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ACTIVATION OF SURFACE IN GAS NITRIDING PROCESS

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ABSTRACT

The authors carried out tests on the possibility of intensifying the introduction of nitrogen into materials by increasing the number of active centres on the material surface. The effect was obtained by prepreparing the surface through bombarding the samples by nitrogen ions accelerated in high-voltage electric field. Later the samples were treated by nitriding in gas atmosphere.

The influence of cathode sputtering parameters on the thickness of nitride layers was investigated. Parameters of sputtering process such as voltage, intensity and time were changed. Moreover, the roughness of the samples after cathode sputtering was measured. It was observed that the higher voltage and intensity were, the thicker nitride layer and the higher content of ε phase were obtained. Time of sputtering had no influence on the thickness and morphology of compound case as well.

KEY WORDS

Gaseous nitriding, cathode sputtering, nitriding kinetics

INTRODUCTION

Chemical reactions during gas nitriding occur in the metal-gas interface. The formation and growth of the surface layer will depend on the relationship between the quantity of the nitrogen atoms (adsorption) and speed of its penetration into the material (absorption) and back into the atmosphere (desorption). If we take gas ammonia as nitrogen carrier then its decomposition takes place on the surface in so called active centres [1, 2].

Activation of the surface before or during nitriding is a very common treatment, which enables the intensification of surface reaction during nitriding. In the present paper the cathode sputtering is suggested as an activation process and its influence on kinetics layer formation was investigated.

Previous investigations of cathode sputtering and its influence on layer formation during gaseous nitriding showed the increase in nitriding kinetics. The thickness measurements of

nitride layer revealed the significant growth of thickness for all the ranges of atmospheres used in comparing with layers after nitriding without cathode sputtering [3-5] – fig. 1.

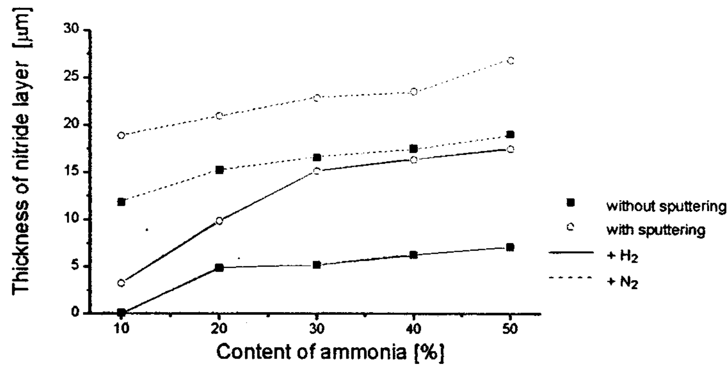

Fig. 1. Thickness of nitride layers after 3 hours of treatment for various nitriding atmospheres.

It was also observed that after cathode sputtering a compound layer developed rapidly on the iron surface during the subsequent nitriding. After 10 mins. the continuous compound case was noticed [3-5] – fig. 2. For samples that had not been pre-treated such a case was even after 1 hour observed.

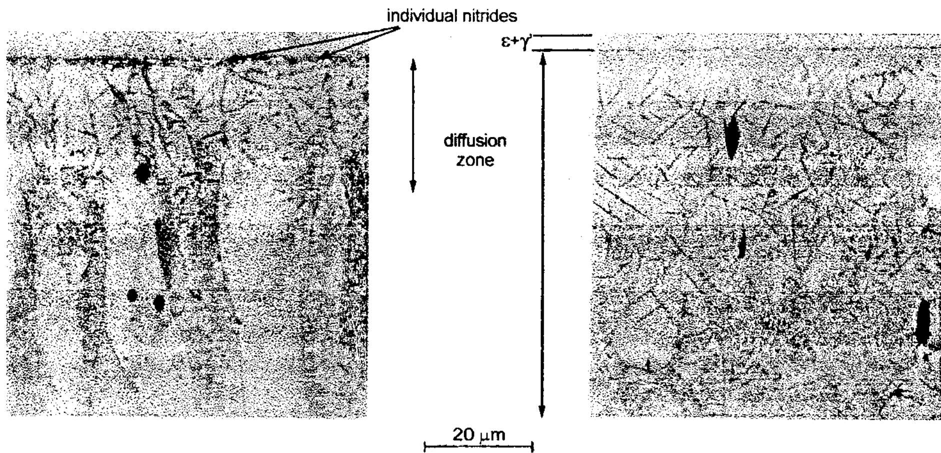

Fig. 2. Cross-section of layers after gaseous nitriding in atmosphere 50%NH_3+N_2, 843 K, after 10 mins. of the treatment: a – without and b – with cathode sputtering

Cathode sputtering process consists in surface bombardment by ions accelerated in the electric field [6]. As a result, the atoms adsorbed on the surface are removed. Moreover defectiveness of upper surface increases and the shape of surface is changed. The latter is observed as a roughness increase of the roughness [7]. Voltage, current intensity (connected with number of ions accelerated in electric field), sputtering time and kind of gas used are the principal parameters of the sputtering process. In the paper the influence of cathode sputtering parameters on kinetics of nitriding was investigated.

