

Microstructure and Tribological Properties of Plasma Nitrided Biomedical CoCrMo Alloys

Xu Lin, Ba Dechun, Wang Qing, Lin Zeng

Northeastern University, Shenyang 110819, China

Abstract: Medical forged CoCrMo alloy was treated by DC plasma nitriding process to alter its surface characteristics and to improve mechanical and tribological properties. The phase composition, microstructures, surface microhardness, and wettability were characterized by X-ray diffraction, scanning electron microscope, micro-hardness tester, and optical dynamic/static contact angle meter. Friction and wear characteristics were investigated on ball-on-disc tribotester under dry sliding conditions. The experimental analysis confirms that the plasma nitriding process is promising in producing thicker, harder, highly hydrophilic and more wear resistance layers on CoCrMo alloy for biomedical applications. At lower nitriding temperatures and for shorter time, the nitrided layer structure is composed of σ -CoCr and CrN phases. At higher nitriding temperatures and for longer time, σ -CoCr and CrN as well as Cr₂N phases appear in nitrided specimens. With the increasing of nitriding temperatures and time, case depth thickness, surface roughness, microhardness and wear resistance increase while water contact angle decreases and becomes highly hydrophilic. Compared with untreated CoCrMo alloy, all nitrided specimens show an important reduction in wear rate and wear scar width, and the nitrided specimen at 800 °C/8 h exhibits the lowest wear rate and the best dry-sliding wear resistance.

Key words: medical grade forged CoCrMo alloy; high-voltage DC plasma nitriding; microhardness; wetting property; tribological property

As one of the most important cobalt-based alloys, cobalt-chromium-molybdenum (CoCrMo) alloy is frequently used not only in aero- and land-based gas turbines technologies for such applications as load bearings, valves, valve seats and bushings sleeves but also in biomedical practices ranging from hip and knee joint replacements, fracture fixation devices to intravascular implants. CoCrMo alloy is featured by perfect mechanical properties such as fatigue strength, tensile strength, superior wear resistance and high corrosion resistance as well as favorable biocompatibility^[1-6]. Owing to its excellent properties, CoCrMo alloy is widely used in metallic orthopedic medical implants.

CoCrMo alloy commonly used in medical fields can be divided into forged CoCrMo alloy and cast CoCrMo alloy. The cast CoCrMo alloy formerly was preferred to be applied to the orthopedic medical implant manufacturing because of

its relatively low cost, high efficiency, ease of fabrication and great treatment capacity. Nevertheless, cast CoCrMo alloy may have some casting defects like gas bubble, hole, coarse grain, dendritic structure, which results in lower tensile yield strength and weaker corrosion resistance than that of forged CoCrMo alloy^[7,8]. Wang et al.^[3] investigated the mechanical and tribological properties of medical grade forged and cast CoCrMo alloy, and found that forged alloy exhibited better properties in higher load environments. Therefore, forged CoCrMo alloy is widely used in manufacturing hip and knee joint implants in recent years. In spite of excellent properties of forged CoCrMo alloy, there is still a concern about wear debris and potential harmful ions generated in the process of mechanical wear and fretting corrosion. These toxic ions such as Co, Cr and Ni ions and abrasive dusts may produce anaphylactic reaction, prosthetic loosening and bone resorption, and even induce cancer^[9]. Due to the wear and

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Corresponding author: Ba Dechun, Ph. D., Professor, School of Mechanical Engineering and Automation, Northeastern University, Shenyang 110819, P. R. China, Tel: 0086-24-83680450, E-mail: lisalunwen@163.com

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corrosion resistance occurring on the surface of CoCrMo alloy, surface treatments can be beneficial to compensate the defects and to improve comprehensive properties.

Surface treatments used in CoCrMo alloy are various, and commonly include ion implantation, plasma nitriding or carburising, plasma surface alloying etc. Because of the formation of hard nitride or carbide precipitates, the wear resistance as well as corrosion resistance of CoCrMo alloy is improved and the release of potential toxicity of Co, Cr and Ni ions declines^[10-12]. Nevertheless, owing to the depth limitation of surface modification layer, the treated CoCrMo alloy is difficult to meet the needs of joint prosthesis. Since plasma assisted thermo chemical surface treatments improve wear, corrosion resistance and fatigue strength, the plasma nitriding or carburizing of forged CoCrMo alloy may be beneficial. But no much study about the plasma nitriding of CoCrMo alloy is reported^[13-15].

