Effect of Electric Potentials on Microstructure, Corrosion and Wear Characteristic of the Nitrided Layer Prepared on 2Cr13 Stainless Steel by Plasma Nitriding

Yang Li¹ · Shang-Zhou Zhang¹ · Jian-Xun Qiu¹ · Yong-Yong He² · Jun-Jie Xiu¹ · Qian-Wen Ye¹ · Zhong-Li Liu¹

Received: 5 June 2018 / Revised: 15 September 2018 / Published online: 9 November 2018
© The Chinese Society for Metals and Springer-Verlag GmbH Germany, part of Springer Nature 2018

Abstract

Plasma nitriding is a widely used technology to enhance the surface performance and extend the service life of alloy parts. The current research mainly focuses on the influences of time, temperature, gas type and pressure parameters on nitriding behavior, while fewer studies have been conducted on the electric potential. This paper mainly reports the effect of the electric potential on nitriding behavior. Test conditions were set using cathodic, anodic and floating potentials in a plasma nitriding furnace. 2Cr13 stainless steel was nitrided at 450 °C for 5 h in an NH₃ atmosphere. The experimental results show that the nitriding treatment can be well performed under the different electric potentials, but differences exist in microstructures, morphologies and performance results of the modified layers. The thickness and hardness values of the nitrided layer are ranked as follows: cathodic > anodic > floating potential. The anodic nitrided surface has an obvious particle deposition layer composed of nitrides and oxides. Electrochemical and tribological experiments show that the corrosion resistance and wear resistance were significantly improved after a nitriding treatment using the three electric potentials. Moreover, the floating nitriding treatment resulted in the best tribological performance and corrosion resistance.

Keywords Nitriding · Stainless steel · Wear · Corrosion

1 Introduction

Plasma nitriding is a modern thermochemical treatment used for increasing the hardness, corrosion and wear resistance of metal parts [1–11]. The parts to be treated (known as the charge) form the cathode, and the furnace wall is the anode. After evacuation, a high voltage is applied between the cathodic table and the furnace wall. The supplied treatment gas is ionized in the electric field. On the surface area that is directly charged by the ions,

nitrogen-rich nitrides are formed and decomposed, releasing active nitrogen onto the surface. During the conventional plasma-nitrided (CPN) treatment where the workpiece serves as the cathode of the discharge system, there will be some problems that are difficult to solve, such as the edge effect [12]. The active screen plasma nitriding (ASPN) technology thus came into use [5, 13–19]. The gas in the furnace is ionized, the surface of metal screen is heated after ion bombardment, and the workpiece reaches nitrided temperature through radiation. As the workpiece has a floating potential rather than a cathodic potential, the edge effect of the CPN technology will be resolved easily.

The current research studies on plasma nitriding technology have mainly focused on the influences of time, temperature, gas type and pressure parameters on nitriding behavior [20, 21]. Li and Bell [22] have investigated the microstructures and corrosion properties of nitrided 410 stainless steels at various temperatures. Fossati et al. [23] studied the influences of the treatment time, temperature [24] and pressure [25] on the microstructure, morphology, mechanical properties and corrosion behavior of the AISI

Available online at <http://link.springer.com/journal/40195>

✉ Yong-Yong He
hey@mail.tsinghua.edu.cn

✉ Zhong-Li Liu
liuzhonglimanor@163.com

¹ School of nuclear equipment and nuclear engineering, Yantai University, Yantai 264005, China

² State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China

316L stainless steel nitrided by the CPN process. The mechanical and tribological properties of AISI 420 and HP13Cr stainless steels nitrided at different temperatures using the cathodic cage design were investigated by Kurelo et al. [26]. Forati Rad et al. [27] investigated the morphology, size and composition of the nitride nanoparticles formed on the surface of the AISI H11 hot working tool steel by plasma nitriding in various gas mixtures under different time and temperatures. Borgioli et al. [28] studied that the influence of the treatment atmosphere on the characteristics of glow discharge treated sintered stainless steels.

In the above-described nitriding process, the roles of the ionized and neutral species, as the active species, generated some controversy [29]. Rusnak and Vıcek [30] considered that the N^+ ions are the dominate incidental species at the nitrided surface, whereas Walkowicz [31] claimed that both the ionized (N_2^+ , N^+) particles and the neutral (N_2 , N) particles are involved in the plasma volume to substrate nitrogen transport during the CPN process. In the current literature, most research shows that the positive nitrogen ions play a decisive role in the nitriding process [32, 33].