EXPERIMENTAL

The experiments were carried out on the samples made of αFe 2x6x20 mm in size. The nitriding atmosphere consisted of ammonia 50%NH_3+$NH_{3dys.}$. Time of nitriding process was 1 hour, temperature 843 K.

The process of cathode sputtering was carried out in a separated chamber. The sample was connected as a cathode. The sample after sputtering was introduced into the reaction zone of the furnace. The whole stand for pre-treatment and nitriding was presented in the previous papers [5, 8].

The nitrogen was used as a sputtering gas. The previous investigation [5, 8, 9] showed that the kind of sputtering gas had no important influence on both the kinetics of layer formation and layer morphology.

Cathode sputtering processes were carried out for parameters that changed in ranges as in Table 1.

Table 1. Ranges of cathode sputtering parameters used in experiment

Voltage [V]	Intensity [mA/cm^2]	Time [mins.]
700-1400	1-4	10-60

For all the samples the nitride layers thickness and phase composition were measured.

Moreover, the influence of cathode sputtering process on surface roughness was investigated. Two types of samples were used: 1 – after grinding (Ra=0.16μm) and 2 – after polishing (Ra=0.05μm).

RESULTS

Roughness

The roughness measurements confirmed that cathode sputtering had an influence on the surface shape. Some increase in surface roughness was observed – Fig. 3. It can be noticed that the lower initial Ra is the bigger roughness changes are observed. Ra increases also with time of sputtering. After 1 hour scattering both types of the samples reached similar level of roughness. In addition, it has been observed, that, there is no relationship between changes of Ra parameters and other sputtering parameters e.g. voltage and intensity.

Thickness

In Table 2 the results of thickness measurements are presented. Approximation analysis of these data enables to obtain the following relation:

$$g = 5.937 + 2.27\, X_U\, X_I \qquad S = 0.567;\ R=0.93,\ F=75 \qquad (1)$$

Where:

g – thickness of nitride layer [mm]

X_U, X_I i voltage and intensity respectively standardised according to formula:

$$X_{stand.} = \frac{X_i - X_{min}}{X_{max} - X_{min}} + 0.5$$

for parameter ranges as in Table 1.
S – standard deviation
R – multidimensional correlation coefficient
F – value of F-Snedecor test
Graphical presentation of Equation (1) is presented in the Fig. 4.

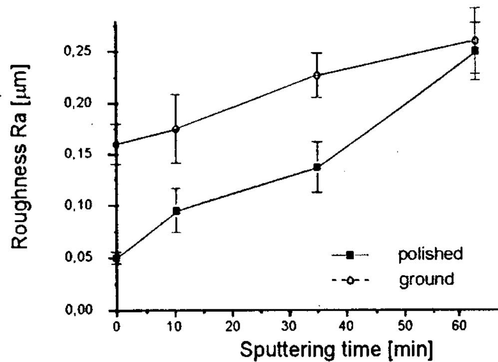

Fig. 3. Change of surface roughness versus time of cathode sputtering. Results were obtained for different parameters of sputtering.

Table 2. Results of thickness measurements for nitride layers obtained after cathode sputtering with different parameters and nitriding (1 hours, 843 K)

Voltage [V]	1025	1025	1025	1025	1350	700	1350	700	1350	700	1350	700	1025
Intensity [mA/cm^2]	4	1	4	1	2.5	2.5	2.5	2.5	4	4	1	1	2.5
Time [mins]	60	60	10	10	60	60	10	10	35	35	35	35	35
Thickness [μm]	9.2	6.8	8.3	6.6	9.6	6.9	9.8	7.6	11.1	8	7.1	6.6	9.1

As it is seen from equation (1) sputtering time has no influence on thickness of nitride layer. Taking into account previous observation about relationship between a parameter and sputtering time it can be stated that roughness contributes very little to the increase of nitriding kinetics. It means that after cathode sputtering higher defectiveness of upper surface plays crucial role in activation of surface for gas nitriding.

