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## Experimental and theoretical study on interaction between lanthanum and nitrogen during plasma rare earth nitriding

C.S. Zhang, M.F. Yan\*, Z. Sun

National Key Laboratory for Precision Hot Processing of Metals, School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China

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### ABSTRACT

In present work, the interaction between lanthanum (La) and nitrogen (N) during plasma rare earth nitriding of M50NiL martensitic steel is analyzed. Phase compositions, elemental contents as well as microhardness profiles of surface layers are investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and microhardness tester to observe the changes of the N contents in treated layers. The results of microhardness, XRD and EDS indicate that the addition of pure La can speed up the denitriding rate compared with the case without La addition. The XPS results reveal that the presence of the La–O and La–N bond reduces the peak intensity of the Me–N bond, which indicates that the addition of La element can reduce the N contents in nitrided layers through the surface oxidation and the attraction of La atoms. The theoretical thermodynamic calculations are employed to further clarify the denitriding function of the surface oxidation and the attraction between La and N atoms.

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### 1. Introduction

Plasma thermochemical treatments as an efficient and environmentally friendly process are widely applied in surface modifications [1]. Rare earth (RE) elements are usually employed in surface thermochemical treatments such as gas carburizing [2] and plasma nitrocarburizing [3] due to their benefits on improving the thickness [4] and mechanical properties of modified surface layers [5]. So far, the effect mechanisms of RE addition during plasma thermochemical treatments are still controversial. The questions concentrate mainly on whether the RE atoms can diffuse into surface layer or not and how they interact with N or C atoms. Works carried out by Yan et al. [6] and Cheng and Xie [7] indicate that the RE atoms could diffuse into the surface layer of steels (several micrometers depth) and will stay mainly at grain boundaries due to their relatively large atomic size (~40% bigger than the iron atom). This might lead to a production of distorted regions and some lattice defects such as dislocations and vacancies, providing fast-diffusion paths for N or C atoms. RE can also act as catalysts to increase nitrogen content in the near surface regions of steel specimens with respect to the improved surface hardness [8,9].

Most RE reagents are dissolved in ethanol in the forms of mixed compounds of RE salt and its oxide containing mainly La and Ce. In

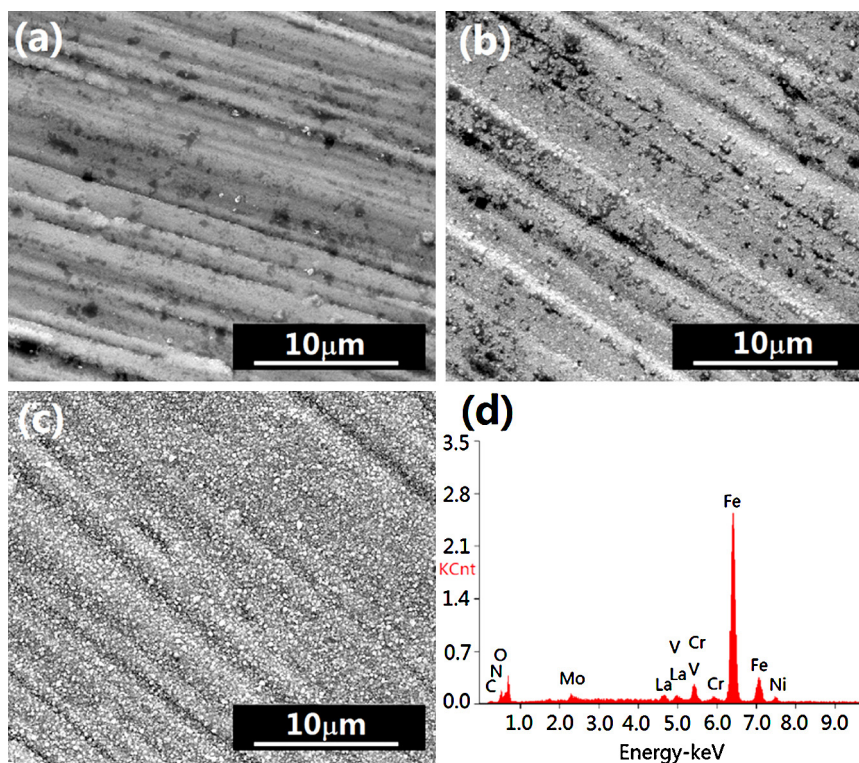
this work, a series of experiments were designed to clarify how La atoms interact with N atoms. Here, to study the interaction between La and N, plasma sputtering was carried out with pure La blocks to exclude other influencing factors (C from ethanol etc.).

### 2. Experimental

The M50NiL martensitic steel was selected as the substrate material with the chemical composition (wt.%) 0.13C, 4.1Cr, 3.4Ni, 4.2Mo, 1.2V, 0.13Mn, 0.18Si, 0.012P, 0.002S and Fe, balance. Before the plasma nitriding, the steel was solution treated at 1150 °C for 1 h. After that, the steel specimens were machined into the size of 12 mm × 12 mm. The flat faces of the specimens were polished by silicon carbide papers (#800), and then ultrasonically cleaned with alcohol and acetone before plasma treatments.

