MICROWAVE PLASMA NITRIDING OF A LOW-ALLOY STEEL

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1. Introduction

A lot of work has been done and published on low pressure plasma nitridation including plasma generation by triode [1-5], r.f. [6,7] and ECR [8,9] discharges. The attention is being paid to these techniques because they promise better process control and higher ionisation compared with diode discharge. They are also more suitable for combining nitridation with PVD or CVD techniques to further improve the properties of processed material. The present paper reports on nitridation of a low-alloy commercial steel in an electron cyclotron resonance (ECR) plasma discharge. The main aim was to study an influence of the current density and the bias on the substrate as well as the gas mixture composition and the temperature of the sample on structure and properties of the nitrided layer.

2. Experimental

The plasma was generated in an RR250PQ ECR source. The reactor has 250 mm diameter and the generator, working at the frequency of 2.45 GHz, is capable to run up to the power of 3 kW.

The substrates made from CSN 15 330 constructional steel were 5 mm thick tablets, 25 mm in diameter. They were ground, polished and then ultrasonically cleaned in ethanol before introducing them into a vacuum chamber. After placing the sample on a substrate holder with an auxiliary heater in a downstream chamber 250 mm away from an output aperture of the ECR reactor, the chamber was evacuated to a pressure lower than $4x10^{-4}$ Pa. Prior to nitriding, samples were sputter cleaned in Ar-H_2 mixture for 15 min to remove a surface oxide layer. The chamber was evacuated again to the base pressure and then the substrates were nitrided under desired conditions. The nitridation was performed in pure nitrogen and in a nitrogen-hydrogen mixture with up to 50 vol% of hydrogen. The substrates were held at the temperatures from 300 to 550 ^{o}C which were measured with a thermocouple introduced into the samples. The incident microwave power was changed from 600 to 1200 W. The pressure varied from 0.15 to 0.31 Pa. The applied substrate bias was in the range from -1000 V and +40 V with respect to the grounded chamber. The treatment times were 2 and 3 hours.

X-ray diffraction analysis, GD-OES (glow discharge optical emission spectroscopy) elemental depth profiling, microhardness testing and optical microscopy were performed in investigation of the treated surfaces.

3. Results

In Fig. 1 the microhardness depth profiles in nitrided steels are shown for various nitriding temperatures at fixed values of the nitriding time, substrate bias and pressure of pure nitrogen. It is seen that nitridation leads to a significant increase in the microhardness of the subsurface region at 500 and 550 °C whereas only poor and no nitriding effect was observed at 400 and 300 °C, respectively.

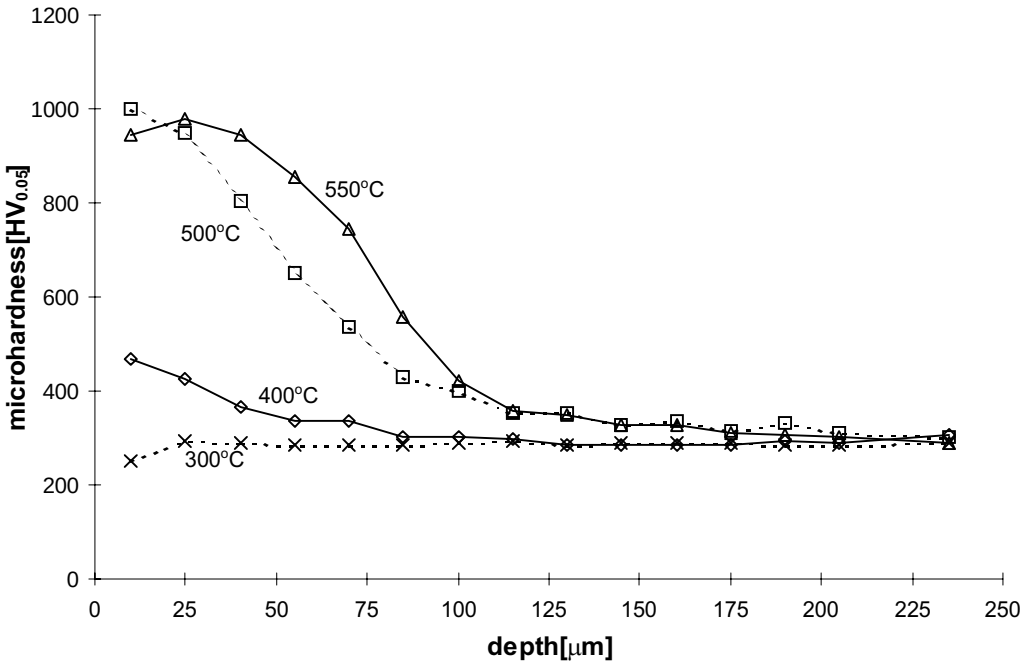

Fig. 1. Microhardness depth profiles for different nitriding temperatures. Nitrided for 2 hours in pure N_2 atmosphere at the bias of -500 V and the pressure of 0.15 Pa. Measured with the Vickers indentor at the load of 50 gf.