Very few investigations have been carried out on the effect of the electric potentials on nitriding behavior or on a comparison among cathodic, anodic and floating potentials. Sousa et al. [34] found that cathodic cage nitriding using a floating potential produced nitrided layers with the same properties as those obtained by the CPN treatment, while totally eliminating edge effects. Zhao et al. [35] studied the ASPN technology of AISI 316L stainless steel at anodic and floating potentials and compared the structures, morphologies and compositions of the two nitrided layers. The nitrided samples using a cathodic potential were bombarded and sputtered by positive ions, the nitrided samples using an anodic potential were bombarded by abundant electrons, and the nitrided samples using a floating potential were mainly nitrided by the adsorption and diffusion of neutral nitrogen substances.

In this investigation, 2Cr13 stainless steel was the study object. The active screens were connected to the cathode of the power supply, and the sample tables were placed on the active screen. The sample tables were located at the cathodic, anodic and floating potentials. The effect of electric potentials on the nitridation behavior of 2Cr13 stainless steel was studied. The surface morphologies and structures of the nitrided layers were analyzed and characterized, and the corrosion and tribological properties were subsequently determined.

2 Experimental

The chemical compositions of the two steels (2Cr13 and 20Cr) are shown in Table 1. The as-received 2Cr13 stainless steel was in the annealed condition (760 °C) and in a form of a round bar with a hardness of 260 HV_{0.1}. Samples were cut from bars of a 20-mm diameter to disks of a 6-mm thickness. Before nitriding, the surfaces were polished with SiC papers (240–2000 grit) followed by polishing with 3.5- μ m diamond paste. The samples underwent ultrasonic cleaning progressively in acetone and ethanol and were then dried in a vacuum dryer.

The plasma nitriding treatment experiments were carried out using a pulsed plasma unit (LDMC-20F, WHRCLS, China) [36]. A 20Cr steel plate was processed to prepare three active screens (16 cm in diameter and 16 cm in height) with the holes uniformly distributed and grooves on the inner wall. The grooves of 5 mm depth and 8 mm width had uniformly distributed 8-mm round holes. The sample table was placed inside the metal screen. The shortest distance from the mesh to the sample edge was approximately 30 mm. The three different electrical arrangements are shown schematically in Fig. 1. The table and the first set of samples to be treated were exposed to a cathodic potential. The second set of samples was exposed to a floating potential and isolated from the cathodic mesh screen. The third set of samples, together with the table and the furnace wall, was electrically grounded and thus formed the anodic potential. The temperature of the substrate was monitored using a thermocouple. The chamber was evacuated to a pressure of 10 Pa before nitriding, using a rotary vane pump. The NH_3 gas flow rate and processing pressure were maintained at 400 sccm and 350 Pa, respectively. The nitriding was performed at 450 °C for 5 h.

The phase compositions of the nitrided layers were determined using an X-ray diffraction meter (XRD, Bruker D8-advance) in the θ – 2θ geometry, with a Cu- $K\alpha$ radiation source. The cross sections of the nitrided samples were characterized by XJL-30 optical microscopy (OM). The untreated and nitrided surfaces were both analyzed by scanning electron microscopy equipped with field emission and energy dispersive spectrometers (SEM–EDS). Microstructural characterization was further conducted in an FEI Tecnai G2 F20 transmission electron microscope

Table 1 Chemical compositions (wt.%) of 2Cr13 and 20Cr steels

	C	Cr	Mn	Si	Fe
2Cr13	0.25	12.5–13.0	0.3–0.5	< 0.50	Bal.
20Cr	0.18–0.24	0.70–1.00	0.50–0.80	0.17–0.37	Bal.

Fig. 1 Schematic representation of the plasma nitriding experimental setup

(TEM). The evolution of the surface morphology was acquired by atomic force microscopic (AFM) examination. All morphology experiments were carried out on an atomic force microscope (NanoScope III) in the ultra-light tapping mode in the atmosphere to prevent scratching of the pre-treated surfaces.

The chemical compositions were characterized by X-ray photoelectron spectroscopy (XPS). The XPS data were collected using a monochromatic Al $K\alpha$ radiation source at 1486.6 eV covering a circular irradiated area with a diameter of 500 μm . XPS spectra were obtained using an Art ion beam to study the chemical composition at different depths. All the binding energies were referenced to the C1s neutral carbon peak at 284.6 eV. XPS spectra were deconvoluted using a nonlinear least squares algorithm with a Shirley baseline and a Gaussian–Lorentzian combination. XPS Peak 4.1 software was used for all data processing. A Bruker Contour GT-K 3D optical microscope equipped with Vision 64 software was used to image the surfaces of the samples. The measurements of the surface micro-hardness were taken by using a Tukon 2500 Automated Hardness Tester with a Vickers indenter under a load of 100 g for 15 s. The surface roughness of the samples was measured using a Form Talysurf PGI 1230.

