed into a tube furnace and the vacuum degree was reduced to 5~10 Pa by opening the vacuum pump. The samples were heated to 800 °C at a rate of 10 °C/min and were maintained at this temperature for 1 h. In this way, any oxide film existing on the titanium surface was removed due to oxygen diffusion which occurs under vacuum conditions and which helps the effective absorption of nitrogen atoms on the surface during the subsequent nitriding process. After maintaining the vacuum degree of 5~10 Pa at 800 °C for 1 h, the pressure in the tube furnace was increased to 0.015 MPa by inserting high purity nitrogen and maintaining this pressure during the nitriding process for 15 min. At the end of the nitriding process, the vacuum degree was again adjusted to 5~10 Pa by opening the vacuum pump and the subsequent diffusion process maintained for 15 min. After this diffusion process, the nitrogen pressure was increased to 0.015 MPa by re-injection of high purity nitrogen. This nitriding process was repeated using the IVGN process for 4 h. Finally, the nitriding samples were cooled to room temperature with a vacuum pressure of 5~10 Pa.

Table 1 Chemical composition of TB8 titanium alloy (wt%)

Mo	Al	Nb	Fe	Si	O	Ti
15.32	3.23	2.86	0.03	0.015	0.13	Bal.

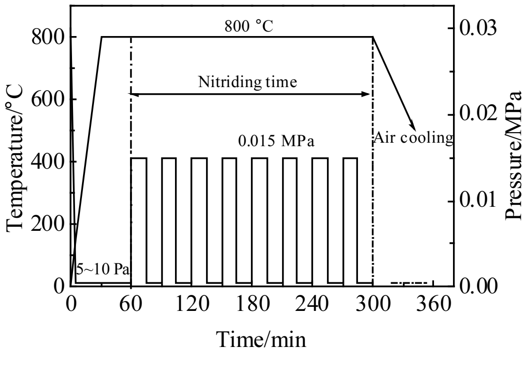

Fig.1 Schematic diagram of the IVGN process for TB8 titanium alloy

After the IVGN treatment, the phase constituents on the surface of the untreated and nitrided samples were examined by X-ray diffraction (PHILIPS PW1800) using Cu-Kα radiation from an angle of 20° to 80° (2θ). The morphology and element distribution were analyzed by SEM (JSM-6490LV) with an energy spectrum analysis X-ray(EDS) (INCA-350X). The hardness of the cross-section nitriding layer was measured under 0.98 N load for 15 s by a micro Vickers hardness tester (MHV-2000). The wear resistance was studied by a pin-on-disk wear tester (MM-U10A). The GCr15 steel bearing with a diameter of 40 mm was used as a counter friction disk material. The friction coefficients were measured under a rotational speed of 200 r/min and a load of 100 N for 30 min and the frictional behaviors were then investigated through the wear surface morphology of the samples.

2 Results and Discussion

2.1 Phase constituents

Fig.2 shows the XRD patterns of the untreated and IVGN samples. It can be seen that α-Ti(N) is the major phase of the untreated sample. After IVGN treatment at 800 °C for 4 h, the diffraction peaks of α-Ti(N) are obviously weakened, and TiN, $TiN_{0.3}$, and Ti_2AlN are formed on the surface of the IVGN sample. Lee et al[13] reported that titanium has a strong affinity with nitrogen as a priority phase and TiN will be first formed on the surface of the titanium alloy during gas nitriding. Due to the formation of a large amount of TiN, the interface

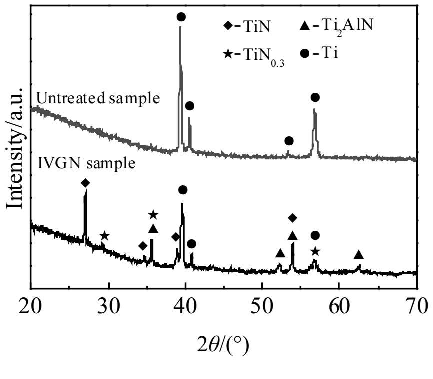

Fig.2 XRD patterns of the untreated and IVGN sample

between the nitrides film layer and the substrate becomes titanium-poor, which will lead to a corresponding increase of aluminum and appearance of an aluminum-rich region[5,14]. In order to dissolve the accumulating aluminum when the aluminum content reaches the specified values, the Ti-Al intermetallic compound formed on the subsurface further reacts with nitrogen to form a Ti_2AlN compound[15,16].

