Comparison of nitriding kinetics of austenitic stainless steel assisted with hollow cathode discharge in different potentials

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Abstract. In the present research 304 austenitic stainless steels were nitrided using hollow cathode discharge-assisted plasma and the effect of potential conditions on the nitriding kinetics was evaluated. The results indicate that nitriding kinetics is significantly promoted in cathode potential. CrN in the anode specimen is more difficult to form than those in the floating and cathode specimens and the temperature affects the modified layers seriously.

1. Introduction
Austenitic stainless steel has played an very important role in various industries for its excellent corrosion resistance, but the low hardness and poor wear resistance limits their use whenever surface hardness is required[1-2]. Plasma nitriding is commonly used to improve the surface hardness and wear resistance of materials[3]. Many researches have been shown that nitriding of austenitic stainless steels at low temperature obtained a modified surface layer consisting of a metastable phase, known as supersaturated or expanded austenitic γN or S-phase, which has proved to have high hardness and very good corrosion resistance [4].

In conventional dc plasma nitriding system the component to be treated is submitted to a high cathode potential so that plasma forms directly on the surface of the component. This causes inherent shortcomings for dc plasma nitriding, such as arc damages to surface, non-uniform appearance of component by the “edging effect”[5-7]. To overcome the problems of dc nitriding, hollow cathode discharge (HCD) assisted nitriding has been recently developed[8,9]. The double or multi-layer screens in plasma nitriding system are employed and HCD is generated between the inner and outer layers when two layers kept in proper distance. The heat radiation is greatly enhanced by the hollow cathode effect that the working space can be easily heated to the temperature required. In addition, the increase of ionization level of hollow cathode will inevitably increase the number of active ions required for surface treatment.[10]. Previous experiment results have shown that low alloy steels can be effectively nitrided in the HCD plasma space [11]. The present work is focused on the kinetics of HCD nitrided layer growth at different potentials. The obtained HCD assisted nitried layers have been investigated with respect to their phase composition, thickness and surface morphology.

2. Experiments and procedures
The specimens used in this study are AISI 304L austenitic stainless steel with the chemical composition of (Table1). Before nitriding each specimen was ground using 240,500,800 grit SiC papers, then polished by mechanical grinding to achieve sleek surfaces.

The nitriding was carried out in a commercial dc plasma nitriding apparatus (Fig.1). Two coaxial cylinders are laid in the center of the chamber. The vacuum chamber wall serves as an anode while two
coaxial cylinders both as cathodes. In present work, the working pressure was 450 Pa, and the pulse dc voltage applied on the cathode cylinders was 600-650 V. Nitriding is conducted in the atmosphere of ammonia (NH₃). The samples were laid on a bench in the middle of the inner cylinder. Some specimens were nitrided in floating potential and some nitrided in the same potential as anode/cathode. The samples were treated at different temperatures of 430℃, 450℃, 480℃, 510℃ and 530℃ for 4h. The cross-section observation for nitrided specimens was investigated by an optical microscope (OLYMPUS), and XRD phase analysis (D/MAX Ultima+, Cu Kα) of the obtained diffusion layers were examined.

3. Results and discussion

Fig.2 exhibits the cross-sectional micrographs of specimens nitrided in different potentials at 430℃ and 480℃ for 4h. At 430℃, all the specimens have similar cross-section morphology -the surface is white bright layer, while the thickness of nitrided layers varies via different potential conditions. However, the specimens at 480℃ behaves a little differently via different potentials, as the precipitation of chromium can be clearly observed in the nitrided layer in floating and cathode potentials, which suggests the corrosion resistance of nitrided layers deteriorated. However, the sample in anode potential at 480℃ still presents uniform modified layers.

Fig.3 indicates the variation of nitriding layer thickness with nitriding temperature. At all temperatures, it is found that the order of nitriding layer thickness is that cathode potential is greater than anode potential than floating potential. In the same HCD auxiliary nitriding device, the cathodic potential nitriding efficiency of low alloy steel is also higher[12]. Under the action of cathodic potential, the surface temperature of the sample will be increased by ion bombardment[13]. On the other hand, ion bombardment can cause a large number of slip systems and defects. However the anion sputtering on the specimens may decrease the diffusion of nitrogen and chromium which impedes migration of nitrogen and chromium atoms to form CrN.

The XRD results in Fig.4 revealed that the specimens are composed of expanded austenite, which are nitrided in anode potential at 480℃ [14]. The existence of chromium nitride in the modified layers in floating and cathode potentials at 480℃ is also confirmed by XRD patterns, which is consistent with the decrease of corrosion resistance of the nitrided layers in floating and potentials in Fig. 2. It should be noticed that the d spacing of the {200} plane with cathode potential specimen is higher than that of the floating and anode specimens, suggesting that cathodic ion bombardment causes higher nitrogen concentration in S phase.

