

# On low temperature ion nitriding of austenitic stainless steel AISI 316

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Received 26.04.2007; published in revised form 01.11.2007

## Manufacturing and processing

### ABSTRACT

**Purpose:** The purpose of this paper is to discuss some problems concerning the extremely high values of the nitride layer hardness and the features of so called S-phase which are formed after low-temperature ion nitriding of high-alloyed austenitic (austenitic-ferritic) steels.

**Design/methodology/approach:** The investigations are performed mainly by using of ray diffraction method after ion nitrided 316 (AISI) steel.

**Findings:** As a result of the work some data, concerning the structure and substructure, the phase composition of the S-phase, crystal lattice, the broadening of diffraction reflexes, mechanism of transformation of  $\gamma'$ - phase into S-phase, its high hardness etc. of the nitrided layer are obtained. It could be concluded that S-phase could be classified as a modified  $\gamma'$ -phase. The extremely high values of the hardness could be explained by the high nitrogen concentration in the solid solution and by the presence of increased density of the defects in the austenitic volume, which is transformed in the new S-phase.

**Research limitations/implications:** The potencionstatic investigations of the electrochemical properties of the nitriding probes, performed by us, confirmed the data, obtained by the literature, but this problem will be discussed in some of the next publications.

**Originality/value:** The high micro- and macro-deformations of the lattice of S-phase could be explained by the considerable registered expansions and the angle replacements of the slope ( $\psi$ ) on the ray diffraction maxima. The registered macro deformations could reach immense values, in the range of  $(1.4 - 2.1) \cdot 10^{-2}$ , which corresponds to macro deformations around 1900 – 2300 MPa (if we accept, for the austenite, the usual module of elasticity of  $2.1 \cdot 10^5$  MPa). For such final decision it is necessary to obtain also some other confirmation facts.

**Keywords:** Thermo-chemical treatment; Nitriding; S-phase; Nitride layer; Austenite supersaturated

## 1. Introduction

The conventional methods (temperatures higher than 500°C) for nitriding of high alloyed corrosion resistant steels determine high degree of hardness of the nitride layer, but at the same time – a worsening of their corrosion resistance, which limits the nitridation of this kind of steels.

But, in the case of thermo-chemical treatment of corrosion

resistance steels, it is necessary to solve the following two problems:

- on the first place – in spite of its very low thickness, the native passive layer is a serious barrier, and in practice, it is impenetrable for the nitrogen and carbon atoms;
- on the second place - traditional thermochemical treatment of such steels, at the normal nitriding temperatures (at approximately 550°C), reduces their corrosion resistance, due to the bonding of the nitrogen and the carbon with the chromium, creating carbides and nitrides and reducing its quantity in the solid solution.

The solving of the first problem could be done by different ways for depassivation of the surface, depending on the nitriding method used. In the case of gas methods, the destroying of the protective oxide layer is done by chemical treatment with chlorine containing solutions or gases, but during the plasma based methods, the “nonpenetrable” oxide layer could be removed, in part or totally, during the stage of “cathode sputtering” [1]. Without going deeper in these possibilities, the authors of this publication pay special attention to the second problem, which is tightly connected with a discussion between the researchers, working in the area of nitriding processes, in connection with morphology of, so called S-phase, obtained during the diffusion saturation of high alloyed austenite stainless steels at low temperatures ( $400\pm 20^\circ\text{C}$ ).

The first information about these low-temperature processes of nitriding and carbonitriding, as well as for the creation of the nitride layer is coming from the period of 1986-1987 [1,9-12]. At present, (during the last four years), the interest to this problem is increased [2,6,8,14,16]. The reason for such interest is in the fact, that there are strong evidences, that in technological sense, it is possible to create a nitriding layer at the above mentioned temperatures, which are “no usual” low for the process of nitriding. Besides that, it is proved that the nitriding layer formed, has new phase composition, containing a new type nitrite phase (S-phase), which provides extremely high hardness and increased corrosion resistance [3-7]. But, at the moment, several new problems are opened for discussion, concerning the morphology of the formed nitriding layer, such as:

- what is the composition and the type of the crystal lattice of S-phase?
- what is the reason for the big enlargement of the diffraction maxima of S-phase?
- is the nitrogen concentration of S-phase in the homogeneity interval of  $\gamma'$ -phase in the matrix?
- what is the transformation mechanism of  $\gamma'$ -phase into S-phase?
- what is the reason for the extremely high hardness and corrosion resistance of S-phase?