2.2 Microstructure

The surface morphology of the IVGN sample is shown in Fig.3a. As can be seen, the TB8 titanium alloy sample nitrided at 800 °C has a smooth surface covered with a large number of tiny nitride particles with diameters of 1~3 μm (see inset in Fig.3). Furthermore, it can be seen that the nitrided surface is very compact and has no defects. Fig.3b shows the EDS result of marked area of the nitrided samples. After the IVGN treatment, the surface is composed mainly of N and Ti elements. Aside from this there are also small amounts of Mo and Al. The N content on the surface is only 25.71%, which proves that a certain amount of nitrogen diffused into the matrix and dissolved into the Ti alloy to form the Ti(N)[17]. For the IVGN process, intermittent vacuuming is used during the diffusion process and the surface nitrides will not form and the N atoms diffuse to the inner substrate. This results in the slowing of the formation rate of surface nitrides and the degree of stress concentration in the nitrides layer is greatly reduced. Therefore, a large number of tiny nitride particles are formed which results in the smooth and compact surface.

Fig.4a shows the cross-section morphology of TB8 titanium alloy samples nitrided at 800 °C for 4 h. It can be seen that a continuous and dense layer is formed on the surface of the nitrided sample. The layer is smooth and exhibits good subsurface combination. This confirms the previous X-ray diffraction analysis, that is, the dense surface layer is a compound layer, which is mainly composed of TiN, $TiN_{0.3}$ and Ti_2AlN, and is about 40 μm thick. Adjacent to the nitride layer, there is a relatively wide zone where appears to have a different microstructure compared to the substrate. As a consequence of solid solution of nitrogen in titanium, this wide zone is known as the nitrogen diffusion zone and is about 90 μm thick[11,18]. When using the IVGN process, other gases and adhesion molecules usually adsorbed onto the surface of samples are discharged out of the furnace, which prevents the formation of the surface gas adsorption layer. The surface activity of samples is greatly improved. Additionally, the reaction gas is constantly replaced and a constant flow maintained by intermittent vacuuming which will significantly increase the number of active nitrogen atoms. Therefore, the nitriding process can be accelerated by IVGN treatment, as well as increasing the density of the nitride layer and depth of the nitrogen diffusion zone on the surface of TB8 titanium alloy at lower temperatures and in a shorter time.

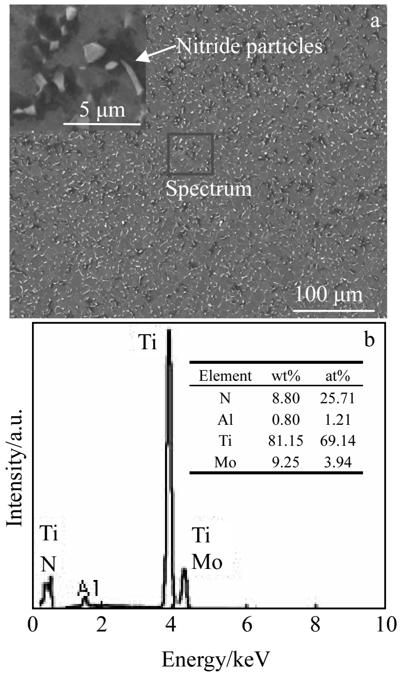

Fig.3 Surface morphology (a) and EDS result of marked area (b) of the IVGN sample

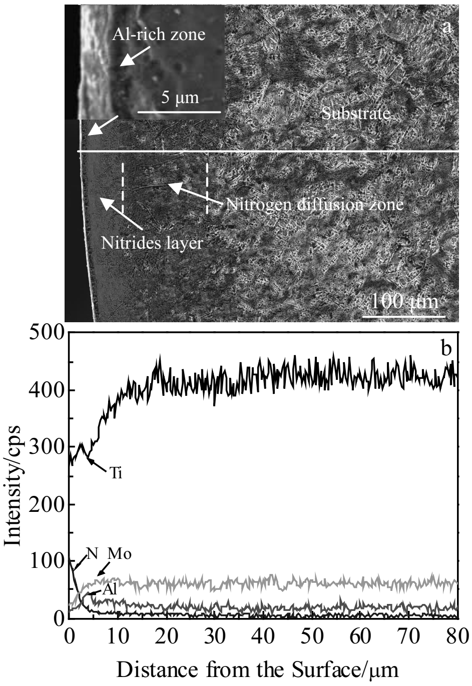

Fig.4 Cross-sectional morphology (a) and EDS linear scanning along baseline (b) of nitrided layer