In the present study, the high voltage DC plasma nitriding process has been selected as a surface treatment technique for medical forged CoCrMo alloy. The aim of this study is to determine the nitriding behavior of a medical grade forged CoCrMo alloy in Ar-N₂ gas mixture with various temperatures and time periods. The structural and compositional characterization of the plasma nitriding layers was investigated by XRD and SEM, respectively. The hardness and surface wettability as well as tribological properties are investigated by microhardness tester, optical dynamic/static contact angle meter and ball-on-disc testing machine.

1 Experiment

Medical grade forged CoCrMo alloy (ISO 5832-12) used in the experiments with chemical composition (wt%) of 27.7Cr, 6Mo, 0.62Mn, 0.76Si, 0.12Ni, 0.1C and balance Co. The tensile strength, elastic modulus and elongation are 700 MPa, 230 GPa and 3.0%, respectively. The test samples with disc-like geometry were cut from cylindrical bars with diameter of 25 mm and thickness of 3 mm. Before plasma nitriding, all the test samples were cleaned with acetone to remove surface contaminations, ground by 320-2000 mesh emery paper, and then finally polished to mirror-like quality. The specimens were separately cleaned with alcohol and distilled water in ultrasonic cleaner for 10 min, and then dried with nitrogen gas.

The nitriding equipment used in this study was constituted of a quartz tube with a length of 1200 mm and a diameter of 80 mm, and can be evacuated to 1×10^{-4} Pa. It was surrounded by a resistance furnace of 500 mm in length to reach a maximum temperature of 1200 °C. The temperature measurement was monitored by a thermocouple located between the tube and the furnace. Prior to the plasma nitriding process, the specimens were subjected to cleaning by argon sputtering for 30 min under a voltage of 500 V and pressure of 200 Pa. Then, the plasma nitriding process was performed in

gas mixture of 70% N₂-30% Ar, with a constant pressure of 100 Pa and process temperatures of 500~800 °C and process time of 2~8 h. Treatments were conducted under working voltage of 600 V. The furnace temperature was increased at a rate of 15 °C/min to the setting temperature, and the specimens were furnace cooled in the working gas after the nitriding process. The detailed processing parameters are listed in Table 1.

XRD (PW3040/60, PANalytical B.V. Co., Nld) operated at 60 kV and 55 mA with CuK α 1 ($\lambda=0.15406$ nm) radiation was used to investigate the phase composition. The X-ray diffraction analysis was run in grazing incidence X-ray diffraction (GIXRD) between 30 ° and 70 °, with step interval 0.1 ° and incidence angle of 5 °. SEM (Ultra plus, Carl Zeiss Co., Germany) observation was done to characterize the surface morphologies and the modified diffusion layers thickness. The roughness of R_a was measured by a roughness tester (TR200, Time Group Co., China). The microhardness and wettability of nitrided layer were measured by microhardness tester (401MVD, Wolpert measuring equipment Co., USA) and optical dynamic/static contact angle meter (SL200, Kino USA industry Co., USA). The applied loads of microhardness test were between 0.98 and 4.9 N and the loading time was 10 s. Surface wettability was evaluated by the water contact angle and the amount of distilled water was 0.5 μ L. In view of the scatter of the microhardness and contact angle data, the microhardness and contact angle values were the average of at least four measurements at different points under the same condition.

The wear tests were conducted on a ball-on-disc tester (HT-500, LICP. CAS, China) at a constant load of 4.9 N under ambient environment conditions without a lubricant. During the whole experiment, a SiN ceramic ball with diameter in 3 mm was used to form wear tracks on the surface of the selected samples. The disc rotated at 168 r/min and a total number of 3000 s was set for each test. The wear rate can be calculated by a equation described in Ref. [3]. Wear scar width and worn regions after wear tests were examined using metallographic microscope (Axiovert 200 MAT, Carl Zeiss Co., Germany).

