



Microstructure and Tribological Properties of Plasma Nitriding Cast CoCrMo Alloy

Qingliang Wang¹†, Chuanhui Huang² and Lei Zhang¹

1) School of Material Science and Engineering, China University of Mining & Technology, Xuzhou 221116, China

2) College of Electro-mechanical Engineering, Xuzhou Institute of Technology, Xuzhou 221008, China

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A medical cast CoCrMo alloy was coated by plasma nitriding process to enhance the wear resistance. The microstructures, phases and micro-hardness of nitrided layers were investigated by atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and micro-hardness. Tribological properties were investigated on a pin-on-disc wear tester under 25% bovine serum solutions. The experimental results showed that plasma nitriding was a promising process to produce thick, hard and wear resistant layers on the surface of CoCrMo alloy. The harder CrN and Cr₂N phases formed on the plasma nitrided layer with the compact nano-crystalline structure. Compared with the untreated sample, all nitrided samples showed the lower wear rates and higher wear resistance at different applied loads and nitriding temperatures. It was concluded that the improvement of wear resistance could be ascribed to the formation of thicker and harder nitrided layers with the specific microstructures on nitrided surfaces.

KEY WORDS: CoCrMo alloy; Plasma nitriding; Microstructure; Tribology

1. Introduction

CoCrMo alloys are widely used for orthopedic applications such as hip and knee joint replacements^[1,2]. The highly biocompatibility of CoCrMo alloy is related closely to the excellent wear and corrosion resistance, imparted by a thin passive oxide film that forms spontaneously on the alloy surface. These films also form on the surfaces of other metal biomaterials, such as stainless steels and titanium alloys, and serve as a barrier to corrosion processes in alloy systems^[3,4]. In spite of the excellent wear and corrosion resistance of CoCrMo alloy, there is still a concern about wear debris and metal ion release from orthopedic implants into the body fluids, such as Co and Cr ions. These metal ions and wear debris, concentrated at the implant-tissue interface, may migrate through the tissue. Over time the level of metal ions may become clinically significant, resulting in implant failure, os-

teolysis and allergic reactions^[5,6].

There are various surface treatments which may increase the wear resistance and prevent and/or reduce the release of potentially harmful metal ions from orthopedic implant materials. One is to thicken the protective oxide layer already present on the surface of metallic biomaterials *via* a process known as passivation^[7]. Another method is to apply coatings or protective layers to increase the wear resistance and reduce the possibility of implant failure and osteolysis^[8,9]. As one of the important surface strengthening processes, nitrogen ion implantation has been shown to improve wear resistance of orthopedic components such as the knee and hip replacements^[10,11]. However, due to the depth limitation, the orthopedics treated in such a way is quite costly and still the lifetime is limited. Since plasma assisted thermo chemical surface treatments improve wear, corrosion resistance and fatigue strength, the plasma nitrided CoCrMo alloy may be beneficial for the medical application^[12]. But no much studies about plasma nitrided CoCrMo alloy were

† Corresponding author. Prof., Ph.D.; Tel.: +86 516 83591918; Fax: +86 516 83591916; E-mail address: wql889@cumt.edu.cn (Q.L. Wang).

Table 1 Treatment conditions of cast CoCrMo samples

Material	Sample No.	Plasma nitriding temperature/°C	Current density /(mA/cm^2)	Voltage /V	Pressure of gas /Pa	Nitriding time /h	Roughness S_a/nm
Cast CoCrMo	CCM1	0	0	0	0	0	15
Cast CoCrMo	CCM2	600	2.4	460	500	9	62
Cast CoCrMo	CCM3	700	3.7	520	500	9	103
Cast CoCrMo	CCM4	800	5.0	580	500	9	165

reported^[13–16]. In the present study, plasma nitriding method has been used to form wear resistance and protective layer on surface of cast CoCrMo alloy. The purpose of this study is to characterize the structures by atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray diffraction (XRD). The tribological properties under bovine serum lubrication are evaluated by a pin-on-disc tribotester. Moreover, the wear mechanisms of plasma nitrided layers are discussed.

