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Surface catalysis gaseous nitriding of alloy cast iron at lower temperature☆

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ABSTRACT

In this paper, the gaseous nitriding at lower temperature and nitriding mechanism from a surface catalysis were studied. Alloy cast iron supported by catalysts on its surface were prepared by alternating currents precipitation way (ACPW) which generates the catalytic surface. The subsequent catalytic decomposition of ammonia and surface adsorption of the free nitrogen were greatly enhanced by the catalysts on its surface. Hence, the nitriding kinetics was improved from 360 °C to 500 °C, and the diffusion activation energy of nitrogen atom was decreased. These works not only study the surface catalysis nitriding mechanism, but also solves the problems in nitriding process. This work widens the field of surface catalysis application.

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1. Introduction

Nitriding is a chemical treatment widely used to form surface nitrides on metal workpiece, which will improve the surface hardness and corrosion resistance by forming of Fe-nitride compounds or nitrogen solid solution. It is well known that gaseous nitriding processes are performed at high temperatures (above 510 °C) for a long duration (up to 80 h) [1]. The high temperatures and long time treatment may induce the porosity in the nitride layer, especially for thin-walled parts example for cylinder liner, which may induce serious parts deformation leading to parts failure. Moreover, the traditional gaseous nitriding technique is using up too much energy and resources.

Recently, the projects about decreasing the nitriding temperature and shorten its duration have attracted great attentions. The researches about gaseous nitriding at lower temperature mainly focus on nitriding by nanocrystallization or nanomaterial. Lu's group reported that the nitriding temperature could be as low as 300 °C depending on the nanocrystallized outer surface of parts (SMAT treatment) [2,3]. However, its nanocrystallization pretreatment was limited by the complex geometry of parts. Inia and Vredenberg reported that gaseous nitriding using NH_3 decomposition on the surface of Fe coated Ni nanoparticles (25 nm) at 325 °C [4]. Ni will prevent the oxidation of Fe by gas impurities and work as NH_3 decomposition catalyst. However, two points is noticeable. Firstly, Ni/Fe bilayer was deposited onto Si substrate using e-beam evaporation. The particle size of Ni/Fe nanocomposite should be in nanometer level, which is similar with nanocrystallization nitriding. Moreover, the effect of oxygen should be discussed. There are some reports which show that the preoxidation nitriding will accelerate the diffusion velocity of nitrogen atom [5]. Baranowska et al. reported gaseous nitrided austenitic stainless steel by electrochemically polished treatment prior to nitriding at 400 °C and 450 °C [6]. However, nitriding is not success for the unpolished treatment at the same conditions. It is a pity that they do not pay enough attention to the relation between the pretreatment and nitrided mechanism at lower temperature. In order to decrease nitriding temperature, it suggests that pretreatment before nitriding is necessary based on previous research.

Generally, as to the bond energy of molecular nitrogen is too high to form free nitrogen atom, it is difficultly to form a nitrided layer on workpiece by using molecular nitrogen as gas resource. For example, Emmett et al. tried and failed to form iron nitride by the action of nitrogen at pressures as high as 200 atmospheres on iron between temperature of 400 °C and 700 °C [7]. On the contrary, highly purified iron powder was successfully nitrogenated at temperature as low as 500 °C [8]. From those results, it should be noticed that the surface morphology and microstructure of samples play an important role during the formation of nitrides. Understanding of the nitriding mechanisms at the lower temperature is still a big challenge in theory and experiment. More important, lower temperature nitriding (<500 °C) might opens new possibilities for greatly improving the tribological performance whilst retaining or even enhancing the excellent corrosion resistance of the untreated material.

Alloy cast iron contains alloying elements (usually nickel, chromium, copper or molybdenum) to increase the strength or

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facilitate heat treatment. Herein, alloy cast iron with catalyst on its surface were prepared and then successfully nitrided at lower temperature in order to improve wear resistance and corrosion resistance used as cylinder linear.

2. Experimental

The compositions of alloy cast iron were presented in Table 1. The samples with the size of 20 mm × 10 mm × 5 mm were firstly annealed at 870 °C for 2 h in order to eliminate stress and later ACP pretreatment prior to nitriding. The pretreatment way refers to our paper [9,10]. The cobalt chloride was added in the electrolyte solution to improve catalytic active. The pretreatment samples were nitrided at temperature of 360 °C, 400 °C, 450 °C, 480 °C for 10 h, and 500 °C for 4 h, respectively.

The samples were investigated as follows: cross section metallography of nitrided layers and the thickness of the compound layers were measured by optical microscope; the diffusion zone thickness was determined by microhardness measurements with unit-load 200 g on cross section of nitrided layer. The distance from the outer surface where the microhardness was 50HV higher than that in matrix was recognized as the thickness of diffusion zone with HV microhardness tester.