Table 1 Different nitriding processes of forged CoCrMo specimens

No.	Temperature/ °C	Voltage/ V	Time/ h	Case depth thickness/ μ m	Roughness, R_a/μ m
1	Untreated	0	0	0	0.05
2	500	600	4	6.5	0.13
3	600	600	4	7.5	0.15
4	700	600	4	10	0.21
5	800	600	4	11.2	0.27
6	800	600	2	9.2	0.22
7	800	600	6	14.7	0.31
8	800	600	8	17.1	0.34

2 Results and Discussion

2.1 XRD analysis

The XRD patterns of all specimens with different nitriding temperatures and time periods are presented in Fig.1 and Fig.2. The untreated specimen has two different crystal phases, mainly α -CoCr (some papers also known as γ) and ε -CoCr cobalt parent phases. The α -CoCr phase with face centered cubic crystal structure is a non-equilibrium phase transformation during cooling, while ε -CoCr phase with hexagonal closed packaged structure is an equilibrium phase and distributes as thin plates in CoCrMo alloy. The specimens used in this experiment show a higher ε phase content. Distinctive phases of the nitrided samples which are σ , CrN and Cr₂N, are largely determined by the nitriding parameters.

As can be seen in Fig.1, σ -CoCr forms at the nearly same angles where the ε -CoCr phase disappears after nitriding treatment. It can be obviously found that the nitrided specimen structure at 500 °C mainly consists of α -CoCr and σ -CoCr cobalt parent phases. When the treatment temperatures reaches 600 °C, the CrN phase forms at about 62.5°. As the temperature continues to rise, except for CrN, α -CoCr and σ -CoCr cobalt parent phases, a new peak of Cr₂N phase at 55° can be observed. Meanwhile, the effects of the nitriding time on specimens are shown in Fig.2. It is found that the diffraction peak intensity of CrN and Cr₂N increases with increasing the nitriding time at this temperature. Moreover, it should be noted that the amount of σ -CoCr phase increases significantly with the elevation of temperature. However, the amount of σ -CoCr phase at about 41° decreases with nitriding time at 800 °C and this phase almost disappears at reaction time of 6 h and above.

Çelik et al.^[6] observed that σ -CoCr phase disappeared in the samples nitrided at 800 °C. Nevertheless, the results obtained from Figs. 1 and 2 show that the plenty amounts of σ -CoCr at about 46.5° still can be detected in the nitriding layers at 800 °C. Meanwhile, the σ -CoCr phase of specimens used in this experiment completely disappears after the treatment temperature up to 900 °C in the subsequence experiments.

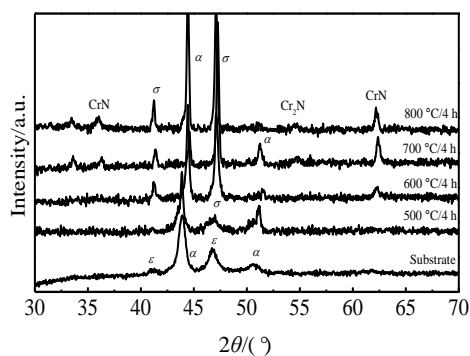


Fig.1 XRD patterns of untreated and nitrided forged CoCrMo alloys at 500, 600, 700 and 800 °C for 4 h

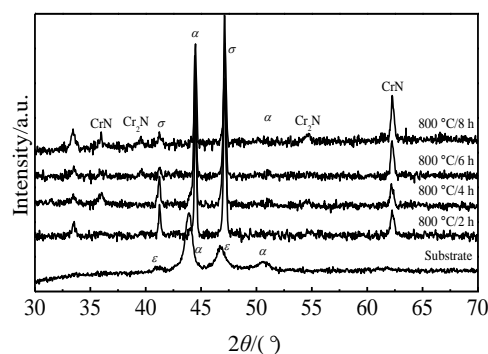


Fig.2 XRD patterns of untreated and nitrided forged CoCrMo alloys at 800 °C for 2, 4, 6 and 8 h

Since the σ -CoCr phase is a cobalt rich phase, the formation of this phase is related to the concentration of cobalt or Co/Cr ration. It has been observed that the intensities of CrN and Cr₂N phases evidently increase with the elevation of temperature and time, which result in decomposition of chromium from the σ -CoCr phase. Therefore, chromium atoms may bond with nitrogen atoms and form CrN and Cr₂N phases.