2. Experimental

Medical cast cobalt-chromium-molybdenum (CoCrMo) alloy (ISO5832-12) has been used in the experiments with a nominal composition of 28.7% Cr, 6.18% Mo, 0.38% Ni, 0.73% Fe, 0.61% Mn, 0.21% C, and balance Co (wt%). Mechanical properties of the yield and tensile strength are 465 and 690 MPa, respectively. Elongation of cast CoCrMo alloy is about 8.5%. The disc specimens were cut from cylindrical bars with diameters of 30 mm and thickness of 5 mm. The pin specimens had a pin-like geometry with a diameter of 4 mm and a length of 20 mm. Before plasma nitriding, all the specimens (including one of the end surfaces for pin sample) were polished to a mean surface roughness of about 15 nm based on 3D surface profiler. The samples were ultrasonically cleaned in alcohol solution and deionized water for 15 min at room temperature, dried and stored under clean room conditions.

The specimens were placed into a holder which was the cathode of plasma nitriding chamber. Prior to the process, the specimens were subjected to cleaning by argon sputtering for 30 min under a voltage of 500 V and a pressure of 100 Pa. Then, the plasma nitriding was performed in gas of pure NH_3 (ammonia), with a constant pressure of 500 Pa and process temperature of 600–800 °C and process time of 9 h. Treatments were conducted using direct current and voltage between 400–600 V depending on desired temperature. The detailed treatment conditions are listed in Table 1.

The friction and wear tests of untreated and nitrided CoCrMo samples were carried out on a universal micro-tribometer (UMT, Type-II, Center Inc., American) under the lubrication condition of 25% bovine serum solution. The same processing CoCrMo pins with a diameter of 4 mm were used as the counterpart materials, such as an untreated pin against an untreated disc and a nitrided pin against a ni-

trided disc. The reciprocating motion pattern was used in evaluating the tribological properties of untreated and plasma nitrided samples. The sliding velocity and distance were 10 mm/s and 10 mm, respectively. All experiments were stopped after 2.5 h or 9000 cycles. The testing contact loads were 2.5, 5.5 and 8.5 MPa, respectively. All specimens were cleaned in an ultrasonic bath of alcohol before tests. To ensure the reproducibility, three parallel experiments were carried out. In order to normalize the wear results in this paper, the commonly used wear rate k ($\text{mg}\cdot\text{N}^{-1}\cdot\text{m}^{-1}$) was calculated by dividing the worn weight Δm (BP211D electron analytical balance with 0.01 mg precision, Sartorius AG, Germany) by the total sliding distance S (m) and applied normal load F (N):

$$k = \Delta m / FS$$

Scanning electron microscopy (SEM, S3000, Hitachi Co., Japan) and atomic force microscopy (AFM, CSPM5500, China) were used to analyze the surface and cross-sectional morphologies for both the untreated and nitrided specimens. X-ray diffraction (XRD, D/MAX-3B, Rigaku Co., Japan) was done in a continuous-scanning mode with $\text{CuK}\alpha$ radiation. Roughness of S_a was measured by ultra-high-precision three-dimensional profiler (3D profiler, MiaoXAM2.5X-50X, USA). At least six readings were taken for each sample. The micro-hardness was measured by micro-hardness meter (HDX-1000, Taiming Test Co., China) with the applied loads from 10 to 500 g.

3. Results and Discussion

3.1 Microstructure and morphology

AFM images of the untreated and treated specimens are given in Fig. 1. It is observed that the surfaces are relatively smooth and featureless. And there only appear some polished textures on surfaces of untreated samples. In contrast, Fig. 1(b) is the image of the cast CoCrMo sample nitrided at 700 °C. The compact nano-crystalline structure can be seen on the plasma nitrided layer and the surface becomes rougher due to nitrogen ion bombardment. Using the 3D profiler, the roughness (R_a) of all cast CoCrMo samples were measured, which can be found in Table 1. Surface roughness of untreated specimen is about 15 nm. But for the as-treated specimens, the surface roughness is measured from 62 to 165 nm. It has been also obtained that the surface roughness increases with