The investigations are performed by using of 316 (AISI) steel, which has been processed by ion nitriding in nitrogen-hydrogen atmosphere, at temperatures  $340\text{-}420^\circ\text{C}$ . In this paper, some data, concerning the structure and substructure, the phase composition and microhardness of the nitriding layer are presented.

The nitriding of austenite steels, at temperatures above  $500^\circ\text{C}$ , leads to the forming of highly recrystallized diffusion layer, but under  $420^\circ\text{C}$ , after nitriding, an austenite-like layer is formed, which is phase separated from the austenite-matrix of the steel.

The ray diffraction (XRD) maxima of this austenite-like phase are highly moved and very highly enlarged, comparing to the austenite-matrix (Fig. 1). The comments, concerning this nitrogen containing new phase, are not in the common direction. Some of the authors [2] define it as “expanded” (elastically deformed) austenite -  $\gamma_x$  ( $X=\text{N,C}$ ) - phase, which even today, is marked by some of the authors as S-phase [10], but some others use  $m$ -phase [10-12]. Latter, in this paper it will be shown that we accept, that it is more correct to use S-phase. In spite of the fact that it is face-centered cubic (f.c.c.) crystal lattice, it is not obvious that it is equal to the austenite, because:

- the parameters of its crystal lattice is quiet different, comparing that of the austenite;
- the homogeneity interval is limited and it is outside of the homogeneity interval of the nitrite austenite;

- the diffraction maxima are highly and abnormally (no uniformly) enlarged, which is the consequence, not only to the concentration gradient in the effectively reflected layer, but to the severe micro- and submicro- tensions;
- the presence of clearly defined frontal border, between the matrix austenite and the newly created phase, is an evidence for the crystal lattice transformation performed;

On the other hand, this new phase, having in mind its diffusion forming and the crystal lattice nature, looks like already well investigated austenite, like  $\gamma'$ -phase ( $\text{Fe}_4\text{N}$ ), from the system Fe-N. If compare their crystallographic models, it could be found, that the S-phase is with a little bit higher parameters and a larger homogeneity interval comparing to  $\gamma'$ -phase. As a consequence of such similarity of these phases, it could be concluded that S-phase could be classified as a phase of penetration with a composition  $(\text{Fe, Cr, Ni})_4\text{N}$ . Its considerable larger diffraction maxima and its increased parameter, concerning the  $\gamma'$ -phase, in the lattice of which, the nitrogen atoms are strictly well-arranged, are the evidence of the presence of some disorder for one part of nitrogen atoms. Probably, this is due to the presence of the alloyed elements (Cr, Ni) in the steel and especially their stabilizing influence on the cubic syngony group.

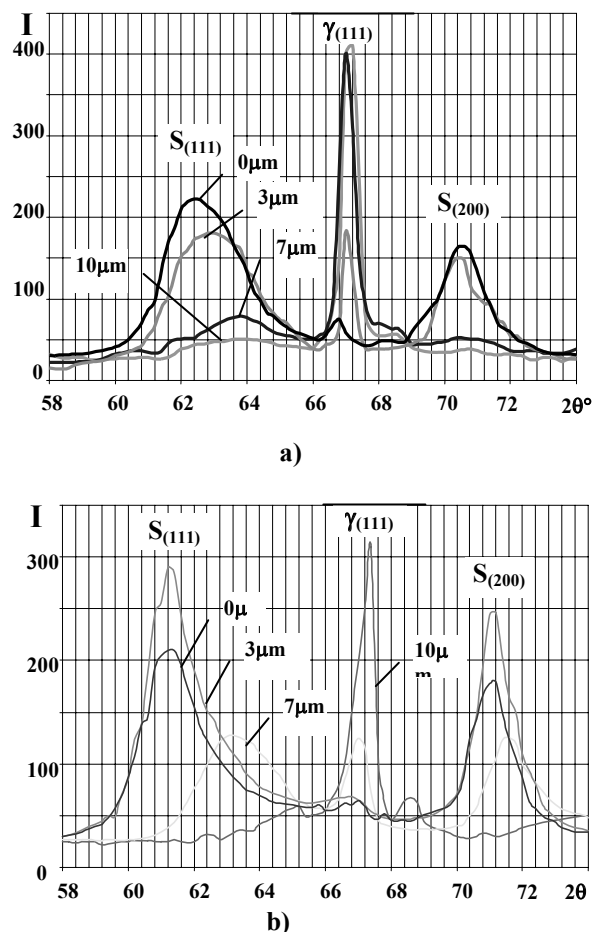


Fig. 1. X-ray diffraction of the S-phase, taken from different analyzing depths of the nitriding layer: a) after gas carbonitriding of X5CrNi18-10 at  $400^\circ\text{C}$ ; b) after ion nitriding of 316 steel at  $420^\circ\text{C}$

