

COMPARISON OF SALT BATH PREOXIDATION AND AIR PREOXIDATION FOR SALT BATH NITRIDING

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Abstract

Salt bath preoxidation was primarily conducted prior to salt bath nitriding, and the effect on salt bath nitriding was compared with that of conventional air preoxidation. Characterization of the modified surface layer was made by means of optical microscopy, scanning electron microscope (SEM), micro-hardness tester and x-ray diffraction (XRD). The results showed that the salt bath preoxidation could significantly enhance the nitriding efficiency. The thickness of compound layer was increased from 13.3 μm to 20.8 μm by salt bath preoxidation, more than 60% higher than that by conventional air preoxidation under the same salt bath nitriding parameters of 560 $^{\circ}\text{C}$ and 120min. Meanwhile, higher cross-section hardness and thicker effective hardening layer were obtained by salt bath preoxidation, and the enhancement mechanism of salt bath preoxidation was discussed.

Keywords: peroxidation, salt bath nitriding, microstructure, hardness

1 Introduction

Salt bath nitriding is a kind of valuable chemical heat treatment widely used for steels to obtain the required properties [1-3]. Compared with other nitriding technologies, salt bath nitriding has obvious advantages, such as with better quality and lower cost [4-6]. After salt bath nitriding, a compound layer is formed, which can significantly improve the performance of metal [7-9]. However, for obtaining the effective thickness of nitrided layer, the nitriding temperature or holding time must be increased [10-12], which would bring out porosity in the nitrided layer, thus may results in side effect on the surface hardness and wear resistance.

It has been reported that preoxidation can enhance the nitriding efficiency, since a thin oxide layer is formed during preoxidation process, which can be decomposed during the followed nitriding process [13, 14]. Traditionally, preoxidation process is conducted in air furnace before salt bath nitriding [15, 16]. Unfortunately, it is found that air preoxidation has little enhancement effect on salt bath nitriding [17, 18].

Based on the efficiency of salt bath nitriding is much higher than that of gas nitriding, it is valuable to study if salt bath oxidation could have much better enhancement effect on salt bath nitriding. Therefore, the goal of this research is to investigate if salt bath oxidation can bring out much better enhancement effect on salt bath nitriding than that of conventional air preoxidation.

2 Experimental

AISI 1045 steel was selected as the substrate material with the chemical composition (wt.%) of: 0.46 C, 0.17 Si, 0.52 Mn, 0.24 Cu, 0.21 Ni, 0.23 Cr, 0.022 S, 0.023 P, and balance Fe. The specimens were machined into a size of 10mm×10mm×10 mm, followed by quenching at 860°C and tempering at 600°C to get uniform microstructure. Then the mechanically polished specimens were treated with emery papers of different granulometry (240, 500, 1500 and 2000 mesh) to achieve a mirror finish. Finally, the specimens were ultrasonically cleaned in anhydrous ethanol and dried before salt bath nitriding treatment. The major chemical constituents of preoxidation salt bath medium are sodium hydroxide (NaOH), sodium nitrate (NaNO₃) and sodium carbonate (Na₂CO₃).

The main treating process was composed of three steps: preoxidation, salt bath nitriding and cooling. Firstly, the samples were preoxidation to 350°C for different time (45, 60min) in air furnace or in salt bath oxidation medium and then nitrided in salt bath nitriding medium at 560°C for 120min. Finally, samples were cooled in water.

The cross sectional microstructure was observed by optical microscopy and the surface of samples was observed by scanning electron microscopy (SEM). Hardness measurements were made in a HXD-1000TMC micro-hardness tester, with the test load of 10g and holding duration of 15s. Each hardness value was determined by averaging at least 5 measurements. The phase constituents were determined by X-ray diffraction (XRD) with Cu-K α ($\lambda = 1.54 \text{ \AA}$) radiation.

3 Results and discussion

3.1 Cross-sectional microstructure and depth analysis

Fig. 1 presents the cross-sectional microstructure of specimens nitrided at 560°C for 120min with different preoxidation method. It clearly shows that compound layer (also called white layer) is formed at the outermost surface after salt bath nitriding under different conditions and the thickness of compound layer is significantly increased by salt bath preoxidation, the thickness of compound layer of 13.3 μm by APON is increased to 20.8 μm by SPON, more than 60% increased. This indicates the salt bath preoxidation can improve the efficiency of salt bath nitriding.