The evaluation of the corrosion resistance of the untreated and nitrided samples was carried out in 3.5 wt.% NaCl solution using an electrochemical workstation (CS-350 Corrtest, China). A typical three-electrode system was used for the polarization tests. The system was composed of a saturated calomel electrode (SCE) as the reference electrode, a platinum rod as the counter electrode and the measured sample as the working electrode. Electrochemical experiments were conducted at room temperature and atmospheric pressure in a three-electrode cell. The polarization curves were obtained in the potential range from

– 1000 to 800 mV with a sweeping speed of 1 mV/s. After the corrosion tests, microscopic analyses were carried out to evaluate the corrosion morphologies and the degree of damage using SEM.

The reciprocating friction wear tests were performed using a universal micro-tribometer (UMT-3, CETR, USA) with a AISI 52100 ball ($d = 4.0$ mm, hardness 62 HRC) as the counterpart. The wear tests were carried out at a sliding speed of 15 cm/s with applied loads of 5 N. The reciprocating sliding system has the amplitude of 15 mm for the frequency of 5 Hz. Each wear test duration was 900 s. Such a short time is mainly to evaluate the tribological properties of the superficial layer of the nitrided sample. All tests were conducted without lubrication in air. After sliding, the surface topography of the wear tracks was measured using SEM and a 3D white light profilometer.

3 Results and Discussion

Figure 2 shows the XRD patterns of the typical nitrided samples at the different electric potentials. The results indicate that the untreated sample was nearly totally composed of two diffraction austenite peaks of $\alpha(110)$ and $\alpha(200)$ at 44.8° and 65.6° , respectively. An evident diffraction peak, indicated as α_N , appears to the left side of the $\epsilon(101)$ peak at approximately 43.7° . By analogy with the designation ‘expanded austenite’ in the earlier researches [22, 37, 38], a solid solution of nitrogen-expanded lattice structure of $\alpha\text{-Fe}$ has developed and shifted the $\alpha(110)$ peak toward a lower diffraction angle. The modified layers of all the nitrided samples mainly consisted of $\epsilon\text{-Fe}_{2-3}\text{N}$, $\gamma'\text{-Fe}_4\text{N}$ and α_N phases. No formation of CrN phase was visible in the spectra of three nitrided samples. From the XRD profiles of the floating sample, the intensity of the

Fig. 2 XRD patterns of the untreated and the different nitrated samples

α_N phase peaks is considerably higher than that of the cathodic and anodic samples. Interestingly, the amount of ϵ - Fe_{2-3}N phase of the anodic sample at 68° is stronger than the cathodic and floating nitrated samples. It is found that the amounts of the ϵ - Fe_{2-3}N , γ' - Fe_4N and α_N phases were different at the three electric potentials.

Figure 3 shows the OM cross-sectional micrographs of the nitrated samples at the different electric potentials. A clear white layer formed on the surface of each nitrated sample. This was because the nitrated layer had better corrosion resistance than the substrate. SEM analysis (Fig. 4) was employed to further examine the cross-sectional morphologies of the different nitrated samples. The thicknesses of the cathodic, anodic and floating nitrated samples were 26, 21 and 16 μm , respectively. Further TEM observations combined selected area electron diffraction (SAED) analyses showed that the CrN precipitate formed in the nitrated layer of the cathodic nitrated sample (see Fig. 4d). It can be attributed to the nitrogen solid solution in α_N phase would decompose into α -Fe and CrN phases [39].

Figure 5 shows the SEM surface morphologies of the nitrated samples at the different electric potentials. Being exposed to ion bombardment and sputtering, the cathodic nitrated surface was clear, showing obvious metal grain characteristics. In contrast, the anodic nitrated surface had obvious characteristics of particle deposition, and there was an ultra-thin film of sediment covering the floating nitrated surface. In our previous study [40], it is found that the top film with the thickness of 100 nm was formed on the floating surface during the ASPN treatment. The ASPN nitrated surfaces were saturated with multiple polyhedral particles on a nanometer scale. Zhao et al. [35] found that the particles on the sample surface of nitrated samples using floating potential were apt to agglomerate into larger particles than those formed from the use of anodic potential.

