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*Published in:*  
Surface and Coatings Technology

*Publication date:*  
1996

*Document Version*  
Early version, also known as pre-print

[Link to publication](#)

*Citation for published version (HARVARD):*  
Briglia, T, Terwagne, G, Bodart, F, Quaeyhaegens, C, D'Haen, J & Stals, LM 1996, 'Study of nitrogen implanted stainless steels by CEMS and TEM', *Surface and Coatings Technology*, vol. 80, pp. 105-108.

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## Study of nitrogen-implanted stainless steels by CEMS and TEM

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### Abstract

Combining TiN coating deposition by PVD and nitriding by nitrogen implantation in stainless steels shows promise for the future if a good adhesion between the coating and the substrate can be obtained. It is therefore necessary to study the structure and composition of the nitrated surface with a view to optimizing the coating adhesion. Implantation of nitrogen at doses of  $1-5 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}$  and with an energy of 50 keV was realized in the nitriding of AISI 304 and AISI 310 austenitic stainless steels. Some samples were heated in vacuo to 400 °C after implantation to simulate the temperature effect during PVD coating. Conversion electron Mössbauer spectroscopy (CEMS) and transmission electron microscopy (TEM) were used to investigate the nitride phases due to nitrogen implantation. These measurements confirm previous results obtained by X-ray diffraction (XRD) and by resonant nuclear reaction analysis (RNRA). CEMS shows an evolution in the phases formed after implantation. At low doses, a solid solution in austenite was formed while a  $\epsilon\text{-(Fe, Cr, Ni)}_{2+x}\text{N}$  nitride was formed at higher doses. For the  $2 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}$  implanted and post-heated sample, CEMS and TEM gave evidence for the presence of a nitrogen solid solution and confirmed the diffusion of nitrogen deep into the specimen.

*Keywords:* Nitriding; Implantation; Stainless steel; Mössbauer

### 1. Introduction

The improvement of the tribological properties of austenitic stainless steels by nitriding and particularly by nitrogen implantation is well established [1–5]. However, the nitriding process can reduce the corrosion resistance owing to changes in the structure of the surface layer [6]. This can be solved by depositing a TiN coating on the specimen by physical vapor deposition (PVD), often used today as a protective, decorative and hard layer to enhance the lifetime of engineering components [7–9]. In view of this, a combination of these two treatments becomes an interesting prospect if good adhesion could be obtained between the coating and the substrate [10,11]. The aim of this work is to study the structure and composition of the nitrogen-implanted surface with a view to optimizing the TiN coating adhesion. This paper presents results of the investigations of nitride phases in nitrogen-implanted AISI 304 and AISI 310 austenitic stainless steels using conversion electron Mössbauer spectroscopy (CEMS) and transmission electron micro-

scopy (TEM). To simulate the temperature effect during PVD, some samples were heated up to 400 °C in vacuo after implantation.

In a previous paper [12], resonant nuclear reaction analysis (RNRA) showed that AISI 304 and AISI 310 give similar nitrogen depth profiles at a temperature below 100 °C. The 400 °C post-heating leads to diffusion of nitrogen into the bulk of the sample. However, for AISI 310 treated steel, a surface peak was observed in the nitrogen depth concentration. TEM is used in this study to identify the nature of this surface accumulation. X-Ray diffraction (XRD) experiments were also made and showed that increasing the nitrogen-implanted dose induces a phase evolution process.

### 2. Experimental details

Samples of annealed austenitic stainless steels AISI 304 and AISI 310 were prepared and implanted according to the procedures given in the preceding paper [12]. The samples had the following compositions: <0.8 wt.% C; <2 wt.% Mn; 17–20 wt.% Cr; 8–11 wt.% Ni; Fe balanced (304) and <1 wt.% Si; <2.5 wt.% C; <2 wt.%

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Mn; 24–26 wt.% Cr; 19–22 wt.% Ni; Fe balanced (310). CEMS experiments were carried out with a  $^{57}\text{Co}$  (50mCi) source in a rhodium matrix. The specimens were placed in a flow proportional counter and only the electrons produced at the surface of the specimen were recorded at room temperature. Typical velocities of  $\pm 5 \text{ mm s}^{-1}$  were used for the source. Mössbauer spectra were fitted using a computer code which gave the parameters such as isomeric shift, quadrupole splitting and magnetic splitting of each Fe-containing phase. As 65% of the information in CEMS came from the first 100 nm of the specimen [13], this method was adequate for the study of nitrogen implanted in stainless steels because the layer analyzed corresponds to the range of the implanted species ( $\pm 55 \text{ nm}$ ) [14].