2.2 Microstructure analysis

The SEM micrographs of the unnitrided and plasma nitrided forged CoCrMo alloys with various temperatures and time periods are given in Fig.3. According to the pictures, the unnitrided specimen exhibits a relatively smooth and featureless surface while the specimen surface becomes rougher after nitriding treatment. From the surface roughness of all the specimens presented in Table 1, it is clearly seen that the surface roughness of the unnitrided sample is about 0.05 μ m and those of the nitrided samples are between 0.13 and 0.34 μ m. In addition to these, it has been also observed that the surface roughness increases with the elevation of temperature and time due to ion bombardment. As can be seen in Fig.3, the surfaces of nitrided specimens are covered by the compact particles with various sizes. As temperature and time increase, the small size particles are inclined to aggregate and form some larger size particles. Thus the surface roughness increases with the increasing of temperature and time.

The cross-sectional micrographs of plasma nitrided forged CoCrMo samples are shown in Fig.4. At lower nitriding temperature, a double layer structure forms on the nitrided surface. It is believed from XRD analysis that the upper layer is CrN layer and the one below is a nitrogen diffused layer. With the increase of the nitriding temperature and time, the possibility of CrN and Cr₂N formation increases and the nitrogen diffused layer decreases until dissolves. As shown in Table 1, it can be easily found that the thickness of the nitrided layer increases with the increasing of nitriding temperature and time, and the thickness shows approximately linear

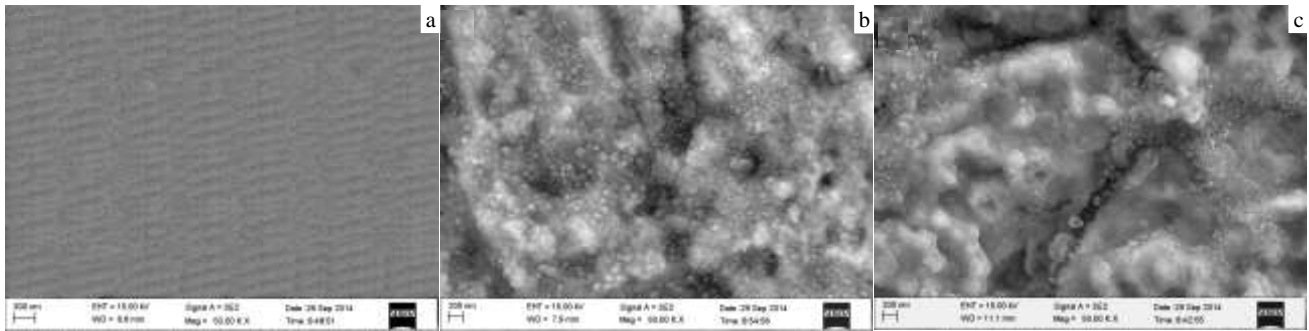


Fig.3 SEM images of untreated and nitrided surfaces for forged CoCrMo specimens: (a) untreated, (b) 700 °C/4 h, and (c) 800 °C/8 h

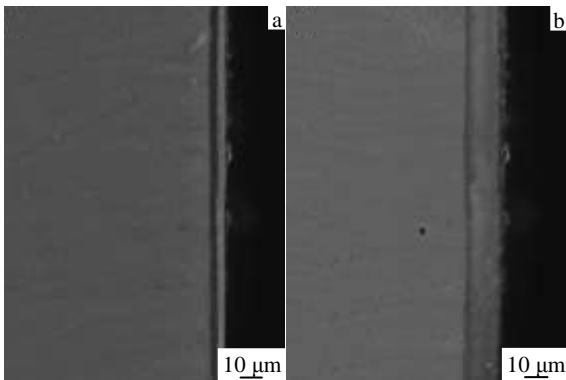


Fig.4 Cross-sectional micrographs of plasma nitrided forged CoCrMo samples: (a) 600 °C/4 h and (b) 800 °C/8 h