The surface roughness was measured using a Form Talysurf PGI 1230 instrument. The roughness, shown in Fig. 6, further demonstrated the surface characteristics of the nitrated samples at different electric potentials. The roughness values of the cathodic, anodic and floating nitrated surfaces were 0.21, 0.18 and 0.11 μm , respectively. The surface roughness of the nitrated sample at floating potential in the ASPN treatment was lower than that of the CPN process [41, 42]. Nishimoto et al. [43] suggested that iron nitride was deposited and grown homogeneously, resulting from the lack of ion bombardment on the surface during the ASPN process. According to the results of our experiments, the surface roughness of the nitrated samples can be ranked in the following order: cathodic > anodic > floating potential.

Figure 7 shows representative topographical and deflection AFM images of the different samples. The untreated surface had obvious polishing characteristics, accompanied by certain scratches, with a small roughness value of only 1.9 nm. The nitrated surfaces were significantly different from the untreated surface. The cathodic and floating nitrated sample surfaces had obvious upheavals at the grain boundaries. The surface roughness values of the cathodic and floating nitrated samples increased to

Fig. 3 OM cross-sectional micrographs of samples nitrated at the different potentials

Fig. 4 a–c SEM cross-sectional micrographs of samples nitrided at the different potentials. **d** TEM cross-sectional micrograph of the cathodic nitrided sample

42.3 and 40.9 nm, respectively. A deposition of fine particles was found on the anodic nitrided surface, and the roughness of the anodic nitrided surface reached as high as 91.7 nm. The particles sputtered from the active screen, and the energetic neutral species in the plasma, flowed through the screen toward the samples [35]. The cathodic sample is bombarded by nitrogen ions, and the surface has low nano-roughness due to the sputtering cleaning function. Compared with the floating sample, the anodic sample acts as small anode and the active screen acts as large cathode. A large number of electrons bombard the anodic surface, thus exerting uniform heating effect. The increase in surface roughness is correlated with the formation of nitrided layer caused by infiltration of nitrogen atoms. The ranking of the roughness on a nanometer scale is in the order of anodic > floating $\approx$ cathodic potential.

Figure 8 shows the XPS fitting map of Fe $2p_{3/2}$, Cr $2p_{3/2}$, N 1s and O 1s peaks on the surface of the nitrided samples at the different electric potentials after sputtered by argon guns for 500 s. The cathodic, anodic and floating nitrided samples were referred to as I, II, and III, respectively.

The values of the bonding energy of the Fe present in the nitrided layer provided evidence of the presence of metallic iron (706.2 eV), iron nitride Fe_xN (706.6 and 707.1 eV) and iron oxides (707.7 and 708.2 eV). The last peak, observed at 709.6 ± 0.4 eV, has been ascribed to the satellites of the ferric compounds, as mentioned previously [44, 45]. It is known that the Fe^{3+} contribution from Fe_2O_3 and Fe_3O_4 is difficult to identify using XPS spectra, and a global value for these two iron oxides was considered [44, 46]. The Fe energy spectra of the nitrided samples from three different potentials were not very different.

The fitting results of the spectra of Cr $2p_{3/2}$ showed that Cr was present as Cr metal, Cr_2O_3 and CrN. For the anodic and floating nitrided samples, the Cr $2p_{3/2}$ spectrum revealed the following three peaks: the 574.4 eV peak was from metallic Cr, the 574.9 eV peak was related to a Cr nitride state, and the 576.2 ± 0.2 eV peak was associated with a Cr oxide state. Lippitz and Hübert [47] reported that the peaks centered at 575.6 should be attributed to CrN, and the peak centered at 577.6 eV should be assigned to Cr_2O_3 . Cr $2p_{3/2}$ has the weakest peak intensity among the four elements, indicating a very low content in the

Fig. 5 SEM surface micrographs of the different nitrided samples

modified surface layer. However, the relative amount of Cr atoms in the cathodic nitrided sample was greater than those of the other nitrided samples. The Cr $2p_{3/2}$ peak of the cathodic nitrided sample was taken from the following four groups of different chemical species: metallic chromium Cr (573.9 eV), chromium nitrides CrN (574.5 eV), Cr_2N (575.2 eV) [47, 48] and chromium oxides (576.4 eV)

[49]. Additionally, the CrN phase in the nitrided layer was observed by TEM (Fig. 4d).