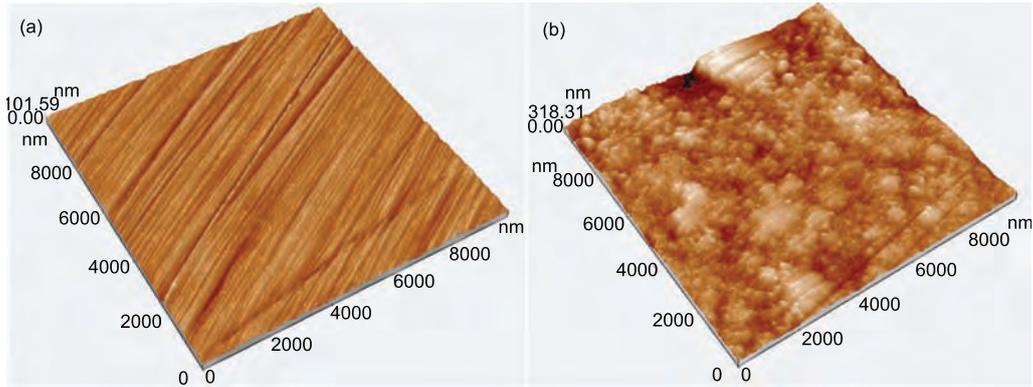


Fig. 1 AFM morphologies: (a) untreated samples, (b) nitrided cast CoCrMo at 700 °C

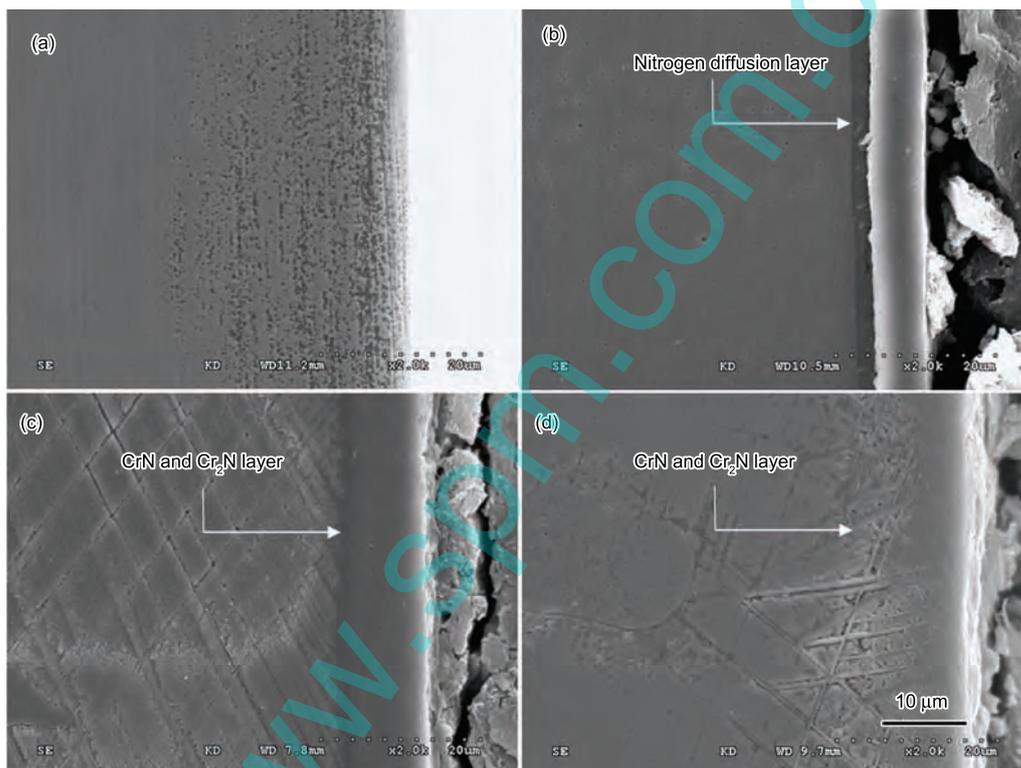


Fig. 2 Cross-sectional SEM images of the untreated sample (a), plasma nitrided samples at 600 °C (b), 700 °C (c) and 800 °C (d)

increasing treatment temperature due to ion bombardment. Since it is desired for prostheses to have smooth surfaces, all samples including the untreated and nitrided ones were slightly repolished to the roughness about 20–30 nm before the wear tests.