For the temperature of 500 to 550 °C the microhardness values from 1100 to 1280 $HV_{0.05}$ were achieved at the surface when the hardness of the untreated steel was 260 $HV_{0.05}$. The temperature had an influence on the thickness and especially on the microhardness profile of the diffusion layer. Its thickness was in the range from 0.09 to 0.10 mm and from 0.11 to 0.12 mm for the temperature of 500 and 550 °C, respectively. The 3 hours treatment time increased the thickness of the diffusion layer by about 15 %. There was

not observed any strong influence of the pressure, bias or gas mixture composition changes on the diffusion layer thickness and microhardness profile shape at a fixed temperature.

From the optical microscopy investigation of the sample cross-section after the nital etch it was possible to determine the compound layer thickness. Its value is strongly dependent on the temperature, bias on the substrate and gas mixture composition. It was found to be around 0.2 μm for 400 °C, 1.5 to 2.5 μm for 500 °C and 3.2 to 4.5 μm for 550 °C at the 2 hours treatment. Both increasing the negative bias and hydrogen content in the nitriding atmosphere decreases the thickness of the compound layer whereas a prolonged treatment increases it.

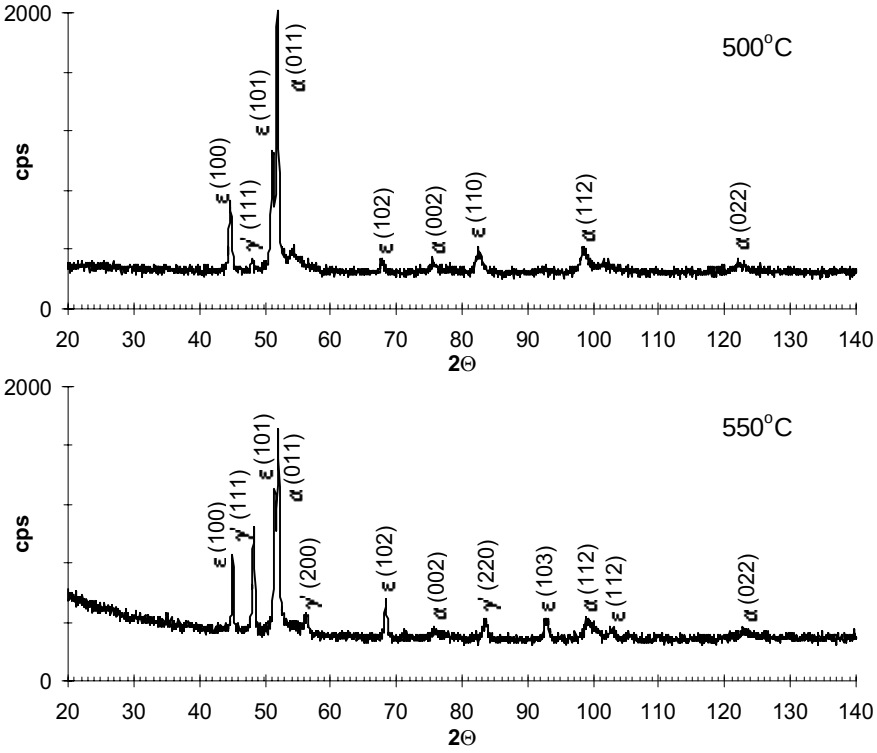

Fig. 2. XRD-patterns of the samples nitrided at 500 °C and 550 °C for 2 hours in pure N_2 at the bias of -500 V and the pressure of 0.25 Pa. The peaks of α-Fe, ε-$Fe_{2\text{-}3}N$ and γ'-Fe_4N are observed.

The X-ray diffraction scans in Fig. 2 provide information on a phase composition of the compound layers. Besides the peaks from the substrate, a presence of the ε-$Fe_{2\text{-}3}N$ phase with a trace amount of the γ'-Fe_4N phase is observed at the surface of the sample nitrided at 500 °C. The higher processing temperature of 550 °C leads to the increase in the content of the γ'-Fe_4N phase, see Fig. 2. Very small peaks of the ε-$Fe_{2\text{-}3}N$ phase were found in the XRD scans of the samples nitrided at 400 °C for 2 hours and no nitride reflections appeared in the scans of the samples nitrided at 300 °C.

The GD-OES elemental depth profiling showed near-surface maximum nitrogen concentrations in the range from 13 to 23 wt% in a dependence on the process parameters. Higher processing temperature increases not only the thickness of the strongly nitrogen-enriched subsurface region but also the nitrogen concentration in the depth of several tens of μm. For example, the concentrations of the nitrogen in the depth of 30 μm were found to be between 0.33 and 0.75 wt%, and between 0.88 and 1.10 wt% for the samples nitrided for 2 hours at 500 °C and 550 °C, respectively. The prolonged 3 hours treatment, carried out under the same conditions, increased the corresponding nitrogen concentrations in the 30 μm depth by about 100%.

4. Conclusion

The used configuration for plasma nitriding in a downstream zone of the microwave system with electron cyclotron resonance provided very good results in nitriding of a low-alloy steel at usual temperatures (500 °C and 550 °C), however, its effectiveness decreased considerably at lower temperatures (400 °C).

Acknowledgements

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