In the N 1s XPS spectra of the anodic and floating nitrided samples, the 397.3 and 397.6 eV characteristic peaks occupied a larger portion of the area, respectively, so it can be classified as iron nitride. The 397.0 eV peak corresponds to the Cr–N bond. The N 1s peak at 398.9 eV

Fig. 6 Surface roughness of the untreated and nitrated samples

was associated with an oxidized nitrogen. The last peak at the highest binding energy was attributed to N–O bonding (oxidized nitrogen) as a result of the oxidation of the nitrogen in the nitride layer [50]. The 398.4 eV peak was classified as an N–C compound state bond energy. This also confirmed that N–C bonding could be detected in the anodic and floating nitrated samples, in contrast to the cathodic nitrated samples. The N 1s spectrum recorded from the cathodic nitrated sample is shown in Fig. 8c. It shows the following three components: the peaks at 397.7 eV and 397.0 eV corresponding to CrN and Cr₂N, respectively, the peak at 399.3 eV, which we associate with

Fe–N, and the last peak at 400.7 eV, which might be associated with the presence of oxidized nitrogen.

The O 1s XPS spectra of cathodic nitrated sample were decomposed into three peaks. A low energy band indicated the existence of the weak Cr–O bond (530.0 eV), while a high energy band indicated the Fe–O bond (530.7 eV), and another energy band indicated the N–O bond (531.3 eV). It was also found that the relative amount of O atoms in the cathodic nitrated sample was less than those of the other nitrated samples. For the anodic and floating nitrated samples, the two strongest peaks were those of 530.4 and 530.9 eV of the Fe–O bond, further proving the existence of these oxides. The component at a binding energy of approximately 530 eV was attributed to Cr oxide, while the other two, due to the deposition, at approximately 531.4 and 532.4 eV, were for C–O and N–O bonds, respectively. It is interesting to note that the amounts of C and O, measured on the modified surfaces of the anodic and floating nitrated samples, were significantly higher than those obtained for the cathodic nitrated sample. It is also possible that the formation of carbonization on the surface of the samples might have interfered with the surface analysis [51].

The XPS analysis showed that relatively more chromium nitrides phases were observed in the modified surface of the cathodic nitrated sample. But, the surface composition of the anodic and floating nitrated samples consisted mainly of iron

Fig. 7 AFM surface micrographs of the different samples: **a** untreated, **b** cathodic, **c** anodic, **d** floating

Fig. 8 XPS deconvoluted profiles for Fe 2p_{3/2} **a**, Cr 2p_{3/2} **b**, N 1s **c**, O 1s **d** peaks on the surface of the samples nitrided using cathodic (I), anodic (II) and floating potentials (III)

nitrides and oxides. The lower Cr concentration is attributed to the deposition of the particles that originate from the particles sputtered from the 20Cr steel screen, which has relatively more iron oxides and relatively few nitrides.

Figure 9 shows the surface micro-hardness values of the untreated and the nitrided samples. It was observed that the hardness values of all the nitrided samples were much higher than that of the untreated sample (260 HV_{0.1}). It is worth noting that the floating nitrided sample had the

lowest hardness value (800 HV_{0.1}) of all the nitrided samples. The micro-hardness values of the cathodic and anodic nitrided samples were approximately 1040 and 940 HV_{0.1}, respectively. Consequently, a comparison of the three different electric potentials revealed that the surface hardness values were ranked as follows: cathodic > anodic > floating potential. The change in the micro-hardness is correlated with phase structure, proportion and the thickness of the nitrided layer.

Fig. 9 Surface hardness of the untreated and nitrided samples

Figure 10 shows the polarization curves of the untreated and three nitrided samples in a 3.5 wt.% NaCl solution. The untreated matrix had a corrosion potential of approximately -0.70 V, and there is an obvious passivation zone (from -0.60 to 0.05 V), in which the passive current density was 5.27×10^{-6} A/cm². When the potential exceeded 0.10 V, the current density increases rapidly with increasing potential, and pitting corrosion of the stainless steel occurred in the Cl⁻ containing solution. This phenomenon is commonly known as pitting corrosion of martensitic stainless steel [22, 52]. The pitting accelerated the surface corrosion, and the corrosion current density was 3.5×10^{-4} A/cm² in the higher potential range of 0.1 – 0.8 V.

The corrosion potential (-0.59 V) of the cathodic nitrided sample was higher than that of the original sample. The polarization curve shows a wide passivation zone, and the passive current density was 2.8×10^{-7} A/cm². When the potential was as high as 0.8 V, no pitting occurred. The corrosion potential of the anodic nitrided sample was

Fig. 10 Polarization curves of untreated and nitrided samples in a 3.5 wt.% NaCl water solution

-0.77 V, as it had shifted to the negative position. The corrosion current density of 9.7×10^{-6} A/cm² was higher than that of the untreated sample, but the increase in potential was not accompanied by the increase of apparent current. The floating nitrided sample has the highest corrosion potential of -0.38 V, which was significantly shifted to the positive potential. However, there was no obvious passivation zone, and the corrosion current density grew slowly as the potential increased, which was obviously lower than the current density of the untreated sample.