3. Results and discussion

Nitriding is a dissociative chemisorption process that takes a few steps of surface reactions including of decomposition reaction of ammonia, adsorption, interface reaction and reaction diffusion [11]. In general, it is considered that nitriding depends on nitriding temperature and time, and reaction diffusion is the rate-determining step during gaseous nitriding process. Our experiments suggest that the surface morphology and microstructure play an important role on the nitriding process. The samples pretreated have similar the surface morphology of the papers [9,10]. The EDS patterns of the pretreatment samples were shown in Fig. 1. Comparing with the results in Table 1, there are several new elements existing on the surface of pretreatment samples. According to line scan of the surface, the atomic ratio of cobalt is up to 3%. Cobalt and its compounds have high activity and stability for the synthesis and decomposition of ammonia [12–14]. The other is chlorine which performs cleaning powder for surface fats oils and oxides.

Both of cobalt and chlorine come from the electroplating bath, which size is no less than nanometer. The fresh and active surface has high catalytic activity for ammonia decomposition and [N] absorption as shown in Fig. 2. Comparing with raw samples, the decomposition rates of ammonia increased notably. This result might attribute to the catalytic activity of cobalt, manganese, nickel and iron deposited by ACPW, which is the catalyst for the synthetic ammonia and ammonia decomposition reaction [11,12]. When increasing the nitriding temperature from 400 °C to 500 °C, the decomposition rates of ammonia increased from 5.0% to 15.2%. The ammonia decomposition rate of pretreatment samples is about 5 times higher than unpretreated sample at the same conditions. Ni catalyst deposited on the surface play a key role in the decomposition of ammonia and the absorption of free nitrogen [N] at lower

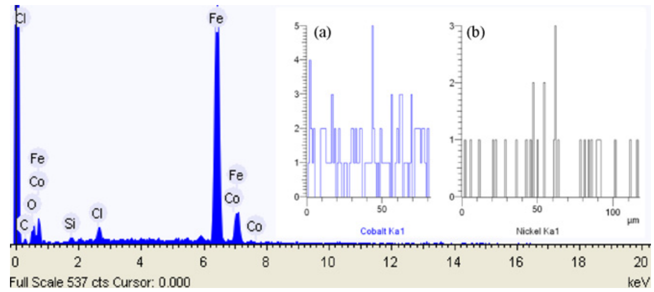

Fig. 1. EDS patterns of the pretreated samples. Inserted the line scan of cobalt (a) and nickel (b).

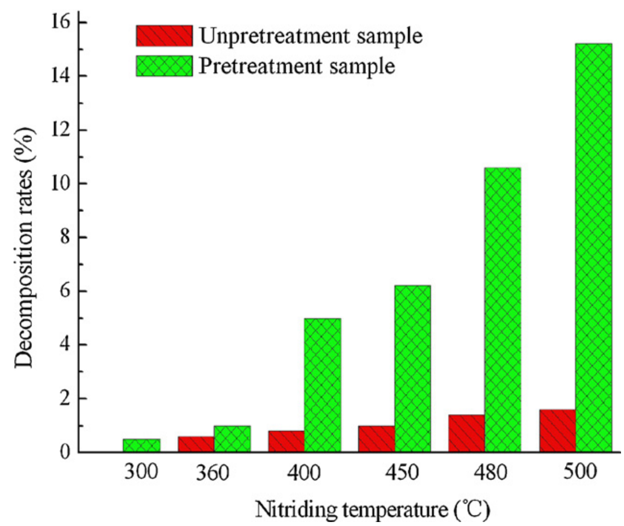

Fig. 2. A histogram is the decomposition rates of NH_3 (%) when the flow rate of NH_3 is 100 ml/min at different nitriding temperature.

temperature. The nanomaterials catalysts have high ratio surface area and high surface energy, and show much higher catalytic activity than traditional catalysts. Our experimental results also confirm the enhanced catalytic property of nanomaterials. And of course, it is necessary to further complete the chemical identification and analysis.

Catalyst will improve decomposition rates and produce [N] absorbed efficiently on the surface at lower temperature. On the other hand, it fails to observe compound layer or diffusion zone for unpretreated sample at the same conditions. It suggests that catalyst can greatly increase the number of active centre and play a very important role on the formation of compound layer. Baranowska reported that the compound layer developed rapidly on the surface during the subsequent nitriding after cathode sputtering [15]. It was also successful for Mijiritskii and Boerma on nitriding by the Ni/Fe deposition the substrate at 300 °C [16]. It is notable that Ni cap layer work as a catalyst and allowed to produce pore-free Fe-nitride layers. The thickness of nanocrystallization obtained by either ACPW, or cathode sputtering treatment, or other pretreatment is much thinner than that obtained by SMAT. However, the same nitriding results were all obtained at the lower temperature. As to the effects of surface nanocrystallization, it will improve the

Table 1
Composition of alloy cast ion.