An Al-rich zone with thickness of 3~5 μm is found in the outmost surface of the nitrides layer (seen inset in Fig.4). According to the X-ray diffraction analysis above, the main reason for this is that a large amount of TiN first form on the surface during gas nitriding, which will reduce the content of titanium at the interface between the nitrides film layer and the substrate. As a consequence of the reduction of titanium, aluminum will increase correspondingly and the subsurface of TiN will become aluminum-rich. To confirm the results of the previous XRD analysis, the cross sections element profile of the nitrided layer are investigated further. As shown in Fig.4b, a maximum peak in the concentration profile of Al atoms on the subsurface of nitrided layer is found, which indicates that segregation of Al elements occurs, thus becoming aluminum-rich. Additionally, the distribution curve of the Ti element exhibits titanium-poor and a distinct change in the N concentration profile exists at the Al peak position.

2.3 Microhardness

Fig.5 shows the cross-sectional hardness indentation and distribution profile of the IVGN sample. The change in hardness can be determined from the size of the indentation. The indentation of the nitrided layer is obviously smaller than that of the substrate. The size of the indentation increases gradually along the depth of the nitrided layer from the surface to the substrate. These changes in the indentation indicate that the surface hardness is greatly improved after IVGN treatment. The surface HV hardness of the modification layer can reach up to 8.5~9.0 GPa when it is nitrided at 800 °C for 4 h, which is about 3 times higher than that of the substrate. The thickness of the hardened layer, which is defined as the vertical distance from the surface of nitriding layer to the core with hardness of 5.0 GPa[10,19], is 100~120 μm.

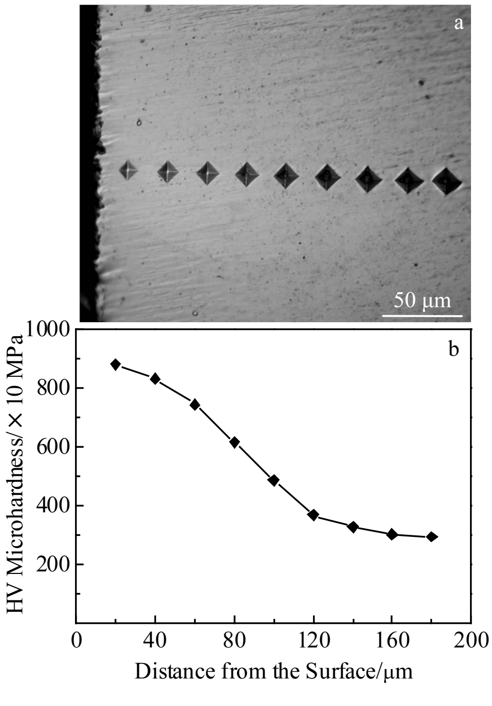

Fig.5 Hardness indentation (a) and distribution profile (b) of the nitrided sample

The hardness of the modified layer is mainly related to the type, thickness and density of the compounds formed on the surface. Using IVGN treatment results in a modified layer, and a high surface hardness can be achieved due to the formation of a thick and dense nitrides layer. Furthermore, the hardness decreases slowly from the surface to the core and exhibits the characteristics of continuous gradient change.

2.4 Wear resistance

Fig.6 shows the changes in the surface friction coefficients of the untreated and IVGN samples. The untreated sample presents a higher friction coefficient during the early stages of abrasion and the maximum friction coefficient can reach 0.46. The frictional contact interface between the untreated samples and the counter face material will increase gradually with time, until the friction coefficient begins to decrease before stabilizing. The average friction coefficient of the untreated sample is 0.34 in the stable stage. In the case of the IVGN process, a low friction coefficient of 0.024~0.038 is maintained for up to about 25 min. After 25 min, the friction coefficient begins to increase rapidly to more than 0.15. Because titanium nitrides possess a low friction coefficient and high hardness, the friction coefficient of the IVGN samples is maintained at a lower level for a longer time. When the nitrides are separated from the base material, the friction coefficient increases suddenly.

