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## **THE CREATION OF ZONE OF PURE IRON AS THE EFFECT OF DENITRIDING OF IRON NITRIDES $\epsilon + \gamma'$ LAYER IN THE ION ETCHING PROCESS**

### **Key-words**

Nitrided layer, ion nitriding, ion etching.

### **Summary**

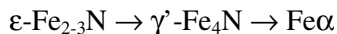
The paper presents research results of the influence of the ion etching process on the intensity of denitriding of iron nitrides  $\epsilon + \gamma'$  layer, obtained by the gas nitriding method on the surface of Armco. The influences of two different types of plasma atmospheres during the ion etching processes were investigated: metallic plasma ( $\text{Cr}^+$ ) and gas-metallic plasma ( $\text{Cr}^+ + \text{N}^+$ ). The ion etching processes were executed by means of the arc sources. After the ion etching processes the CrN coating with the thickness of about 2-3  $\mu\text{m}$  was deposited with the use of the arc-evaporation method. The structure obtained by ion etching and CrN deposition processes has been determined by means of scanning microscopy and EDS analysis. Thanks to the testing, the thickness of pure iron zone, which was created during the ion etching process, as the effect of denitriding of iron nitrides  $\epsilon + \gamma'$  layer, was define. Based on the obtained results the influence of the different type of plasma atmosphere during the ion etching process of iron nitride layer, on the intensity of creation of pure iron zone, was determined.

## 1. Introduction

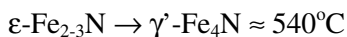
The fast development pace of many modern industrial branches, which has been observed in the recent time, was mainly determined by surface engineering capabilities [1–4]. Thanks to new material and technological developments enabling the modification of machines' and tools' functional properties, they could have been adjusted to work in worsening maintenance conditions, e.g. at high mechanical and thermal loading, intensive wear or corrosive effect of the environment. However, industry's expectations towards new types of layers concern not only a greater mechanical durability, wear resistance by friction or thermal resistance, but also effective parallel resistance to several external factors affecting the material simultaneously. The above expectations result in the development of new layers with a complex structure, the "hybrid layers" [5-6], which means the application of complex technological processes called multi-stage technologies or hybrid technologies [7–9]. So far, the best known hybrid layer created with the use of hybrid technologies consists of nitrided layer with deposited PVD coating [10–14]. Thanks to the interaction of those two elements, i.e. nitrided layer and PVD coating, the whole structure is characterised by properties unachievable for each of the elements separately. The conservation of the individual components constituting the hybrid layer of the nitrided layer/PVD coating type and the common effect of their interaction in different maintenance applications were demonstrated in [15–17].

In the most often applied PVD application methods, i.e. magnetron-sputtering and arc-evaporation, the stage of layer deposition is preceded by a substrate ion etching. In case on the nitrided substrate, an iron nitride  $\epsilon+\gamma'$  layer occurs, then during the ion etching process, as a result of denitriding, its decomposition and the creation of a soft layer of pure iron on the surface of a nitrided element can occur. In [18], it has been proved that among four different PVD layers, TiN, Ti(C,N), (Ti,Cr)N, CrN, deposited by the arc-evaporation method on EN X38CrMoV5.1 steel with a created nitrided layer containing iron nitride on the surface, all coatings containing titanium, immediately after their deposition, lost adhesion to the substrate completely. However, the adhesion lost has not been observed for the nitrided layer consisting exclusively of a diffusion zone without iron nitride layer on the surface. An effective coating of nitrided steel, both without and with iron nitrides layer on the surface, was possible solely for the CrN coating. A more precise analysis of the etching process in metallic plasma containing  $Ti^+$  ions carried out by the author of this paper in [19], as well as data by Sun and Bell presented in [20], have proved that the reason for the decomposition of iron nitrides layer was the temperature increase above 500°C.

Baek et. all. have proved [21], by means of calorimetric method, that the creation of pure iron on the nitrided layer can occur as a result of thermal decomposition of iron nitrides:



Temperatures at which the particular stages of this process start amount to correspondingly:



However, the decomposition of iron nitrides and the creation of pure iron were also observed at considerably lower temperatures. The authors of this paper observed this phenomenon [18–19] already at the temperatures 400°C and 500°C; however, Sun and Bell [20] observed this phenomenon at the temperature 450°C. Therefore, the claim assuming that lowering the temperature of iron nitrides decomposition necessitates an additional supportive factor seems to be justified from author's point of view. Sun and Bell indicate [20] the presence of argon in the atmosphere of the ion etching process as a factor supporting the decomposition of iron nitrides. However, the author's paper [19], as well as papers of other researchers [22–23], did not confirm this fact. Baek indicates [22] a positive effect of nitrogen in the atmosphere of the etching process. According to him, the decrease of the difference between the concentration of nitrogen in the layer of iron nitrides and the atmosphere of etching process will effectively eliminate the depletion of iron nitrides  $\varepsilon$  and  $\gamma'$  into nitrogen preventing, at the same time, their decomposition and the creation of pure iron Fe $\alpha$  layer. On the other hand, the outcomes in [18], as well as lack of literature information on the occurrence of iron nitrides decomposition in ion etching process with metallic ions other than Ti (eg. Cr or Zr), clearly indicate a significant destructive role of titanium ions in this process. Disputable conclusions on the decomposition of iron nitrides during ion etching processes formulated in literature induced the author to conduct studies aimed at explaining the influence of a particular type of metallic ions as well as nitrogen ions on the course of this process.

## 2. Experimental details

In order to elucidate the impact of particular types of metallic ions and nitrogen ions on the course of iron nitrides decomposition during the ion etching processes an armco, ion etching with the layer of iron nitrides on the surface was executed. In the experiment, two different types of plasma were applied: metallic Cr<sup>+</sup> and gas-metallic Cr<sup>+</sup>+N<sup>+</sup>. The etching processes were carried out with the use of arc sources according to parameters presented in Table 1. The layer of iron nitrides with a clear multi-layer structure and the total thickness of about 13 $\mu\text{m}$  obtained as a result of gas nitriding process on the surface of armco was demonstrated in Fig. 1.

Table 1. Ion etching parameters

No.	Pressure p [mbar]	Ion types	Substrate bias voltage $U_{\text{bias}}$ [V]	Maximum temperature T [°C]	Time t [min]
1	$<10^{-3}$	Cr	-750 / 10min -800 / 20 min -950 / 41min	550	71
2	$10^{-3}$	Cr+N	-750 / 10min -800 / 20 min -950 / 39min	550	69

Directly at the border with the diffusion layer, there is a 2–3  $\mu\text{m}$  thick iron nitride layer  $\gamma'$ - $\text{Fe}_4\text{N}$ , and above it there is about 10 $\mu\text{m}$  thick zone constituting a mixture of  $\epsilon$ - $\text{Fe}_{2-3}\text{N}$  +  $\gamma'$ - $\text{Fe}_4\text{N}$ . For each sample, constant etching times at pressure parameters  $U_{\text{bias}} = -750$  V i  $U_{\text{bias}} = -800$  V were assumed that amounted to respectively:  $t_{(-750)}=10$  min,  $t_{(-800)} = 20$  min. Next, the value of substrate bias voltage was being gradually increased to  $U_{\text{bias}} = -950$  V. The etching time at this bias voltage was an end time for the etching surface to obtain a constant temperature value  $T_{\text{max}} = 550^\circ\text{C}$ . Then, for the substrate heated in this way, the processes of CrN coating deposition were carried out. An exemplary course of process parameters alterations is presented in Fig. 2.

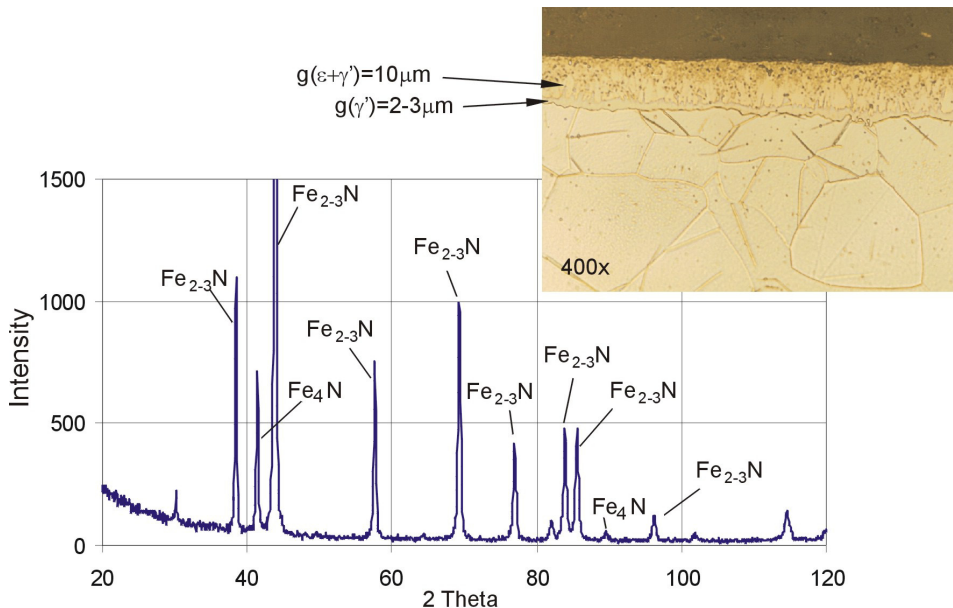


Fig. 1. Diffraction pattern and microstructure of nitrated armco iron with the layer of iron nitrides at the surface