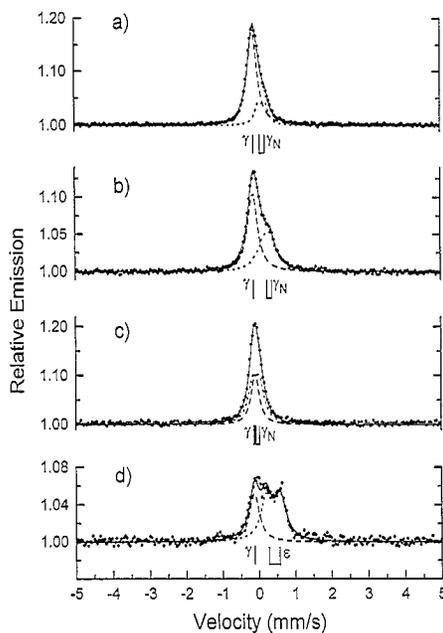


Fig. 1. CEMS data and computer fits for (a)  $1 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}$  implanted 304 SS; (b)  $2 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}$  implanted 304 SS; (c)  $2 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}$  implanted 304 SS and post-heated at  $400 \text{ }^\circ\text{C}$  during 20 min; and (d)  $5 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}$  implanted 304 SS. Sticks indicate the subspectra and corresponding phases.

TEM examinations were carried out with a CM12 Philips microscope.

### 3. Results and discussion

#### 3.1. CEMS measurements

The results of CEMS studies on AISI 304 implanted at three different doses and with a low current density ( $\pm 10 \mu\text{A cm}^{-2}$ ), keeping the temperature below  $100 \text{ }^\circ\text{C}$ , are presented in Fig. 1. Both steels show the same behavior. At low dose ( $1 \times 10^{17}$  and  $2 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}$ ), we observe in the Mössbauer spectrum a singlet due to the paramagnetic austenitic substrate and a doublet due to an interstitial nitrogen solid solution phase called  $\gamma_{\text{N}}$ -expanded austenite phase. For the highest dose ( $5 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}$ ), a doublet with hyperfine parameters close to those of  $\epsilon\text{-Fe}_{2+x}\text{N}$  is observed as well as the substrate signal [15]. We assign this doublet to  $\epsilon\text{-(Fe,Cr,Ni)}_{2+x}\text{N}$ . As this phase is paramagnetic (doublet), we can conclude that  $x$  is close to zero since it is similar to pure Fe-nitrides where  $\epsilon\text{-Fe}_{2+x}\text{N}$  is magnetic for  $x > 0.5$  [15,16]. There is a phase evolution in the implanted layer when the implanted dose increases. The nitrogen solid solution at low dose transforms into  $\epsilon\text{-(Fe,Cr,Ni)}_{2+x}\text{N}$  at high dose. This confirms our previous results obtained by XRD and is comparable to the results obtained by Williamson et al., except for the fact that they implanted at a higher temperature ( $t^\circ = \pm 400 \text{ }^\circ\text{C}$ ) owing to the elevated flux of the implanted species [1,17]. If we calculate the relative fraction of each phase in the Mössbauer spectra (Table 1), we observe that the nitride phase increases relative to the substrate with increasing dose, indicating that there is no dose saturation, as confirmed by RNRA profiles.

We post-heated (in vacuo, to  $400 \text{ }^\circ\text{C}$ , during 20 min) two samples of each stainless steel type implanted with  $2 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}$ . CEMS results are given in Table 1 and shown in Fig. 1(c) (for AISI 304). They provide evidence that the  $\gamma_{\text{N}}$ -expanded austenite phase is still

Table 1

Hyperfine parameters resulting from CEMS analysis,  $\delta$  is the isomer shift,  $\Delta$  is the quadrupole splitting and  $F$  is the relative area which is correlated to the abundance of the phase. Parameters are given in  $\text{mm s}^{-1}$

Dose ( $\times 10^{17} \text{ N}^+ \text{ cm}^{-2}$ )	AISI 304			AISI 310			Phase
	$\delta$	$\Delta$	$F$	$\delta$	$\Delta$	$F$	
1	-0.137		0.78	-0.179		0.66	$\gamma$
	0.122	0.192	0.22	0.064	0.192	0.34	$\gamma_{\text{N}}$
2	-0.139		0.53	-0.122		0.57	$\gamma$
	0.172	0.307	0.47	0.201	0.287	0.43	$\gamma_{\text{N}}$
5	-0.136		0.34	-0.132		0.23	$\gamma$
	0.389	0.393	0.66	0.369	0.483	0.77	$\epsilon$
2 (+ $400 \text{ }^\circ\text{C}$ post-annealing)	-0.099		0.38	-0.099		0.24	$\gamma$
	-0.068	0.198	0.62	-0.053	0.220	0.76	$\gamma_{\text{N}}$

present after annealing but its relative area has increased. The same behavior was observed for both types of steel (Table 1). This can be interpreted, using RNRA and XRD, as proof of a diffusion mechanism towards the bulk of the material. Indeed, since about 95% of the information comes from the first 300 nm [13], and as RNRA shows that implanted nitrogen maximum depth is 150 nm before annealing, a diffusion process beyond this 150 nm will increase the information received from the  $\gamma_N$  phase.