Having in mind these crystallographic and morphological features of the S-phase, it is possible to characterize it as one type modified  $\gamma'$ -phase ( $M_4N$ ), but the authors of the present paper think that, for such final decision, it should be necessary to obtain also some other confirmation facts. This is the reason to accept the opinion, that on this stage, it is more correct, this system to be defined as a new type phase.

More precise analysis of the structure of the diffusion layer, formatted on the base of the S-phase (Fig. 2), shows several typical features, which are not observed in the case of other nitride phases, as follows:

- S-phase is separated from the matrix austenite ( $\gamma$ ) by abrupt intermediate phase border, which could be seen only as a result of step in the concentration of the nitrogen, penetrating from the front side. Something more, between S- and  $\gamma$ -phases, a thin intermediate layer is found, which could be seen better by using of an inclined polishing (sampling), specially prepared for more clearly development (Fig. 3). The phase composition of this layer is still not defined. There are not data for it in the literature investigated;
- there is a clear structural heredity, proving the orientation dependence of S-phase and the matrix austenite (the borders of the austenite grains substructure are preserved during its formation in the grains of S-phase) - Fig. 2 a);
- in their nitriding volume, it could be observed a dispersal separated nitrogen phase. Some abrupt intermediate phase border, in the ferrite grain, is not formatted, which is an evidence for the presence of abrupt change in the nitrogen concentration;
- the ferrite grains (for duplex steel), which are at the diffusion zone, they are not transformed in S-phase, and at the boundary S/ $\alpha$ , it could be seen a special sub structural state in the both phases, which is characterized by an increased defect density from the group of deformation origin (Fig. 4).

The nature of the extremely high values of the hardness (up to 1700 HV), in case of plasma nitriding of stainless steels, is not clear at the moment. There is a domination of the hardness explanation by the mechanism of the solid solution, namely by the high nitrogen concentration in the solid solution.

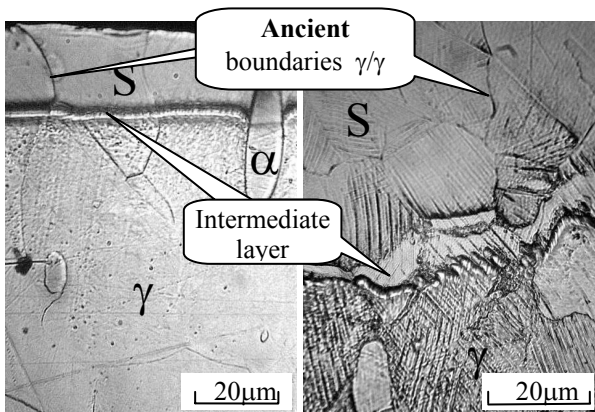


Fig. 2. Structure of the nitriding layer after ion nitriding of steel 316 at 420°C; a) cross polishing, b) inclined polishing

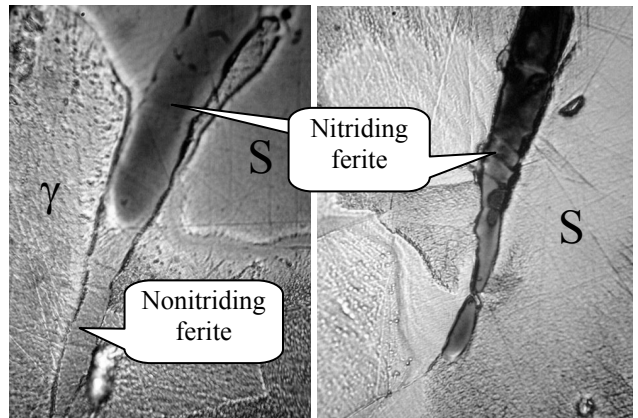


Fig. 3. Ferrite structure at the boundary S/ $\alpha$  a), and in the volume of the S-phase b)