The cross sectional SEM micrographs of the plasma nitrided cast specimens are given in Fig. 2. At low nitriding temperature, a double layer structure forms on the nitrided surface. The thickness of the first layer is measured about 7 μm and the second layer is about 2 μm at 600 °C in Fig. 2(b). It is believed from XRD analysis that the second phase is CrN formed on the first nitrided layer. The one below

is the nitrogen diffusion layer due to nitrogen atoms taking interstitial places among the parent structure and forming surface layers by expanding the lattice. With increasing nitriding temperature, the possibility of the formation of CrN and Cr₂N layer increases and therefore this layer dissolves. At nitriding temperature of above 700 °C shown in Fig. 2(c) and (d), only a widened CrN and Cr₂N layer is seen to form uniformly throughout the parent microstructure, and the thickness of nitrided layer increases to about 12 μm for 700 °C and 14 μm for 800 °C. Therefore, it can be seen that the thickness of nitrided layers increases with the nitriding temperatures.

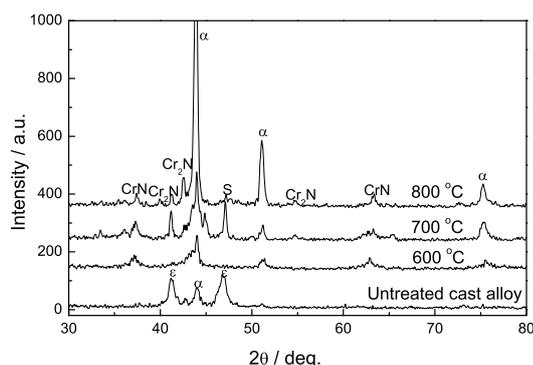


Fig. 3 XRD patterns for untreated and nitrided CoCrMo alloys

3.2 XRD analysis

The XRD results for cast CoCrMo specimens are shown in Fig. 3. For the untreated sample, the structure appears to be a mixture of α -CoCr and ε -CoCr Co parent structure with solid solution Cr and Mo. And there is a higher concentration of the ε -CoCr phase or ratio of ε/α . The presence of ε -CoCr phase with hcp structure is consistent with the equilibrium Co/Cr phase diagram. The presence of α -CoCr existing in an fcc structure above 450 °C is possibly indicative of a non-equilibrium transformation during cooling. Distinctive phases of the nitrided specimens which are CrN, Cr₂N and S-phase, depend on the treatment temperature. At treatment temperature of 600 °C, it is observed that the ε -CoCr phase almost disappears and CrN phase forms at peaks of about 37.2 and 62.8 deg. When the temperature increases to 700 °C, S-phase occurs at the nearly same angles of ε -CoCr phase. And there are the clear diffraction peaks of Cr₂N phase at about 44.2 and 55.1 deg. After the temperature up to 800 °C, it is seen that the diffraction intensity of Cr₂N diffraction peaks increases obviously, which reveals that the content of Cr₂N phase improves with increasing temperature. At the same time, S-phase reduces significantly.

Lanning and Wei^[13] observed CrN and Cr₂N phases for the cast and forged CoCrMo alloy. However, Celik *et al.*^[15] reported that Co₂N phase was formed for cast alloy at 600 °C, in addition to CrN and Cr₂N phases. As can be seen in Fig. 3, CrN and Cr₂N phases are found and Co₂N phase cannot occur on nitrided layers at different treatment temperatures. S-phase is a cobalt rich phase with a metastable and interstitial supersaturated phase, the formation of which requires either a higher concentration of Co or a higher temperature according to Co/Cr phase diagram^[17,18]. It has been observed that the amounts of Cr₂N increase with increasing nitriding temperature, which may induce the decomposition of Cr from S-phase. Thus Cr atoms may bond with N atoms and form Cr₂N phase. Conse-

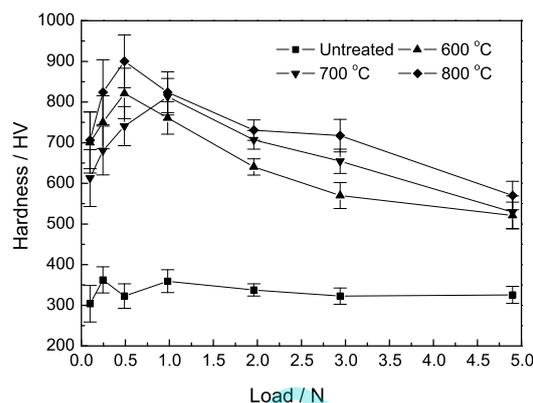


Fig. 4 Micro-hardness of untreated and nitrided CoCrMo alloys

quently, the effects of nitriding and elevated temperature have altered the distribution of phases for cast CoCrMo alloy.