### 3.2. TEM measurements

The RNRA profile for post-heated AISI 310 sample shows a diffusion mechanism towards the bulk and the surface marked by a clear surface peak (Fig. 2). To determine the origin of this peak, TEM measurements were made on post-heated AISI 304 and 310 specimens. These indicated that for both substrates, the lattice parameter of the austenite phase is 1% or 2% larger than the tabulated one. This means that the surface layer contains expanded austenite. For AISI 304, study of the diffraction patterns (Fig. 3) allowed the identification (in addition to the austenitic substrate) of  $\gamma$ -CrN (fcc,  $a=0.414$  nm). This phase was not detected by XRD, maybe because the clusters were too small. Nevertheless, this phase is unexpected in AISI 304 where the Cr content is smaller than in AISI 310. TEM being the only proof of the presence of  $\gamma$ -CrN, this information needs more investigation. For AISI 310, only expanded austenite was observed and no explanation for this surface nitrogen accumulation can be given at present. Further investigations will be made to explain this phenomenon.

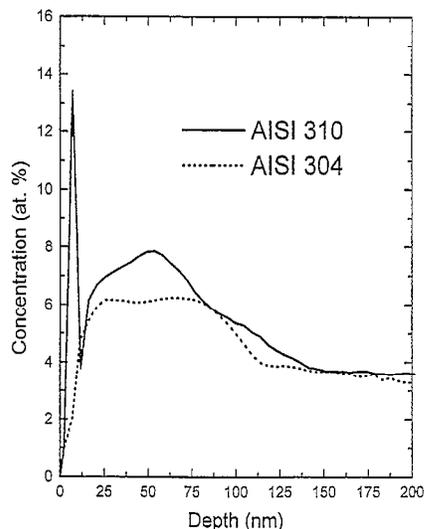


Fig. 2. RNRA nitrogen depth profiles for AISI 304 and AISI 310 implanted at unmonitored temperature ( $<100$  °C) with a dose of  $2 \times 10^{17}$   $N^+$   $cm^{-2}$  and then post-heated at 400 °C during 20 min.

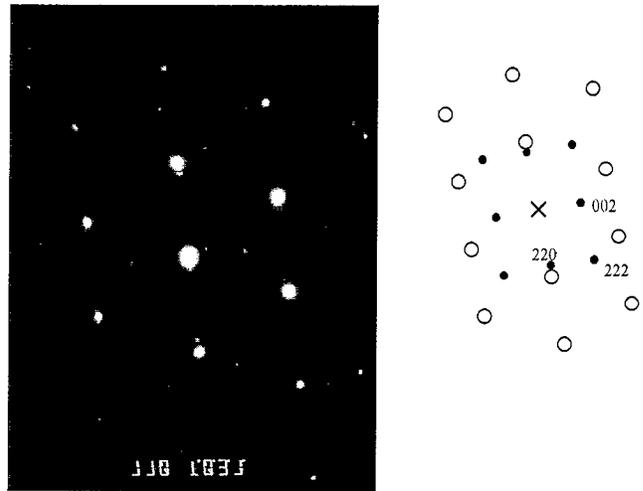


Fig. 3. Electron diffraction pattern of AISI 304 implanted with  $2 \times 10^{17}$   $N^+$   $cm^{-2}$  and post-heated at 400 °C during 20 min: (O)  $\gamma$ -austenite, (●) CrN.

### 4. Conclusions and perspectives

Conversion electron Mössbauer spectroscopy has provided evidence of a phase evolution process in the surface layer as AISI 304 and AISI 310 austenitic stainless steels were implanted with 50 keV nitrogen ions with doses increasing from  $1 \times 10^{17}$   $N^+$   $cm^{-2}$  to  $5 \times 10^{17}$   $N^+$   $cm^{-2}$ . While a nitrogen solid solution in austenite, called  $\gamma_N$ -expanded austenite, was observed at low doses, this phase was transformed into  $\epsilon$ - $(Fe,Cr,Ni)_{2+x}N$  with low  $x$  for a higher dose. This behavior was the same for both steels. If a post-heating treatment was undertaken after a  $2 \times 10^{17}$   $N^+$   $cm^{-2}$  dose, the solid solution was still present but seemed to diffuse into the bulk. Transmission electron microscopy studies of the post-heated samples confirmed this result but also showed the presence of  $\gamma$ -CrN in the AISI 304 surface layer which could not be confirmed by the other methods. The presence of this  $\gamma$ -CrN phase will be investigated in the future. No explanation has yet been put forward concerning the nitrogen surface enrichment found by RNRA in post-heated AISI 310. Therefore, PVD coating process will be executed on a solid solution of strengthened stainless steel [1].

Further investigations in the  $2$ – $5 \times 10^{17}$   $N^+$   $cm^{-2}$  dose range will be performed to study the decomposition of the expanded austenite phase. TiN coating by PVD will be performed in order to characterize the adhesion and the influence of the coating on the treated surface.

### Acknowledgments

This study was sponsored by the Belgian program of Interuniversity Poles of Attraction, initiated by the Belgian State, Prime Minister's Office — Science Policy

Programming. Scientific responsibility is assumed by the authors.

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