increase with process parameters. The thickness of nitrided samples has been measured from 6.5 μm to 17 μm and the maximum and minimum values are at 500 °C/4 h and at 800 °C/8 h, respectively. Due to the low diffusion rate of nitrogen atoms at low temperature, the forming of nitrided layers depends mainly on lattice expansion induced by nitrogen atoms taking interstitial places among cobalt parent structure. With the increasing of the treatment temperatures and time, the opportunity of forming CrN or Cr₂N layer increases because of faster diffusion rate or intensive movement of nitrogen atoms and the thickness of nitrided layer increases^[16].

2.3 Wettability

Surface wettability is an important factor to characterize material properties and it is usually measured by contact angle. The Young’s equation reveals that the wetting behavior is determined by the balance of forces at the contact line arising from the three interfacial tensions occurring at the solid-liquid, solid-vapor and liquid-vapor interface^[17]. Fig.5 shows the change of contact angles with nitriding temperature and time. It is observed that the contact angle decreases with the increasing of nitriding temperature and time and the surface wettability is inclined to hydrophilicity. For example, the contact angle is about 30 ° at 500 °C/4 h, and then the contact angle decreases to about 10 ° at 800 °C/8 h. The measurements

of contact angles mainly depend on the heterogeneity,

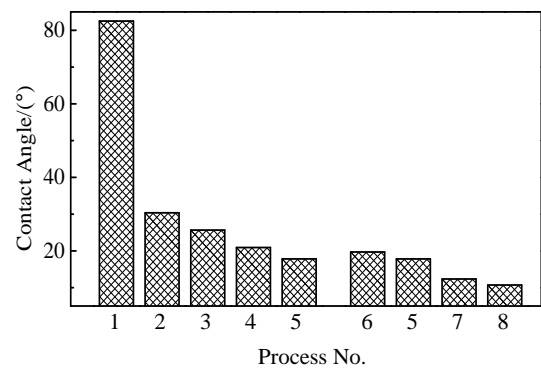


Fig.5 Contact angles of CoCrMo alloys nitrided at various process parameters

chemical composition and surface roughness. Wenzel’s equation properly predicts the effect of surface roughness on contact angle and it shows that the roughness may reduce the contact angle if the contact angle of untreated sample is lower than 90 °. Thus, it is not surprising to find that the specimen nitrided at 800 °C/8 h with the highest roughness has the lowest contact angle. Nevertheless, since the surface roughness difference among nitrided specimens is not so much, much difference could not be expected.

2.4 Microhardness

The variation of surface microhardness of unnitrided and nitrided CoCrMo specimens with different process parameters are shown in Fig.6. As shown in Figs.6a and 6b, the microhardness of all plasma nitrided specimens at different applied loads are improved after nitriding treatments, and the hardness values increase with the increase of temperatures and time. It should be noted that the hardness of the nitrided specimens at lower applied loads have larger fluctuation due to the smaller indentation depth and the larger errors. The specimen nitrided at 800 °C/8 h exhibits the highest microhardness measured as about HV_{0.2} 8.9 GPa, increasing more than two times than that of unnitrided specimen, while the hardness of substrate is measured as about HV 3.2 GPa. The improvement of the microhardness depends on the