Fig. 5 indicates the case hardness of nitrided specimens at 430 ℃ - 510 ℃ for 4h. All surface microhardness measurements were carried out with a Vickers diamond indenter under the load of 50 g. The results show that the case hardness of all nitrided specimens increases with the treatment temperature, regardless of the potential. The main reason for the increase of hardness is the formation of compressive stress and deformation in the high nitrogen rich layer. The specimens nitrided at low temperature (430℃) with different potentials indicate similar surface hardness of Hv300-370. Because the nitrided layer obtained at 430 ℃ is relatively thin, the case hardness partly reflects the hardness of the soft substrate. For the samples with thicker nitrided layers obtained above 450℃, the hardness difference of samples with different potentials at the same temperature reflects the difference of nitriding layer thickness, which is consistent with the results of nitrided layer thickness in Fig. 3.

4. Conclusions

The 304 austenitic stainless steel were effectively nitrided assisted with HCD in floating, anode and cathode potentials and the shortcomings of traditional DC plasma nitriding are totally eliminated. Nitrided layers in cathode potential leads to a thicker nitried layer than the specimens in floating and anode at the same temperature. The defects produced by cathode ion bombardment might benefit the nitriding efficiency of the specimens in cathode potential. When specimens nitriding at 480℃ in floating and cathode potentials, CrN formed in the nitried layer leads to a sharp decrease in corrosion resistance.
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References
[1] L.C. Gontijo, R. Machado, S.E. Kuri, L.C. Casteletti, P.A.P. Nascente 2006 Corrosion resistance of the layers formed on the surface of plasma-nitrided AISI 304L steel Thin Solid Films 515 p 1093
[2] Esfandiari M, Dong H 2007 The corrosion and corrosion-wear behaviour of plasma nitrided 17-4PH precipitation hardening stainless steel Surf Coat Technol 202(3) p 466
[3] L. Trabzon, M.C. Igdir 2006 On the materials properties of thin film plasma-nitrided austenitic stainless steel Surface and Coatings Technology 200 p 4195
[4] Y. Sun, X. Y. Li, T. Bell 1999 X-ray diffraction characterisation of low temperature plasma nitrided austenitic stainless steels Journal of Materials Science 34 p 4793
[5] Kim Sang-Gweon, Yeo Kook-Hyun, Cho Yong-Ki, Okumiya Masahiro 2018 The Phenomenon of High Hardness Values on the S-Phase Layer of Austenitic Stainless Steel via Screen Plasma Nitriding Process Advances in Materials Physics and Chemistry 08 p 257
[6] Samandi M., Shedden, B.A., Smith, D.F.I., Collins, G.A., Hutchings, R., Tendys 1993 Corrosion and Tribological Behaviour of Plasma Immer-sion Ion-Implanted Austenitic Stainless Steel Surface and Coatings Technology 59 p 261
[7] L. Han, J.T. Dai, X.R. Huang, C. Zhao 2013 Study on the Fast Nitriding Process of Active Screen Plasma Nitriding Physics Procedia 50 p 94
[8] L. Kenéz, N. Kutasi, E. Filep, Laszlo Jakab-Farkas 2018 Anodic Plasma Nitriding in Hollow Cathode (HCAPN) 73 p 96
[9] Fontoura Cristian Padilha, Rodrigues Melissa Machado, Garcia Charlene Silvestrin Celi 2020 Hollow cathode plasma nitriding of medical grade Ti6Al4V: A comprehensive study Journal of biomaterials applications 35 p353
[10] Yu. G. Khusainov, K. N. Ramazanov 2019 Local Ion Nitriding of Martensitic Structural Steel in Plasma of Glow Discharge with Hollow Cathode Inorganic Materials: Applied Research 10 p544
[11] E. Menthe, K.T. Rie 1999 Further investigation of the structure and properties of austenitic stainless steel after plasma nitriding Surface and Coatings Technology 116-119 p 199
[12] Duralar Technologies LLC 2020 Plasma Nitriding With Pecvd Coatings Using Hollow Cathode Ion Immersion Technology in Patent Application Approval Process (USPTO 20200140988) [J]. Energy Weekly News
[13] Chen, Li, Ji, Khan, Fuentes 2013 Nanomechanical properties of duplex treated 42CrMo4 steel Surface Engineering 29 p 462
[14] Liang Wang, Shijun Ji, Juncai Sun 2006 Effect of nitriding time on the nitrided layer of AISI 304 austenitic stainless steel Surface & Coatings Technology 200 p 5067