To further verify the wear characteristics, the wear surface morphology of the untreated and IVGN samples are shown in Fig.7. For the untreated sample, the wear surface has local plastic deformation and adhesive tearing marks. A large number of deep and wide grooves are formed on the surface along the frictional sliding direction (Fig.7a). Titanium belongs to the highly active metal elements, has low thermal conductivity, its surface is easily torn by friction, and it has poor adhesive wear resistance. Due to low surface hardness, titanium alloy samples are easily impacted by micro-protrusion of the counter friction disk material which generates grooves, showing that titanium alloys have poor abrasive wear resistance. As

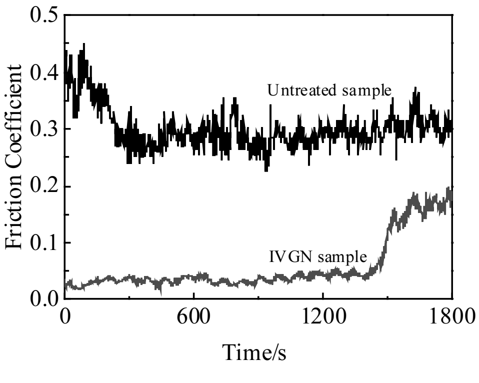

Fig.6 Surface friction coefficient of the untreated and IVGN samples

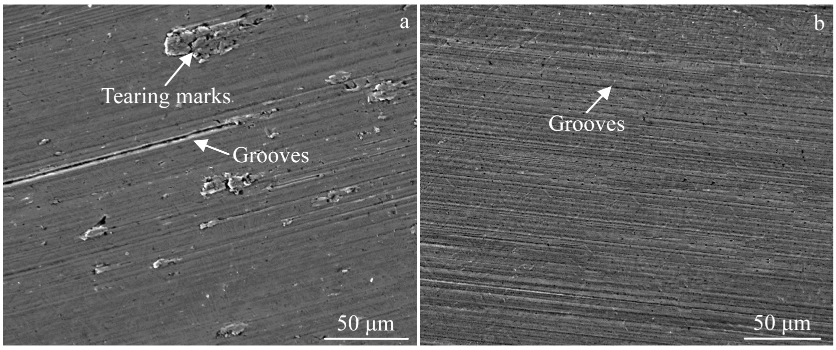

Fig.7 Wear surface morphology of TB8 titanium alloy: (a) untreated sample and (b) IVGN sample

shown in Fig.7b, the grooves formed on the surface of the IVGN sample are relatively narrow and the adhesive tearing phenomenon is not seen on the surface of the sample, that is, the surface is not damaged and appears to have a high wear resistance. After IVGN treatment at 800 °C for 4 h, a hardened layer with the thickness of 100~120 μm is formed with a dense nitride layer and a good bonding strength with the substrate. The surface HV hardness is greatly improved and reaches 8.5~9.0 GPa. Additionally, due to the formation of a wider nitrogen diffusion zone and a thick hardened layer, the wear resistance of the IVGN samples is greatly improved.

3 Conclusions

1) Due to the diffusing of nitrogen into the substrate, the dense nitride layer and thick nitrogen diffusion zone are formed on the surface of TB8 titanium alloy by the IVGN process.

2) TiN, $TiN_{0.3}$, and Ti_2AlN are the major phases of the nitrided surface after the IVGN treatment at 800 °C for 4 h.

3) The surface HV hardness of the IVGN sample can reach up to 8.5~9.0 GPa, which is nearly three times as much as that of the substrate hardness.

4) The thickness of the hardened nitriding layer is 100~120 μm. The wear resistance is greatly improved, which is attributed to the formation of the thick hardened layer, having good bond strength with the substrate, and high surface hardness.

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TB8 钛合金间歇式真空气体渗氮层的组织与耐磨性

杨 闯，马亚芹，刘 静

(贵州师范大学，贵州 贵阳 550025)

摘 要：为了提高耐磨性，对 TB8 钛合金进行间歇式真空气体渗氮处理。利用 XRD 和 SEM 分析了改性层的物相组成和显微组织，并对改性层的表面硬度和耐磨性进行了研究。结果表明，TB8 钛合金经 800 ℃间歇式真空气体渗氮 4 h 后，表面改性层物相主要由 TiN、$TiN_{0.3}$、Ti_2AlN 及 α-Ti 组成，渗氮层组织致密，与基体结合良好，表面 HV 硬度为 8.50~9.0 GPa，是基体硬度的 3 倍，硬化层厚度为 100~120 μm。由于表面形成的硬化层较深，故耐磨性得到了极大改善。

关键词：TB8 钛合金；间歇真空；气体渗氮；组织；耐磨性

作者简介：杨 闯，男，1976 年生，博士，教授，贵州师范大学材料与建筑工程学院，贵州 贵阳 550025，电话：0851-84351718，E-mail: 276905017@qq.com