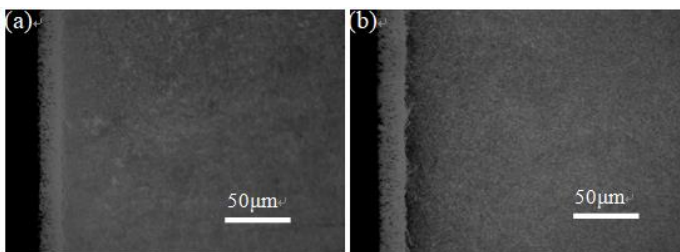


Fig. 1 The cross-sectional microstructure of specimens nitrided at 560°C for 120min with different preoxidation methods (a) APO 350 °C×45 min; (b) SPO 350 °C×45 min

3.2 Micro-hardness profile

Fig. 2 shows the micro-hardness profile of specimens nitrided at 560°C for 120min with different preoxidation methods. It clearly shows that the cross-section micro-hardness can be significantly increased by salt bath nitriding with different preoxidation methods. The specimen treated by SPON has higher cross-section micro-hardness than that treated by APON. Meanwhile, the effective hardening layer thickness, defined as the layer with hardness 50HV_{0.01} higher than that

of substrate, is evidently increased with salt bath preoxidation. This indicates the salt bath preoxidation enhancement effect on salt bath nitriding is greater than air preoxidation.

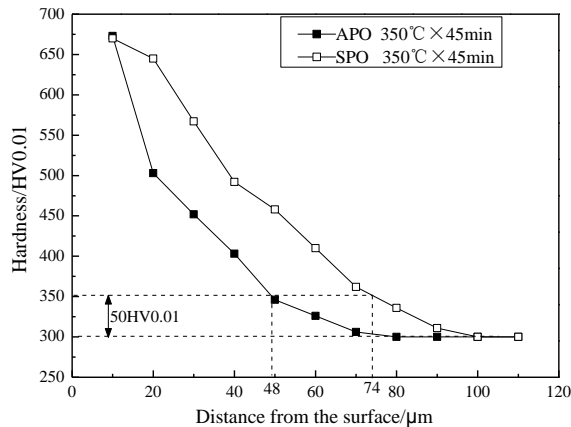


Fig. 2 The micro-hardness profile of specimens nitrided at 560°C for 120min with different preoxidation methods

3.3 XRD analysis

Fig. 3 shows XRD diffraction patterns of samples after different preoxidation methods. It clearly shows that though Fe_3O_4 phase formed on the surface after different preoxidation process, the relative content of Fe_3O_4 is different, which can be obtained by calculating the ratio of the strongest peak of Fe_3O_4 to the strongest peak of $\alpha\text{-Fe}$ [19, 20], and it can be seen that the relative content of Fe_3O_4 treated by salt bath preoxidation is much higher than that treated by air preoxidation. Therefore, the salt bath preoxidation enhancement effect on salt bath nitriding is greater than air preoxidation. Meanwhile, when air preoxidation time increases to 60 min, the Fe_2O_3 phase is formed on the surface, which indicates that too long holding time results in excessive oxidation and is unfavorable for subsequent nitriding [21, 22].

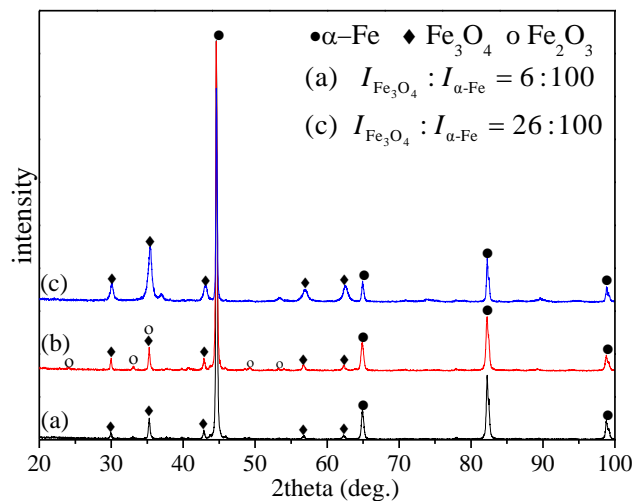


Fig. 3 XRD diffraction patterns of 45 steel samples treated by different preoxidation (a) APO 350°C×45 min; (b) APO 350°C×60 min; (c) SPO 350°C×45 min