Plasma nitriding was performed using a LDMC-30 plasma nitriding unit. Before the application of a glow discharge, the furnace chamber was evacuated to 20 Pa by a rotary pump. Plasma nitriding was conducted at a constant furnace pressure of 300 Pa in a gas mixture containing N<sub>2</sub> and H<sub>2</sub> with the ratio of 1:5 at 400 °C for 4 h (the nitrided specimen was identified as N400, the last three numbers represent the treatment temperature). Then the nitrided specimens were divided into two groups (group A and B). The group A (identified as N400 + H560RE) was plasma sputtered (tempered) with La addition (six 2.3 g-blocks of pure La were hang above the specimens) at 560 °C for 6 h in the furnace containing mixed gas (H<sub>2</sub> and Ar) without N. The group B (identified as N400 + H560)

\* Corresponding author. Tel.: +86 451 86418617; fax: +86 451 86413922.  
E-mail addresses: [yanmufu@hit.edu.cn](mailto:yanmufu@hit.edu.cn), [prsm804@163.com](mailto:prsm804@163.com) (M.F. Yan).



**Fig. 1.** Surface morphologies of M50NiL steel plasma treated at (a) N400; (b) N400 + H560; (c) N400 + H560RE; (d) EDS results associated with (c).

was plasma sputtered without La and all other conditions were the same for group A.

The cross-sectional microhardness profiles of the treated specimens were determined with a microhardness tester (HV-1000) under an indentation load of 100 g for 20 s. Three microhardness indentations were made in each position of the same depth from the surface to prepare the microhardness profiles.

In order to define the phase composition of the treated layers, X-ray diffraction (XRD) with Cu K $\alpha$  radiation ( $\lambda=0.15405$  nm) was carried out in the range of glancing angles 20–100° at 40 kV and 50 mA with 0.05° interval step mode using a D/max-rB diffractometer. The existence of the N and La elements were analyzed using scanning electron microscope (SEM, FEI QUANTA 200 F) equipped with an energy dispersive X-ray analyzer (EDS). To make sure of the accuracy of the measured content profiles, ten points placed at the same depth would be tested.

X-ray photoelectron spectroscopy (XPS) was employed to clarify the chemical composition and states of the treated specimens accurately. The XPS analysis was performed using a Thermo Scientific K-Alpha spectrometer with a monochromatic Al K $\alpha$  (12 kV, 6 mA) excitation. The base pressure of the analytical chamber was 10<sup>-6</sup> Pa and the diameter of the analyzed area was 400  $\mu$ m. The high-resolution XPS spectra were collected using an analyzer pass energy of 50 eV and 0.1 eV steps after a survey scans (0–1350 eV). The collected spectra included the following elemental peaks: carbon (C 1s), nitrogen (N 1s), oxygen (O 1s), iron (Fe 2p) and lanthanum (La 3d). All peaks were calibrated by C 1s peak with binding energy of 285.0 eV.

The aims of the XPS data analysis were to determine the chemical states and relative amounts of all detected elements, which are based on the curve fitting of the XPS spectra. The XPS peaks fitting were performed using an available software (XPS Peak 4.1) with Gaussian (80%)–Lorentzian (20%) combination curves and Shirley background algorithm [10]. The relative amounts of detected

elements (C, N, O, Fe and La) were calculated as the following equation [11]:

$$C_x = \frac{(I_x/S_x)}{\sum_i(I_i/S_i)} \quad (1)$$

where  $I$  was the peak areas obtained from the XPS spectra after background correction and  $S$  was atomic sensitivity factors.

### 3. Results and discussion

Fig. 1 gives the surface morphologies of plasma treated specimens N400, N400 + H560 and N400 + H560RE. It can be seen that a large amount of fine particles overlaps on the surface of the N400 + H560RE specimens (see Fig. 1c) compared with the N400 and N400 + H560 ones (see Fig. 1a and b). Some particles are LaFeO<sub>3</sub> phase probably, which will be identified by the subsequent XRD results. The EDS results show that there is a considerable amount of La atoms with the content of 2.68 at.% on the treated layer.

The microhardness and N content profiles in the surface layer of the N400, N400 + H560 and N400 + H560RE specimens are shown in Fig. 2. Fig. 2b represents that both the microhardness of the N400 + H560RE and N400 + H560 specimens are lower than that of the N400 ones. The measured N contents in the surface layers by EDS (see Fig. 2d) exhibit the same evolution as the microhardness profiles, i.e. the lower microhardness corresponding to the lower N content. The N contents in the surface layers of the N400 + H560 and N400 + H560RE specimens dramatically decrease, due to firstly the inward diffusion of N atoms and secondly the denitriding process caused by the sputtering of Ar<sup>+</sup> or surface oxidation. Additionally, both the microhardness and N content of the N400 + H560RE specimens are slightly lower than those of the N400 + H560 ones, which imply that La atoms could further reduce N contents in the nitrided layers. It should also be pointed out that the La profile (see Fig. 2c) drops rapidly from a higher level on the treated surface (~2.68 at.%)

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