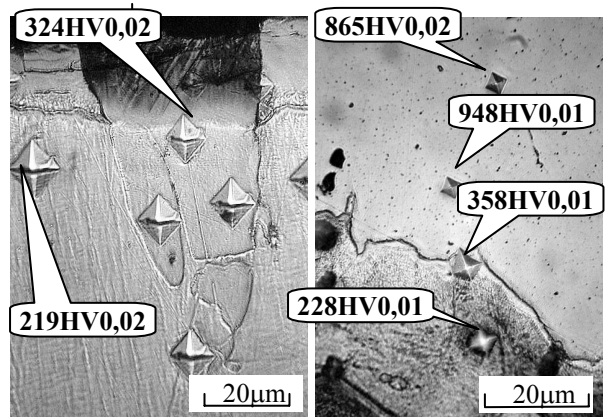


Fig. 4. Substructure of S-phase on the boundary with a) and in the central zones of the layer b) – inclined polishing (sampling)

The presence of increased density of the defects, in arranging of the transformed austenite volume in the new S-phase, could have a contribution to the increased hardness. As a prove for the increased density of deformation defects, in the arrangement, this is the registered contrary dislocation of the diffraction maxima (111) and (200) of the S-phase [15,16]. As far as the high hardness of this phase is its own feature, and it is as a result of the new face-centered cubic lattice and its considerable micro-deformations, following the increased nitrogen contents in it, the increased hardness of nitrided ferrite is due to the dispersed chromium-nitride depositions.

Obtained during the nitriding of the duplex steel (Fig. 5). The real proofs for the high micro- and macro-deformations of the lattice of S-phase, from one side, these are the considerable registered expansions and the angle replacements of the slope ( $\psi$ ) on the ray picture of the diffraction maxima (Fig. 6).

This extremely high translation of the x-ray maximum (311) (with several degrees  $2\theta$ ), confirms the ultrahigh macro deformations (macro-tensions) of pressure, mentioned also by some other authors [12,16]. In the experiments, the registered macro deformations could reach immense values, in the range of

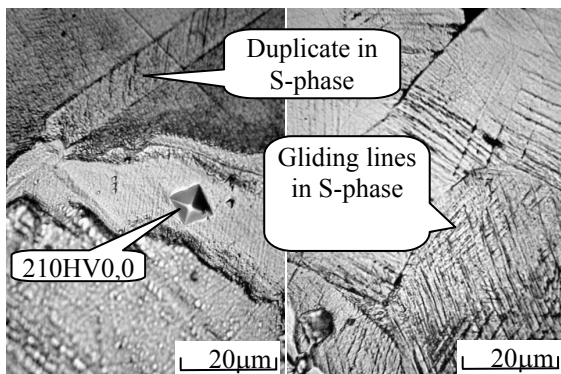


Fig. 5. Microhardness in the different phases of the nitriding layer for 316 steel: a) in the austenite and ferrite of ion nitriding austenite-ferrite steel; b) in the intermediate layer and S-phase in the gas carbonitriding austenite steel

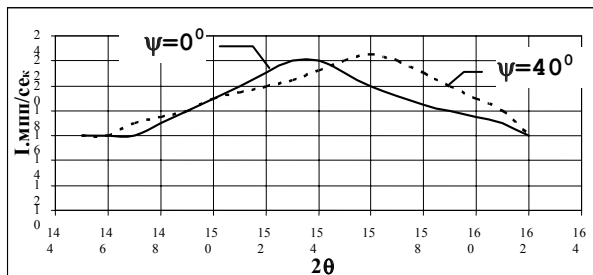


Fig. 6. Expansion and translation of diffraction maximum of the line (311) of S-phase, in case of different slope angles ( $\psi$ ) of the ray picture

$(1.4 - 2.1) \cdot 10^{-2}$ , which corresponds to macro deformations around 1900 – 2300 MPa (if we accept, for the austenite, the usual module of elasticity of  $2.1 \cdot 10^5$  MPa).

During the last years, the low temperature nitriding processes investigators, pay special attention to the corrosion characteristics of the nitride layers. The reason is the fact, that by contrast with the conventional nitriding of highly doped austenite steels, during which, the corrosion strength is reduced, in case of low temperature nitriding, the opposite desired effect, of keeping and even increasing of the corrosion strength could be obtained [2,3,8]. The potencionstatic investigations of the electrochemical properties of the nitriding probes, performed by us, confirmed the data, obtained by the literature, but this problem will be discussed in some of the next publications.

## Acknowledgements

This paper presents some results from the work on the Project No. BY-TH 215/2006 at Ministry of Education and Sciences of Bulgaria.

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