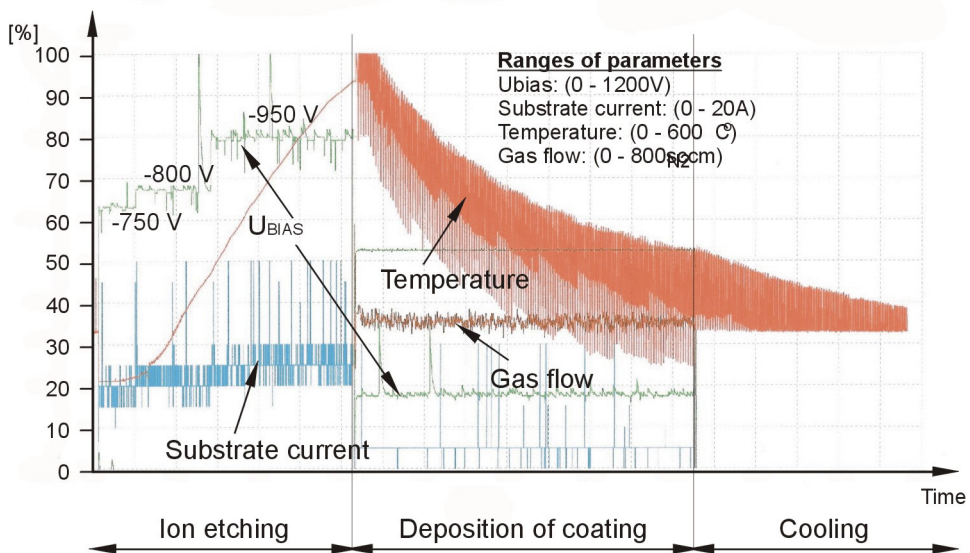


Fig. 2. The alteration course of ion etching parameter values in metallic plasma  $\text{Cr}^+$  and deposited coating  $\text{CrN}$

### 3. Results and discussion

The assessment of the impact of ion etching on the intensity of iron nitrides layer decomposition was carried out based on the linear analysis of chemical composition executed by means of EDS method. The obtained results (Fig. 3a,b) confirmed that the occurrence of nitrogen in ion etching atmosphere considerably limits the decomposition of iron nitrides layer. After etching in metallic plasma  $\text{Cr}^+$ , the thickness of the created iron layer amounted to about  $2.5\mu\text{m}$  (Fig. 3a). However, in case of applying metallic and nitrogen plasma  $\text{Cr}^+\text{N}^+$ , the thickness of the created iron layer amounted to merely about  $0.6\mu\text{m}$ . The results indicate an important role of denitriding the iron nitrides layer during the ion etching process, especially when applying metallic plasma. The obtained results allow to state that the occurrence of nitrogen in the atmosphere of ion etching process effectively limits the intensity of iron nitrides  $\epsilon$  and  $\gamma'$  decomposition and pure iron layer formation. They also revealed that the decomposition of iron nitrides  $\epsilon$  and  $\gamma'$  also occurs during ion etching in plasma which does not contain titanium ions. Based on the above the theses stated in [19], the assumption that a considerable effect of titanium ions on this process becomes dubious.

Naturally, the intensity of iron nitrides decomposition can differ depending on the quantitative share of phases  $\epsilon$  and  $\gamma'$ , ion etching time, and substrate temperature. The occurrence of carbon in the zone of  $\epsilon + \gamma'$  compounds seems less than meaningless, the effect of which during ion etching can be similar to the

effect of nitrogen in the etching atmosphere. According to the author of this paper, the diversity of properties (*structure, chemical composition*) and the diversity of ion etching parameters (*atmosphere composition, time, temperature*) distinguishing nitrated layers are the reason for the different information in publications on the decomposition of iron nitrides layer in the process of ion etching.