Element	C	Si	Mn	Cu	Cr	B	P	S
Concentration (%)	2.8–3.2	1.6–2.0	0.7–1.0	0.8–1.2	0.25–0.4	0.03–0.05	0.15–0.25	<0.12

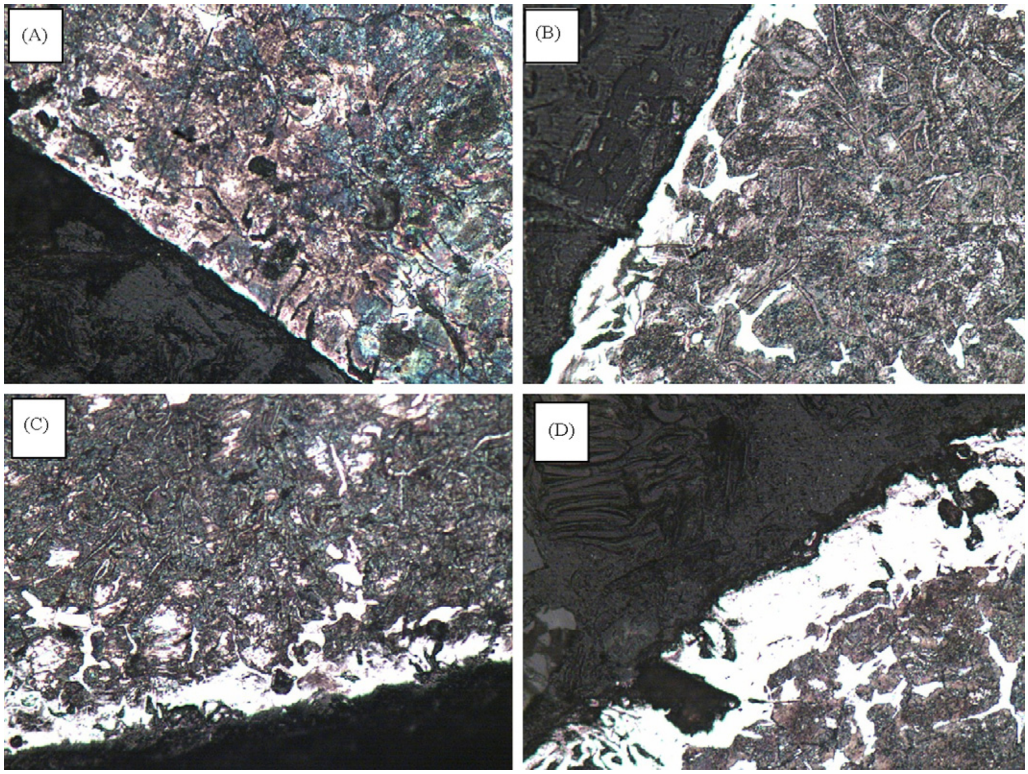

Fig. 3. Cross-sectional OM of samples nitrided at different temperatures (200×) for 10 h. (A) 360 °C, (B) 400 °C, (C) 450 °C, and (D) 480 °C.

catalytic activity and interface reaction other than provide reaction diffusion channel. Combine with the previous results on nitriding at lower temperature, we found the pretreatment prepared using nanocrystallization, or deposition, or cathode sputter is the crucial factor to decrease nitriding temperature and improve diffusion rate.

The cross-sectional OM of samples nitrided at different temperatures was shown in Figs. 3–5. With the nitriding temperature increasing from 360 °C to 480 °C, the thickness of compound layer and diffusion zone will increase. Compared with the pure iron, there are lots of alloy elements in alloy cast iron which will disturb the nitrogen diffusion. The surface microhardness and cross-sectional microhardness were shown as Figs. 6 and 7, respectively. However, there is a compound layer at 360 °C and surface hardness can reach up to 632HV. The thickness of continuous compound layer is about 5 μm and the microhardness is 727HV at 400 °C. Compound layer creased to 10 μm in thickness and the microhardness is 766HV at 480 °C. It is notable that both the compound layer and surface hardness are growing quickly and peak at 30 μm in thickness and 991HV in hardness at 480 °C. Nitrogen concentration of compound layer is about 12.3% at atomic rate as shown by EDS analysis in Fig. 4. Base on the Fick diffusion law, as the temperature increase, the diffusion of nitrogen atom will be faster. It is also agreement with the catalytic nitriding. When temperature is increase to 500 °C only for 4 h nitriding duration, there is continuous compound layer with about 20 μm in thickness and microhardness is up to 876HV. According to the microhardness curves along with the depth, the nitriding depth is up to 70 μm which is deeper than surface nanocrystallization nitriding [2]. The influence of catalyst on the complex compound layer including of ε-$Fe_{2\text{-}3}N$ and γ-Fe_4N will be analysis in other paper.