3.3 Micro-hardness of CoCrMo

Fig. 4 presents the apparent surface Vickers micro-hardness as a function of the applied load from 10–500 g. The hardness number is the average of 6 data points. It is observed that all the hardness of nitrided samples is still much higher than that of the untreated sample at different loads. And the nitrided samples at high temperatures exhibit high hardness. This strengthening of the surface will allow an important reduction of the surface wear in friction and wear. The improvement of hardness is believed due to the formation of CrN and Cr₂N mixed phases consisting of nano-crystalline structures. At low nitriding temperature of 600 °C, less hard CrN phase on nitrided layer is conducive to the improvement of alloy hardness. At high nitriding temperature, CrN, S-phase and Cr₂N are the main phases in a parent structure of α -CoCr. The hardness of S-phase is similar or even harder than that of quenched Fe–C (950HV)^[18]. But the hardness of CrN and Cr₂N phase is up to 2740 and 2175 HV^[12], which leads to the higher hardness of nitrided CoCrMo alloys at higher temperatures. Although some authors assign this behavior to the presence of nano-crystalline inside the coating, this result is also due to the intrinsic hardness of the deposited compound^[19].

3.4 Friction and wear

Fig. 5 shows the friction coefficients of untreated and nitrided cast CoCrMo samples under the lubrication of 25% bovine serum solution at stresses of 2.5, 5.5 and 8.5 MPa, respectively. As can be seen, the friction coefficients of all samples start high and then decrease to the steady values after about 4000 running cycles. In addition, the friction coefficients basically show the decreasing trend with increasing applied

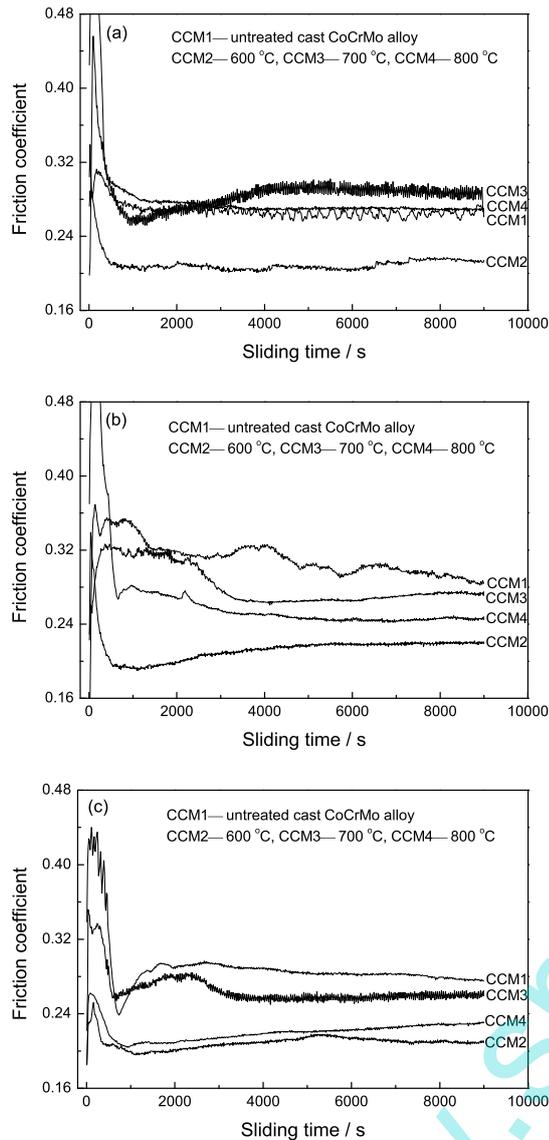


Fig. 5 Friction coefficients of untreated and nitrided cast CoCrMo alloys: (a) 2.5 MPa, (b) 5.5 MPa, (c) 8.5 MPa

stress. At the low stresses in Fig. 5(a), the friction coefficients of nitrided samples at high temperatures of 700 and 800 °C are about 0.29 and 0.27, respectively, which are close to or slightly higher than the value of 0.27 for untreated alloy. At the high stresses in Fig. 5(b) and (c), the values of all nitrided samples are obviously lower than those of the untreated one.