Figure 11 shows the SEM morphologies of the untreated and nitrided samples after the polarization tests in a 3.5 wt.% NaCl solution. As seen in Fig. 11a, the untreated 2Cr13 steel surface had obvious corrosion pits, and comprehensive corrosion can be observed with the naked eye in the corrosion test area. According to Fig. 11b, d, it can be seen that the cathodic and floating nitrided surfaces were almost unaffected by corrosion, with only slight spot corrosion pitting occurring in a particular zone, which was consistent with the results of the polarization curve (Fig. 10). The surface of the anodic nitrided sample had small and shallow spots, as shown in Fig. 11c, but no obvious pitting was observed on the surface by the naked eye. The samples nitrided at the different electric potentials had better corrosion resistances than the untreated sample, due to the formation of a nitrided compound layer.

The friction coefficient–sliding distance curves of the untreated and nitrided samples are shown in Fig. 12. The friction coefficient of the untreated matrix rapidly increased to 1.05 in the initial sliding stage and reduced to 0.7 after a sliding distance. Then, the friction coefficient gradually rose to 0.95 and fluctuated violently within this range. However, the friction coefficients of the nitrided samples were small and had slight fluctuations. The friction coefficients of the cathodic, anodic and floating nitrided samples were 0.88 ± 0.03 , 0.81 ± 0.02 and 0.78 ± 0.05 , respectively. The changes in the friction coefficients were attributed to the changes in the element concentrations and microstructures of the modified layers [52, 53]. The floating nitrided sample had the lowest friction coefficient, which is related to the lowest amount of surface roughness after nitriding.

The wear morphologies of the untreated and the nitrided samples are shown in Fig. 13. The untreated substrate exhibited severe wear, a groove with wide polishing scratches (Fig. 13a), and obvious protrusions on both sides of the groove, indicating the occurrence of plastic deformation. Figure 14a shows that many small parallel furrows were distributed on untreated sample, and both ends of the polishing scratches were slightly deformed. It was determined that the wear mechanism of the untreated matrix was

Fig. 11 SEM surface images of the untreated and nitrated samples after the polarization tests

Fig. 12 The variation of friction coefficient versus time of the untreated and nitrated samples

mainly abrasive wear accompanied by a slight plastic deformation.

Figure 13b–d shows the wear morphologies of the nitrated samples. Compared with the untreated surface, all the nitrated surfaces had shallow scratches, which indicated the abrasion of the nitrated surfaces was not significant. The ranking of the morphologies of the white light interference evaluation of abrasion are ranked as follows: cathodic > anodic > floating potential. The SEM morphologies revealed no significant damage to the three nitrated samples (Fig. 14). Some black, irregular wear spots were found in the polishing scratches, which can be considered to be a result of transfer from the relatively soft part of the friction pair. An EDS analysis found the significant presence of oxygen in polishing scratches. The main wear mechanism of the nitrated samples was slight oxidative wear. In particular, the oxygen content of the

Fig. 13 White light interferometer results of the worn surfaces of the different samples: **a** untreated, **b** cathodic, **c** anodic, **d** floating

floating nitrided sample was 26.0 at.%, which was twice that of the other two electric potential samples. In addition, the lower roughness of the floating nitrided sample also further reduced the degree of wear.

4 Conclusions

In a pulse plasma nitriding furnace, 2Cr13 stainless steel was subjected to nitriding treatment at cathodic, anodic and floating potentials. The following conclusions have been drawn from the experiments:

1. The nitrided layers at the three potentials all consisted of ϵ -Fe₂₋₃N, γ' -Fe₄N and α_N phases, but the phase proportions of the three nitrided layers were different. Nitrided layer thickness and hardness values were ranked as follows: cathodic > anodic > floating potential. Different potentials also exert a significant effect on the morphology and roughness of the nitrided

surface. On a microscale, the influences of the three potentials rank as follows: cathodic > anodic > floating potential. On a nanoscale, as determined by AFM, the sequence is as follows: anodic > cathodic $\approx$ floating potential.

2. The XPS data of the cathodic nitrided sample showed that the sample had a relatively high chromium content, and that CrN and Cr₂N phases were observed on the modified surface. However, in the anodic and floating nitrided samples, the surface composition consisted mainly of iron nitrides and oxides.
3. The corrosion resistance of the untreated 2Cr13 steel was improved after being nitrided at the three electric potentials, and the corrosion resistance was closely related to the surface morphologies and phase composition of the modified layer.
4. The tribological properties were improved after being nitrided at the three electric potentials. The main wear mechanism for the untreated matrix was abrasive wear

Fig. 14 SEM and EDS results of the worn surfaces of the different samples: **a, b** untreated; **c, d** cathodic; **e, f** anodic; **g, h** floating

accompanied by mild plastic deformation, while that for the nitrided samples was slight oxidative wear. Of the three methods, the floating nitrided sample had the best friction and wear performance.