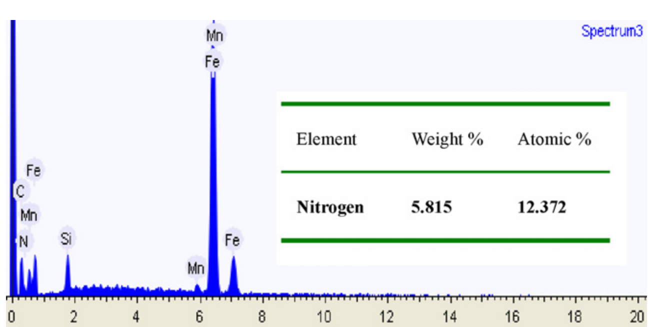

Fig. 4. EDS patterns of the pretreatment samples at 480 °C for 10 h. Inserted is nitrogen concentration by line scan.

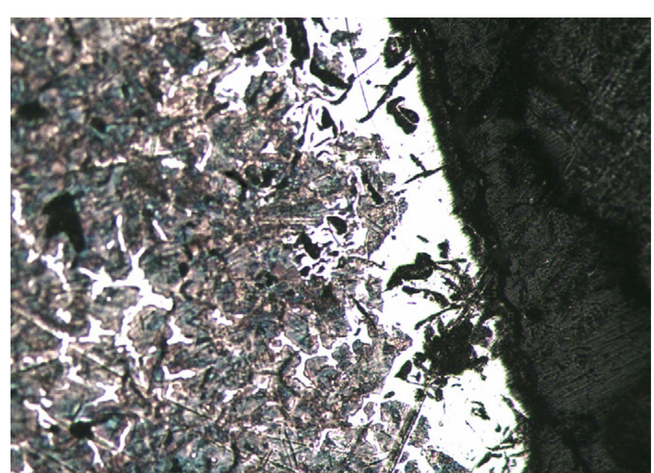

Fig. 5. Cross-sectional OM of samples nitrided at 500 °C for 4 h.

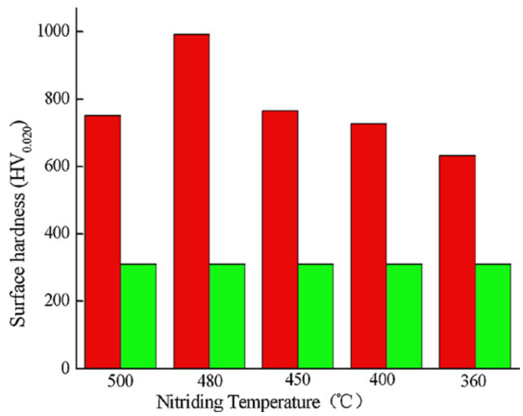

Fig. 6. Red color histogram of surface microhardness varying with temperature. Blue color histogram is the core microhardness. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

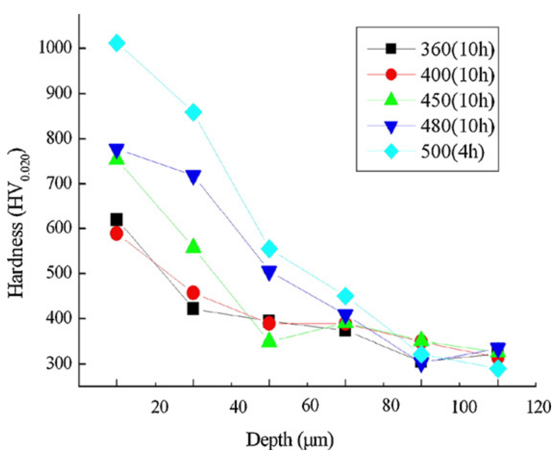

Fig. 7. Microhardness curves along the depth from the top surface layer to the substrate.

In summary, we achieved the surface catalysis gaseous nitriding of alloy cast iron at lower temperature. The results indicated that the hardness, thickness and bright layer could be controlled by nitriding temperature and time. Based on our experimental results, it concluded that pretreatment of alloy cast iron will change the mechanism for the formation of the diffusion layer, that is to say, the gas–solid with adsorption and interface reaction were the rate limiting step. Although the diffusion depends on the temperature and nitriding potential of the atmosphere, it believe that the surface reaction kinetics determines the rate of the total process.

4. Conclusion

In conclusion, alloy cast irons with the catalyst on the surface were prepared and then were successfully nitrided at lower temperature. Catalyst could enhance ammonia decomposition and the free nitrogen adsorption, hence, the gas–solid adsorption and interface reaction were the rate limiting step in the nitriding process. The experiment provides the new understanding on nitriding mechanism, which will attach importance to surface catalysis gaseous nitriding both in theoretical analysis and applicable research.

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