The wear rates of untreated and nitrided cast CoCrMo samples at different applied stresses are given in Fig. 6. Compared with untreated cast samples, the wear rates of all nitrided samples decrease clearly. Under the conditions of different applied loads, nitrided samples at high treated temperature have the low wear rates and show the better wear resistance. However, the samples nitrided at 700 °C show the lowest wear values at different loads. The average wear rate is only about 25% of that for the untreated sample. As expected, the wear re-

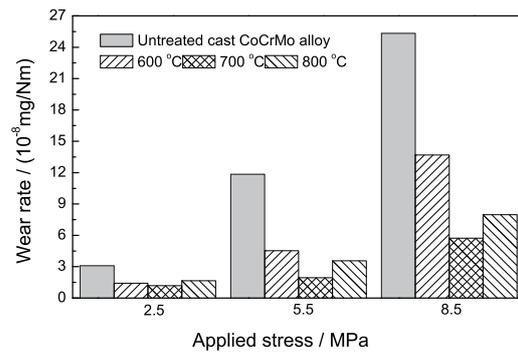


Fig. 6 Wear rates of untreated and nitrided CoCrMo alloys at different applied loads

sistance of nitrided samples increases nearly 3 times as compared to that of the untreated sample.

The wear tracks of SEM and 3D profiler micrographs for untreated and plasma nitrided CoCrMo samples at stress of 5.5 MPa are given in Fig. 7. It is quite observed that the wide and deep abrasive damages are demonstrated on the worn surface of untreated sample in Fig. 7(a) and (b), which imply that very serious abrasive wear must have played an important role in the wear process. Another wear feature is worthy of our attention. Lots of wear debris can be seen in partial plowing grooves. The wear tracks for nitrided samples at different treated temperatures are shown in Fig. 7(c)–(h). Although parallel abrasion grooves are also observed in wear tracks, they are much finer as compared with those found in the wear tracks of untreated sample. These morphologies indicate that very mild abrasive wear might have dominated the wear process of nitrided samples. It is noted that some much spalling areas can be found on the wear surface of nitrided sample at 800 °C in Fig. 7(g), which may lead to the high-wear values in comparison to the nitrided samples at 700 °C in Fig. 6.

In general, the wear resistance of nitrided samples increases basically with the nitriding temperature, which is determined by the CrN and Cr₂N formation consisting of the compact nano-crystalline structure and the thicker nitrided layers form at high temperature with a higher hardness. Although enough hardness and thickness as well as a good adhesion nitrided layer effectively improve the wear resistance for nitrided samples at high nitriding temperature, the damage resistance and durability of the layer are likely to be equally important. As seen in Fig. 6, the wear resistance of nitrided sample at 800 °C is not further improved compared with nitrided sample at 700 °C. On the one hand, the hardness and wear resistance of Cr₂N are less than those of CrN phase^[12], the increase of which does not further improve the wear resistance of nitrided alloys. On the other hand, it is seen in Fig. 2 that some micro-cracks have formed on the nitrided layer as the process temperature increases. These cracks may break off the film