Acknowledgements This project was supported by the National Key Basic Research Program of China (No. 2014CB046404), the Shandong Provincial Natural Science Foundation, China (No. ZR2018MEE016), the Shandong Provincial Key Research and Development Plan, China (No. 2017GGX20140) and the National Natural Science Foundation of China (No. 51301149).

References

- [1] Y.X. Wang, Z.B. Chen, C.S. Zhang, Y. You, *Acta Metall. Sin. (Engl. Lett.)* **31**, 371 (2018)
- [2] A. Zhecheva, W. Sha, S. Malinov, A. Long, *Surf. Coat. Technol.* **200**, 2192 (2005)
- [3] Y. Sun, *Wear* **362**, 105 (2016)
- [4] B.C.E.S. Kurelo, G.B. de Souza, S.L.R. da Silva, F.C. Serbena, C.E. Foerster, C. Alves, *Appl. Surf. Sci.* **349**, 403 (2015)
- [5] L.A. Espitia, H. Dong, X.Y. Li, C.E. Pinedo, A.P. Tschiptschin, *Wear* **376–377**, 30 (2017)
- [6] Y.T. Xi, D.X. Liu, D. Han, *Surf. Coat. Technol.* **202**, 2577 (2008)
- [7] W.Y. Tang, M.H. Chuang, S.J. Lin, J.W. Yeh, *Metall. Mater. Trans. A* **43**, 2390 (2012)
- [8] D.X.L. Y.T. Xi, D. Han, Z.F. Han, *Acta Metall. Sin. (Engl. Lett.)* **21**, 21 (2008)
- [9] Q. Wang, C. Huang, L. Zhang, *J. Mater. Sci. Technol.* **28**, 60 (2012)
- [10] J.C. Díaz-Guillén, G. Vargas-Gutiérrez, E.E. Granda-Gutiérrez, J.S. Zamarripa-Piña, S.I. Pérez-Aguilar, J. Candelas-Ramírez, L. Álvarez-Contreras, *J. Mater. Sci. Technol.* **29**, 287 (2013)
- [11] F. Zhang, M. Yan, *J. Mater. Sci. Technol.* **30**, 1278 (2014)
- [12] M. Olzon-Dionysio, M. Campos, M. Kapp, S. de Souza, S.D. de Souza, *Surf. Coat. Technol.* **204**, 3623 (2010)
- [13] C.E. Pinedo, S.I.V. Larrotta, A.S. Nishikawa, H. Dong, X.Y. Li, R. Magnabosco, A.P. Tschiptschin, *Surf. Coat. Technol.* **308**, 189 (2016)
- [14] C.X. Li, J. Georges, X.Y. Li, *Surf. Eng.* **18**, 453 (2002)
- [15] M. Naeem, M. Shafiq, M. Zaka-ul-Islam, A. Ashiq, J.C. Díaz-Guillén, M. Shahzad, M. Zakaullah, *Mater. Des.* **108**, 745 (2016)
- [16] Y. Hoshiyama, R. Mizobata, H. Miyake, *Surf. Coat. Technol.* **307**, 1041 (2016)
- [17] P. Hubbard, J.G. Partridge, E.D. Doyle, D.G. McCulloch, M.B. Taylor, S.J. Dowey, *Surf. Coat. Technol.* **204**, 1145 (2010)
- [18] M. Naeem, M. Shafiq, M. Zaka-ul-Islam, M.I. Bashir, J.C. Díaz-Guillén, C.M. Lopez-Badillo, M. Zakaullah, *J. Alloys Compd.* **721**, 307 (2017)
- [19] M.I. Bashir, M. Shafiq, M. Naeem, M. Zaka-ul-Islam, J.C. Díaz-Guillén, C.M. Lopez-Badillo, M. Zakaullah, *Surf. Coat. Technol.* **327**, 59 (2017)
- [20] Y. Li, Z. Wang, L. Wang, *Appl. Surf. Sci.* **298**, 243 (2014)
- [21] H. Dong, *Int. Mater. Rev.* **55**, 65 (2010)
- [22] C.X. Li, T. Bell, *Corros. Sci.* **48**, 2036 (2006)
- [23] A. Fossati, F. Borgioli, E. Galvanetto, T. Bacci, *Surf. Coat. Technol.* **200**, 3511 (2006)