Morphology

For all the samples phase composition by XRD was measured. Nitride layers of every sample were consisted of ε and γ' nitrides. After approximation analysis of the phase composition of the compound layers the following relation was obtained:

$$a = 0.513 + 3.6 * X_U * X_I \qquad R = 0.876; \; S = 1,29; \; F = 36,39 \qquad (2)$$

where:
a – ratio of content ε and γ'
X_U , X_I , R, S and F – like in Equ. (1)
Graphical representation of Equ. (2) is presented on Fig. 5.

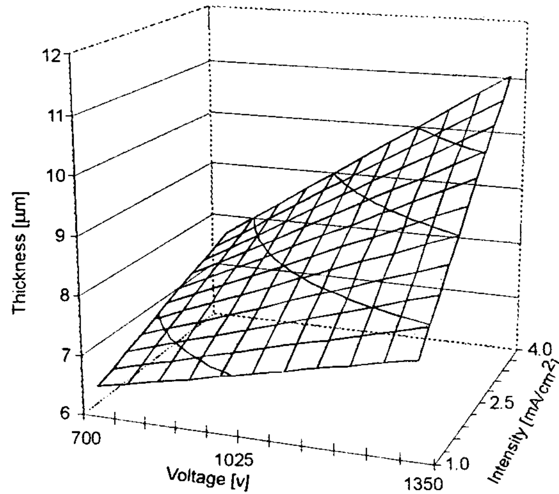

Fig. 4. Thickness of nitride layers versus voltage and intensity used in sputtering process – graphical presentation of equation (1).

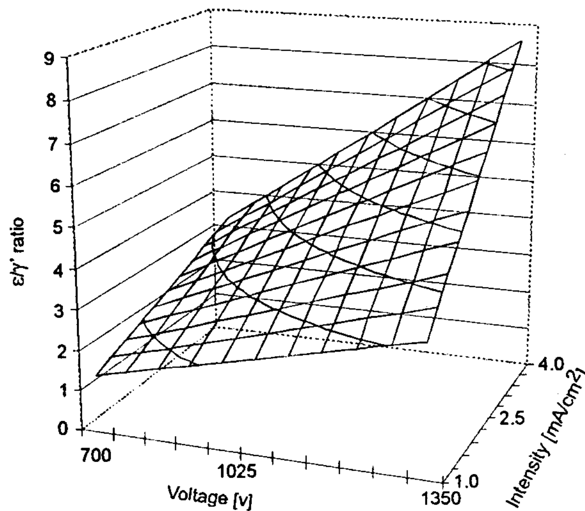

Fig. 5. Phase composition of nitride layer versus voltage and intensity used in sputtering process – graphical presentation of equation (2).

As we can see the composition of compound layer is also independent on time of sputtering. However voltage and intensity used in sputtering process have an influence on the morphology of the layer. If both parameters increase the ratio ε/γ' also increases. It means that content of ε phase is higher. By comparing Equ. (1) and (2) we obtain the relation between phase composition and thickness of the layer:

$$a = 1.09 + 3.64 * X_g^2 \qquad R = 0.906;\ S = 1.13;\ F = 50.41 \qquad (3)$$

where:
a – ε/γ' ratio
X_g – thickness of nitride layer standardised in range as in Table 2
R, S and F – like in Equ. (1)

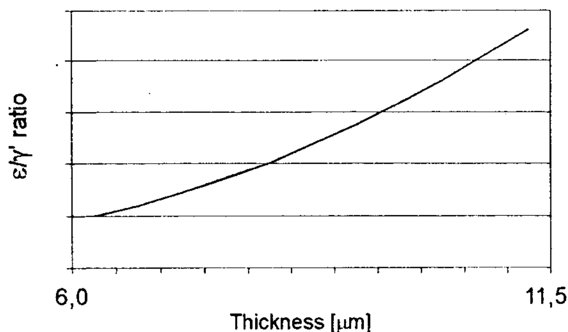

Fig. 6. Phase composition versus thickness of the nitride layer – graphical presentation of equation (3).

Equation (3) and fig. 6. indicate that the content of ε phase is directly proportional to the thickness of the compound layer. It means that ε phase appears at very beginning stage of nitriding and during subsequent growth of nitride layer only this nitride is formed. It confirms previous observation [3-5] that cathode sputtering before nitriding causes that during gaseous nitriding higher quantity of nitrogen is absorbed by the surface than in case of samples that was not pre-treated in this way.

SUMMARY

Cathode sputtering process used as a pre-treatment before gas nitriding increases nitriding kinetics. Increasing such sputtering parameters as voltage and intensity causes linear increase of nitrogen content in the nitride layer (higher content of ε phase). Sputtering time has no influence on the thickness and phase composition of the nitride layer.

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