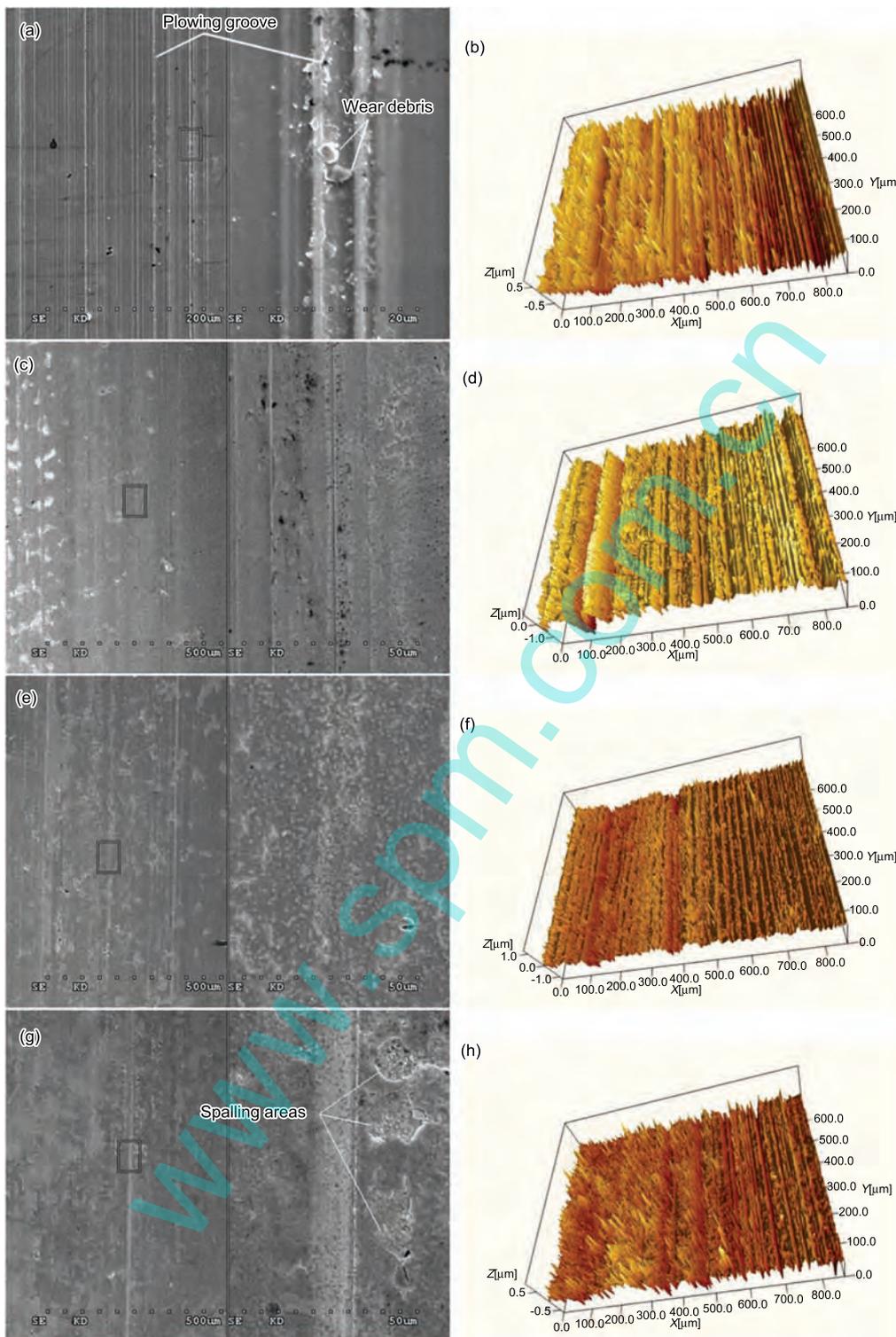


Fig. 7 SEM and 3D profiler micrographs of wear surfaces of untreated alloys (a) and (b), and nitrided cast CoCrMo alloys at 600 °C (c) and (d), 700 °C (e) and (f), 800 °C (g) and (h)

during sliding to cause high wear rates for nitrided samples at 800 °C. Consequently, the nitriding temperature of 700 °C is more suitable for forging CoCrMo alloy.

4. Conclusion

Plasma nitriding is a promising process to produce thick, hard and wear resistant layers on the surface

of CoCrMo alloy. The results from the nitrided cast CoCrMo samples have indicated that the harder CrN and Cr₂N phases form on the nitrided layer. All plasma nitrided samples exhibit an important increase of the surface hardness. At the low loads, the friction coefficients of nitrided samples at high nitrided temperatures are close to or slightly higher than that of untreated alloy. At the high loads, the values of all nitrided samples are lower than those of the untreated one. Compared with the untreated sample, nitrided alloys show lower wear rates and higher wear resistance under different loads and nitriding temperatures. The adhesive wear is the main mechanism for untreated and nitrided CoCrMo alloys. It is concluded that the improvement of wear resistance is ascribed to hard nitride formation of CrN and Cr₂N phases on nitrided surfaces.

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