- [24] F. Borgioli, A. Fossati, E. Galvanetto, T. Bacci, *Surf. Coat. Technol.* **200**, 2474 (2005)
- [25] F. Borgioli, A. Fossati, E. Galvanetto, T. Bacci, G. Pradelli, *Surf. Coat. Technol.* **200**, 5505 (2006)
- [26] B.C.E.S. Kurelo, G.B. de Souza, S.L. Rutz da Silva, N.d.F. Daudt, C. Alves Jr., R.D. Torres, F.C. Serbena, *Surf. Coat. Technol.* **275**, 41 (2015)
- [27] H. Forati Rad, A. Amadeh, H. Moradi, *Mater. Des.* **32**, 2635 (2011)
- [28] F. Borgioli, E. Galvanetto, T. Bacci, G. Pradelli, *Surf. Coat. Technol.* **149**, 192 (2002)
- [29] H. Martínez, F.B. Yousif, *Eur. Phys. J. D* **46**, 493 (2008)
- [30] K. Rusnak, J. Vicek, *J. Phys. D Appl. Phys.* **26**, 585 (1993)
- [31] J. Walkowicz, *Surf. Coat. Technol.* **174–175**, 1211 (2003)
- [32] H. Michel, T. Czerwec, M. Gantois, D. Ablitzer, A. Ricard, *Surf. Coat. Technol.* **72**, 103 (1995)
- [33] A. Bogaerts, E. Neyts, R. Gijbels, J. van der Mullen, *Spectrochim. Acta B* **57**, 609 (2002)
- [34] R. de Sousa, F. de Araujo, K. Ribeiro, T. Dumelow, J. da Costa, C. Alves, *Surf. Eng.* **24**, 52 (2008)
- [35] C. Zhao, L.Y. Wang, L. Han, *Surf. Eng.* **24**, 188 (2008)
- [36] Y. Li, Y. He, S. Zhang, X. He, W. Wang, B. Hu, *Vacuum* **146**, 1 (2017)
- [37] Y. Li, Y. He, J. Xiu, W. Wang, Y. Zhu, B. Hu, *Surf. Coat. Technol.* **329**, 184 (2017)
- [38] Y.T. Xi, D.X. Liu, D. Han, *Appl. Surf. Sci.* **254**, 5953 (2008)
- [39] P. Corengia, G. Ybarra, C. Moina, A. Cabo, E. Broitman, *Surf. Coat. Technol.* **187**, 63 (2004)
- [40] Y. Li, Y. He, W. Wang, J. Mao, L. Zhang, Y. Zhu, Q. Ye, J. Mater. Sci. Eng. Perform. **27**, 948 (2018)
- [41] K.J.B. Ribeiro, R.R.M. de Sousa, F.O. de Araújo, R.A. de Brito, J.C.P. Barbosa, C. Alves Jr., *Mater. Sci. Eng. A* **479**, 142 (2008)
- [42] K. Nagatsuka, A. Nishimoto, K. Akamatsu, *Surf. Coat. Technol.* **205**, S295 (2010)
- [43] A. Nishimoto, A. Tokuda, K. Akamatsu, *Mater. Trans.* **50**, 1169 (2009)
- [44] T. Yamashita, P. Hayes, *Appl. Surf. Sci.* **254**, 2441 (2008)
- [45] F.Z. Bouanis, C. Jama, M. Traisnel, F. Bentiss, *Corros. Sci.* **52**, 3180 (2010)
- [46] L. Freire, M.J. Carnezim, M.G.S. Ferreira, M.F. Montemor, *Electrochim. Acta* **55**, 6174 (2010)
- [47] A. Lippitz, T. Hübert, *Surf. Coat. Technol.* **200**, 250 (2005)
- [48] D.J. Li, F. Liu, M.X. Wang, J.J. Zhang, Q.X. Liu, *Thin Solid Films* **506**, 202 (2006)
- [49] A. Conde, A.B. Cristóbal, G. Fuentes, T. Tate, J. de Damborenea, *Surf. Coat. Technol.* **201**, 3588 (2006)
- [50] F.Z. Bouanis, F. Bentiss, M. Traisnel, C. Jama, *Electrochim. Acta* **54**, 2371–2378 (2009)
- [51] J. Baranowska, S.E. Franklin, *Wear* **264**, 899 (2008)
- [52] M.F. Yan, R.L. Liu, *Surf. Coat. Technol.* **205**, 345 (2010)
- [53] J. Yang, Y. Liu, Z. Ye, D. Yang, S. He, X. Li, *Appl. Surf. Sci.* **256**, 4072 (2010)