thickness of case depths and the formation of σ -CoCr, CrN

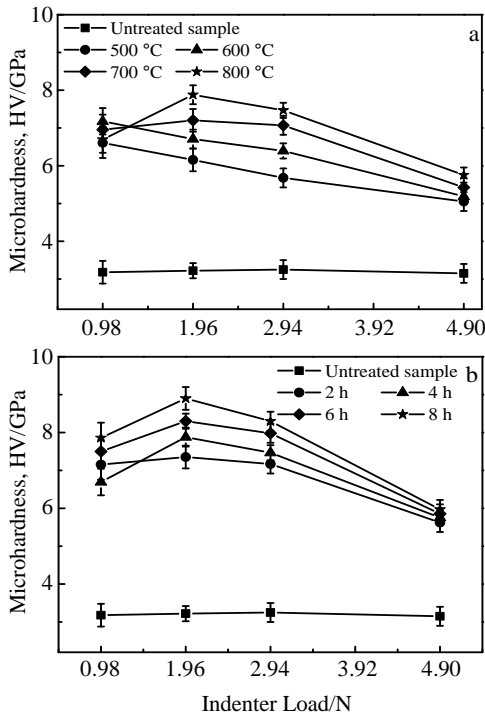


Fig.6 Surface microhardness of untreated and nitrided samples of forged CoCrMo alloys as a function of the applied load: (a) at 500, 600, 700, 800 °C for 4 h and (b) at 800 °C for 2, 4, 6, 8 h

and Cr₂N phases. The hardness of the σ -CoCr phase is similar to or even harder than that of quenched Fe-N (HV 8 GPa) and the hardness of CrN or Cr₂N phase is up to HV 20 GPa^[18,19]. At lower treatment temperature, the nitrided specimen structure mainly consists of σ -CoCr cobalt parent phase and the thickness of case depth is relatively small and the increasing range of hardness is lower. At higher treatment temperature, the hardness of nitrided samples exhibit an important increase due to the formation of CrN or Cr₂N phase and the thicker case depth. The strengthening of the surface may lead to the reduction of the surface wear in friction and wear.

2.5 Friction and wear

The wear rates and wear scar widths of all specimens are shown in Fig.7. Compared with the untreated specimen, the wear rates and wear scar widths of all nitrided specimens significantly drop, which show the better wear resistance in dry conditions. The wear rates and wear scar widths decline with the increase of nitrided temperatures and time. The nitrided specimen at 800 °C/8 h exhibits the lowest wear rate and wear scar width, and the wear resistance increases more than two times than that of the untreated specimen. The reasons for the improvement of wear resistance in nitrided specimens are related to the CrN and Cr₂N phases formed in the nitrided layer. The CrN and Cr₂N phases are the higher hardening phases and have better adhesion. As the nitriding temperature and time increase, intensity of CrN and Cr₂N phases, nitride layer

thickness and surface microhardness increase and the wear rate

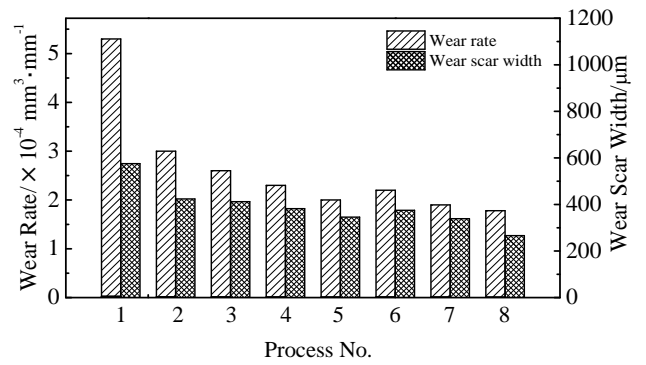


Fig.7 Wear rate and wear scar widths of untreated and nitrided samples of forged CoCrMo alloys

and wear scar width decrease. As can be seen in Table 1, the nitride layer thickness of the sample nitrided with lower temperature and shorter time is thinner and the SiN ceramic ball may easily contact to the substrate, which lead to the poor wear resistance. On the other hand, high hardness, enough thickness and good adhesion of the nitrided layer induced by higher temperature and longer time may effectively hinder the contact between the friction ball and substrate.