3.4 Surface morphology

Fig. 4 shows the surface morphology of sample treated by different preoxidation process. It clearly shows that the structure of oxide layer treated by air preoxidation is lamella in shape. But the sample treated by salt bath preoxidation has a rough oxide layer with a lot of nano- pores. Obviously the sample treated by salt bath preoxidation has bigger specific surface area than that treated by air preoxidation, thus has larger contact area with the active nitrogen atoms in salt bath nitriding medium. Therefore, the oxide layer formed by salt bath preoxidation is easier to be reduced by active nitrogen atoms than that formed by air preoxidation. Meanwhile, nano-pores can help the active nitrogen atoms to diffuse into the substrate.

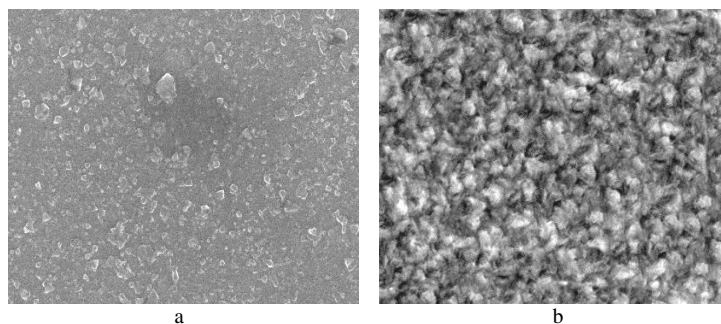


Fig. 4 The surface morphology of sample treated by different preoxidation methods (a) APO 350°C×45 min; (b) SPO 350°C×45 min

4 Discussion

During preoxidation reaction, the chemical bonds of NO_3^- (comes from NaNO_3) in salt bath preoxidation medium and O^2 in air are decomposed to generate active oxygen atoms by absorbing energy, and the bonding energy of O-N and O=O is 206kJ/mol and 498kJ/mol, respectively, which illustrates that O-N in salt bath medium is much easier to decompose and form active oxygen atoms than that of O=O in air. Therefore, the reaction between Fe and molten NaNO_3 is much faster than that between Fe and O_2 at the same preoxidation temperature, leading to higher relative content of Fe_3O_4 by salt bath preoxidation (**Fig. 3**). In addition, when air preoxidation time increases to 60min, the Fe_2O_3 phase is formed on the sample surface. This indicated that too much holding time result in excessive oxidation to form Fe_2O_3 phase, which was unfavorable for subsequent nitriding [22, 23]. Therefore, the enhancement effect of air preoxidation cannot be consistently increased through extended holding time.

Fig. 4 shows that the sample treated by salt bath preoxidation has bigger specific surface area than that treated by air preoxidation, thus the oxide layer formed by salt bath preoxidation is easier to be reduced by active nitrogen atoms. Meanwhile, nano- pores can help the active nitrogen atoms to diffuse inward to the substrate.

5 Conclusions

The effect of salt bath preoxidation and air preoxidation on salt bath nitriding was compared, and The results showed that salt bath preoxidation has better enhancement effect on salt bath nitriding. The thickness of compound layer is only 13.3 μm treated by air preoxidation, and increased to 20.8 μm treated by salt bath preoxidation while nitrided at 560°C for 120min. Meanwhile, the sample treated by salt bath preoxidation has higher cross-section hardness than that treated by air

preoxidation. The enhancement mechanism is that the sample treated by salt bath preoxidation has higher relative content of Fe_3O_4 , which can react with active nitrogen atoms in salt bath nitriding to accelerate the growth of Fe_3N .

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