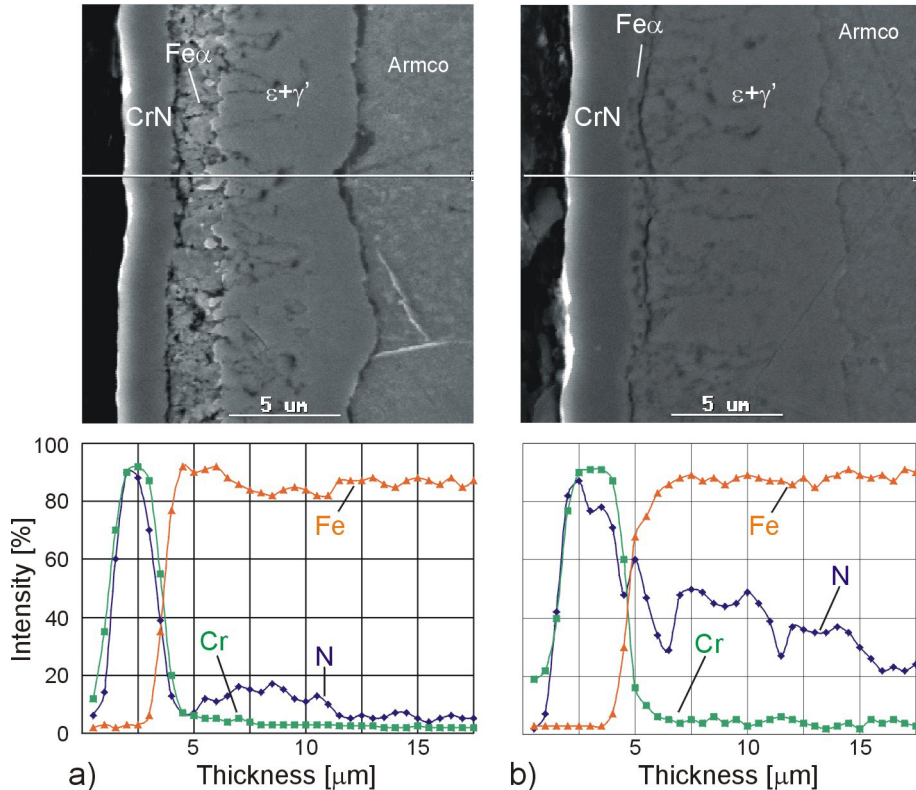


Fig. 3. The results of the linear analysis of chemical composition for nitrated layer with iron nitrides layer on the surface after ion etching and CrN coating deposition: a) etching in metallic plasma Cr, b) etching in gas-metallic plasma Cr+N

#### 4. Conclusions

Based on the obtained results of the studies, the following conclusions were formulated:

1. A significant effect of nitrogen in the atmosphere of ion etching process on limiting the decomposition intensity of iron nitrides  $\epsilon$  and  $\gamma'$  and the creation of pure iron layer indicates a dominating role of the process of denitrating iron nitrides.

2. The results of the conducted studies, which revealed that the decomposition of iron nitrides  $\epsilon + \gamma'$  and the creation of pure iron layer, also occur in the ion etching process in metallic plasma  $\text{Cr}^+$  as well as the literature information confirming the decomposition possibility of iron nitrides in ion etching process with the contribution of  $\text{Ti}^+$  [18-20] indicate the occurrence possibility of iron nitrides decomposition  $\epsilon + \gamma'$  and the creation of pure iron layer on the surface of nitrated layer, independently from the types of metallic ions used in ion etching process. In effect, the nitrated layer structure that can be effectively used to create hybrid layers of the nitrated layer / PVD coating type without loss of PVD coating adhesion should be limited to the nitrated layer containing merely a diffusion zone.

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Recenzent:  
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### **Powstawanie warstwy żelaza jako efekt odazotowania warstwy azotków żelaza $\epsilon+\gamma'$ w procesie trawienia jonowego**

#### **Słowa kluczowe**

Warstwa azotowana, azotowanie jarzeniowe, trawienie jonowe.

#### **Streszczenie**

W artykule przedstawiono efekt wpływu procesu trawienia jonowego na intensywność odazotowania warstwy azotków żelaza  $\epsilon + \gamma'$  wytworzonej w procesie azotowania gazowego na żelazie Armco. Procesy trawienia jonowego zrealizowano w plazmie metalicznej ( $\text{Cr}^+$ ) oraz metaliczno-gazowej ( $\text{Cr}^+ + \text{N}^+$ ) z wykorzystaniem źródeł plazmy łukowej. Bezpośrednio po procesie trawienia jonowego na trawionym podłożu osadzano warstwę CrN o grubości 2–3  $\mu\text{m}$  metodą łukowo-próżniową. Dla wszystkich badanych próbek, z wykorzystaniem mikroskopii skaningowej oraz liniowej analizy składu chemicznego metodą EDS, określono grubość warstwy czystego żelaza wytworzonej w wyniku procesu odazotowania podczas trawienia jonowego warstwy azotków żelaza  $\epsilon + \gamma'$ . Na podstawie uzyskanych wyników dokonano oceny wpływu składu środowiska plazmowego na intensywność procesu odazotowania analizy azotków żelaza  $\epsilon + \gamma'$  i tworzenia się warstwy czystego żelaza.