The wear tracks of the untreated and nitrided CoCrMo alloys under dry conditions are illustrated in Fig.8. In Fig.8a, a lot of abrasive debris and plowing grooves occur in the wear track of the untreated sample, and the scratching is wide and deep. Excessive adhesion and plastic deformation is evidently observed on the worn surface at the initial friction stage, which confirms that adhesive wear is the dominating wear mechanism of the untreated sample. The wear mechanisms are different for the untreated and the treated CoCrMo alloys during different

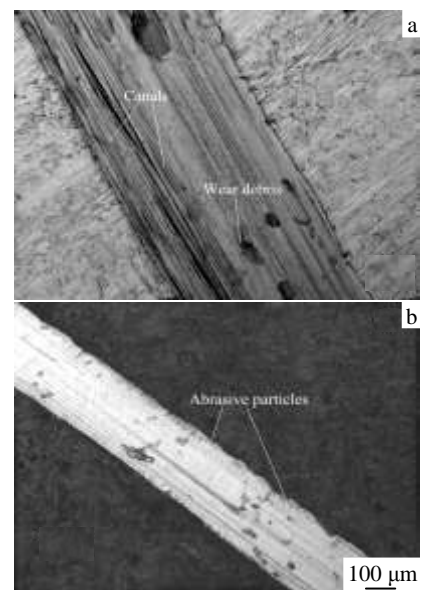


Fig.8 Micrographs of wear tracks on the forged CoCrMo alloys under

dry conditions: (a) untreated and (b) nitrided at 800 °C/4 h friction stages, and the adhesive wear may transform to abrasive wear if the nitrided layer breaks down and creates debris with the increase of friction time and sliding distance. Combined with Fig.7 and Fig.8, the widths of the wear tracks extensively decrease after the plasma nitriding treatments. In Fig.8b, shallowing scratching and less abrasive debris are observed on the worn surface of the specimen nitrided at 800 °C. The thick nitrided layer effectively prevents the ball to contact to the substrate and decreases the amount of plastic deformation. As a result, the main wear mechanisms for the nitrided specimens are fatigue wear, abrasive wear and slight adhesive wear.

3 Conclusions

1) At lower nitriding temperatures (below 700 °C) and for shorter time (close to 2 h), the nitrided layer structure is composed of σ -CoCr and CrN phases; at higher nitriding temperatures (above 700 °C) and for longer time (more than 2 h), σ -CoCr and CrN as well as Cr₂N phases appear in nitrided specimens.

2) With increasing of nitriding temperatures and time, case depth thickness, surface roughness, microhardness and wear resistance increase while water contact angle decreases and becomes highly hydrophilic.

3) Compared with untreated CoCrMo alloy, all CoCrMo alloys after plasma nitriding treatments have lower wear rates and narrow wear scar widths.

4) The wear mechanism for the untreated specimen is mainly adhesive wear while the nitrided specimens change the wear mechanism to fatigue wear, abrasive wear and slight adhesive wear because of breakage of nitrided layers.

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医用锻造 CoCrMo 合金等离子氮化微观结构及摩擦性能

徐 林, 巴德纯, 王 庆, 蔺 增

(东北大学, 辽宁 沈阳 110819)

摘 要: 采用高压直流等离子体氮化技术, 对医用锻造钴铬钼合金进行表面氮化处理, 考察了氮化温度及时间对钴铬钼合金摩擦性能及润湿性能的影响。运用 X 射线衍射仪及场发射扫描电镜分析氮化层物相组成及表面微观结构; 用显微硬度计和光学动/静态接触角仪测试合金表面显微硬度及接触角数值; 利用球-盘摩擦试验机在干摩擦条件下对氮化层的摩擦磨损性能进行测试。结果表明: 钴铬钼合金试样经直流等离子体氮化处理后, 氮化层厚度、表面粗糙度及显微硬度值显著增加, 亲水性能及耐磨损性能得到明显改善。在较低的氮化温度及较短的氮化时间内, 氮化试样物相主要由 σ -CoCr 相及 CrN 相组成; 随着氮化温度及时间的增加, 氮化试样物相中还检测到硬质化合物相 Cr₂N。与未处理试样相比, 氮化试样的磨损率及磨痕宽度减小, 氮化参数为 800 °C/8 h 时磨损率最低, 磨痕宽度最窄, 耐磨损性能最佳。

关键词: 医用锻造钴铬钼合金; 高压直流等离子体氮化; 显微硬度; 润湿性; 摩擦性能

作者简介: 徐 林, 女, 1985 年生, 博士, 东北大学机械工程与自动化学院, 辽宁 沈阳 110819, 电话: 024-83680450, E-mail:

