



On the formation of expanded austenite during plasma nitriding of an AISI 316L austenitic stainless steel

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Abstract

Plasma nitriding of an AISI 316L austenitic stainless steel at low (400 °C) and high temperatures (550 °C) was performed under different nitriding gas mixtures. Nitrided surfaces were characterized by XRD using the Rietveld method. Expanded austenite “ γ_N ” with a special triclinic (t) crystalline structure was formed during the low-temperature nitriding treatment. Minor volume fractions of Fe₃N, Fe₄N and Cr₂N nitrides were also found. The expanded austenite phase showed a distortion ε of the lattice angles due to a very high nitrogen content dissolved in austenite, supersaturating the solid solution and leading to a 10% lattice distortion and to high compressive residual stresses at the surface.

After nitriding the specimens at 550 °C the case was composed primarily by a high volume fraction of Fe₄N, Cr₂N and CrN nitrides, leading to a low distortion of the parent austenitic phase, maintaining the original cubic lattice.

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1. Introduction

Austenitic stainless steels (ASS) can not be conventionally nitrided at temperatures near 550 °C due to intense precipitation of chromium and iron nitrides in the diffusion zone [1–4], during the nitriding cycle. The precipitation of chromium nitrides increases the hardness and promotes compressive residual stresses at the surface but impairs severely the corrosion resistance. Plasma nitriding allows introducing nitrogen in the steel at temperatures below 450 °C. During this treatment a very hard (~1500 HV) and corrosion resistant metastable phase, expanded austenite “ γ_N ”, is formed at the surface of the steel [5–7]. This phase is a nitrogen supersaturated solid solution (austenite) with a distorted crystalline lattice.

Several papers in the literature describe the structure of the diffusion zone of high-temperature nitrided ASS as a mixture of chromium and iron nitrides while the low-temperature nitriding treatment induces the formation of homogeneous expanded austenite free from precipitated nitrides.

In this paper a detailed X-ray diffraction study of the phases formed during plasma nitriding of AISI 316L austenitic stainless steel — ASS, using the Rietveld method shows that expanded austenite, chromium and iron nitride precipitates are always present after both high- and low-temperature nitriding treatments. The effect of the nitrogen content of the nitriding gas mixture on the sequence of precipitation was also studied.

2. Experimental

Slices of AISI 316L austenitic stainless steel, received as round bars 28.6 mm in diameter were cut 5 mm thick. Test specimens for plasma nitriding were fine grounded and diamond polished. The chemical composition of the steel is shown in Table 1.

Plasma nitriding treatments were carried out in a pulsed-DC plasma reactor with a hot wall chamber, from ELTROPULS GmbH. A 1 h sputtering step using pure hydrogen plasma was carried out, in order to remove the passive film and activate the surface. For the low-temperature nitriding cycle the sputtering step was performed at 350 °C and for the high-temperature nitriding cycle the sputtering step was carried out at 400 °C. The nitriding step was conducted at 400 and 550 °C, during 12 h.

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Table 1
Chemical composition in mass %

| C | Si | Mn | Cr | Ni | Mo | N | Fe |
|-------|------|------|------|------|------|-------|---------|
| 0.011 | 0.31 | 1.81 | 18.8 | 14.7 | 2.45 | 0.014 | Balance |

Gas mixtures of $1\text{N}_2:3\text{H}_2$ and $3\text{N}_2:1\text{H}_2$ were used. The nitriding pressure was 250 Pa, and the voltage was 470 V.

The phases formed in the nitrided layer were characterized by XRD in a Phillips diffractometer using CuK_α radiation, $\lambda=0.1542$ nm, with a conventional $\theta/2\theta$ Bragg-Brentano symmetric geometry. Rietveld method [8] was used to analyze the X-ray diffraction patterns.

Hardness of the nitrided layer was assessed using a Vickers nanoindentation method on a Fischerscope 100 equipment using 25 mN as a test load.

3. Results and discussion

Figs. 1–4 show the X-ray diffraction patterns of the nitrided layers after processing the raw data using the Rietveld method. Table 2 shows the phases formed, their amount and lattice parameters. Figs. 1 and 2 show that after nitriding at 400 °C, the presence of expanded austenite predominates, although iron and chromium nitrides are also detected. Figs. 3 and 4 show that during plasma nitriding at 550 °C, intensive nitride precipitation occurs, although expanded austenite is also detected.

The X-ray diffraction patterns analyzed by the Rietveld method, Figs. 1 and 2, show that at low temperature not only expanded austenite is formed during plasma nitriding. At 400 °C iron and chromium type nitrides $\epsilon\text{-Fe}_3\text{N}$, $\gamma'\text{-Fe}_4\text{N}$, and Cr_2N , can also be found. Volume fraction for Fe_2N and CrN are lower than 1% and can not be considered. According to the chemical composition of this steel Fe, Cr and Mo are expected to be dissolved on iron and chromium nitrides [9], but nitrides stoichiometry can not be evaluated in the present analysis.

Broadening and shifting of austenite peaks due to nitrogen supersaturation in the lattice correspond to expanded austenite

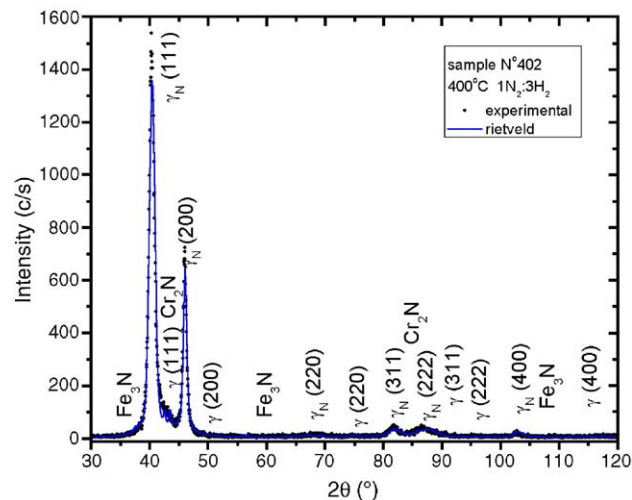


Fig. 2. AISI 316L nitrided at 400 °C, 12 h, 25% N_2 /75% H_2 .

γN . The expanded austenite γN {200} planes are more widely spaced than any other planes indicating a deviation from the cubic fcc unit cell. Different candidate unit cells for expanded austenite were analyzed using the Rietveld refinement method: tetragonal (fct) and (bct), monoclinic and triclinic structures. The described distortion can not be represented by a monoclinic or a tetragonal (bct) unit cell, the tetragonal (fct) unit cell being the only one that reproduces the (111) and (200) positions of the diffraction peaks. An orthorhombic distortion of the lattice is insufficient and it is necessary to consider unit cells in which the angles deviate slightly from right angles. Therefore, the expanded austenite can be best described by a special triclinic (t) crystalline structure [3], with a distortion ϵ of the lattice angles due to the presence of nitrogen in solid solution. According to the model proposed by Fewell et al. [10], the triclinic structure gives the best description of the present data and represents very well the distortion found in the expanded austenite lattice.

The shift of the austenite peaks to lower angles indicates compressive residual stresses in the nitrided layer. When plasma

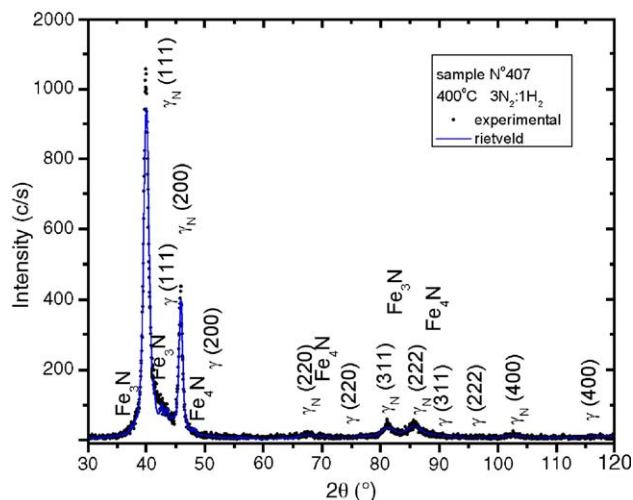


Fig. 1. AISI 316L nitrided at 400 °C, 12 h, 75% N_2 /25% H_2 .

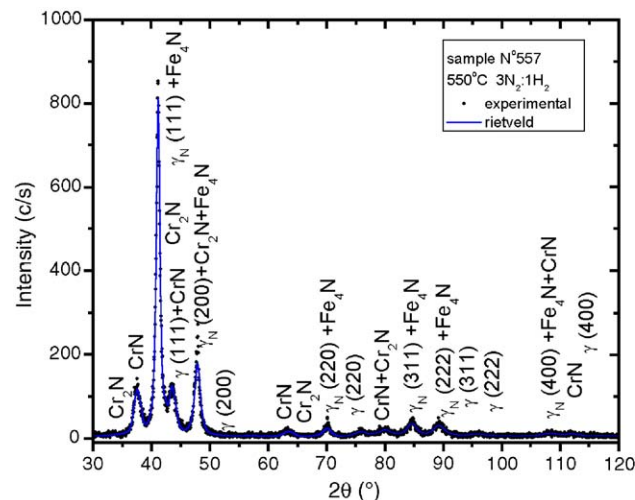


Fig. 3. AISI 316L nitrided at 550 °C, 12 h, 75% N_2 /25% H_2 .

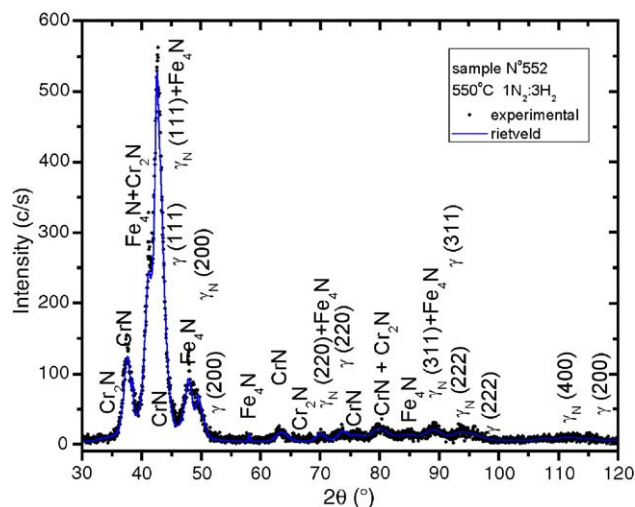


Fig. 4. AISI 316L nitrided at 550 °C, 12 h, 25%N₂/75%H₂.

nitriding is carried out with high nitrogen content in the gas mixture expanded austenite content is lower due to the high iron and chromium nitrides volume fraction, and a lower distortion ε in the austenitic lattice is found. Increasing nitrogen content in the gas mixture expanded austenite lattice parameters are only slightly different.

When nitriding is performed at 550 °C nitride precipitation controls the overall formation of the layer. Circa 80% of the layer is composed by nitrides, according to Table 2. For nitrogen to hydrogen ratio 1N₂:3H₂, CrN is the major phase in the diffusion zone. When the nitrogen potential of the atmosphere is increased to 3N₂:1H₂, γ -Fe₄N nitrides predominate. In this case, a better corrosion resistance is expected for plasma nitriding at high temperature using high nitrogen content in the

Table 3

Austenite lattice expansion and FWHM parameter

| Condition | 400 °C — 3N ₂ :1H ₂ | 400 °C — 1N ₂ :3H ₂ | 550 °C — 3N ₂ :1H ₂ | 550 °C — 1N ₂ :3H ₂ |
|------------------|--|--|--|--|
| $\Delta a/a$ (%) | 10.05 | 9.72 | 5.21 | 2.41 |
| C_N | $C_N=46.28\%$ | $C_N=44.86\%$ | $C_N=24.00\%$ | $C_N=11.09\%$ |
| FWHM (°) | (111) 1.10 (200) 1.18 (220) 2.28 (311) 4.88 | (111) 1.12 (200) 1.76 (220) 2.34 (311) 5.63 | (111) 0.58 (200) 0.69 (220) 1.15 (311) 1.57 | (111) 0.72 (200) 0.82 (220) 1.24 (311) 1.67 |

gas mixture due to a lower depletion of chromium in the matrix. However, corrosion resistance for low-temperature nitriding will be always higher because of the low volume fraction of nitride precipitation.

For 550 °C nitriding treatments the differences are more noticeable. In the nitride layer a greater nitride precipitation leads to lower nitrogen content in the matrix. As a consequence one can see a lower volume fraction of expanded austenite with a lower distortion of the austenitic lattice. The distortion of the lattice is small enough to give a face centered cubic crystalline structure.

Table 3 shows the relative expansion of the austenite parameter (γ_N) when compared to virgin austenite, $\Delta a/a_\gamma$ (%), where $\Delta a = a_{\gamma_N} - a_\gamma$, and the nitrogen content of expanded austenite C_N , calculated according to Picard's [7] equation:

$$a_{\gamma_N} = a_\gamma + AC_N$$

where A is the Vegard's constant (0.0078 Å).

Table 3 also shows the Full-Width Half-Maximum (FWHM) of austenite peaks. The greater expansion of the austenitic lattice parameter, observed at 400 °C, is responsible for the increase in

Table 2

Phases, volume fraction and lattice parameter in the nitrided case using Rietveld method

| Condition | Expanded austenite γ_N | Fe ₂ N | Fe ₃ N | Fe ₄ N | CrN | Cr ₂ N |
|----------------------------------|---|-------------------|---------------------------------------|------------------------|------------------------|---------------------------------------|
| 400 °C | (t) | (hp) | (hp) | (fcc) | (fcc) | (hp) |
| 3N ₂ :1H ₂ | 89.60% $a=0.395$ nm $\alpha=89.24^\circ$ $\beta=91.51^\circ$ $\varepsilon=1.51^\circ$ | 0.05% | 4.70% $a=0.272$ nm $c=0.422$ nm | 3.70% $a=0.378$ nm | 0.14% | 1.80% $a=0.481$ nm $c=0.450$ nm |
| 400 °C | (t) | (hp) | (hp) | (fcc) | (fcc) | (hp) |
| 1N ₂ :3H ₂ | 96.70% $a=0.394$ nm $\alpha=88.82^\circ$ $\beta=92.34^\circ$ $\varepsilon=2.34^\circ$ | 0% | 0.80% | 0% | 0% | 2.50% $a=0.481$ nm $c=0.450$ nm |
| 550 °C | (fcc) | (hp) | (hp) | (fcc) | (fcc) | (hp) |
| 3N ₂ :1H ₂ | 7.42% $a=0.378$ nm | 0.28% | 0.03% | 60.00% $a=0.379$ nm | 27.00% $a=0.414$ nm | 5.00% $a=0.486$ nm $c=0.442$ nm |
| 550 °C | (fcc) | (hp) | (hp) | (fcc) | (fcc) | (hp) |
| 1N ₂ :3H ₂ | 15.00% $a=0.369$ nm | 0.68% | 0.32% | 31.00% $a=0.379$ nm | 47.00% $a=0.414$ nm | 6.00% $a=0.491$ nm $c=0.448$ nm |

(hp): Hexagonal primitive.

(t): Triclinic.

(fcc): Face centered cubic.

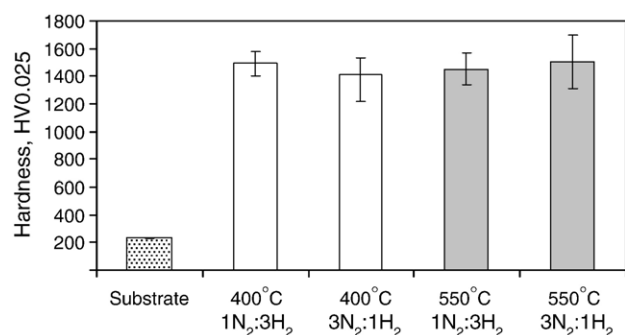


Fig. 5. Hardness of the nitrided layer after plasma nitriding at 400 °C and 550 °C.

the field of compressive residual stresses in this phase, resulting in a strong hardening effect.

High-temperature nitriding induces precipitation of iron and chromium nitrides which hardens the specimen's surface. Low-temperature nitriding treatment leads to the formation of a hard expanded austenite layer and Fig. 5 shows hardness values for the nitrided case of all plasma nitriding conditions. Both low- and high-temperature nitriding treatments lead to surface hardness up to 1500 HV.

4. Conclusions

After plasma nitriding an AISI 316L austenitic stainless steels it was observed that the nitrided layer of specimens nitrided at 400 °C shows predominantly expanded austenite although some chromium and iron nitride precipitation is also observed. The expanded austenite is better described by a

special triclinic (t) crystalline structure, with a distortion ϵ of the lattice angles due to the presence of high nitrogen supersaturating the solid solution. The high nitrogen content (circa 45 at.%) dissolved in the γ_N crystalline lattice leads to a noticeable expansion of the lattice (10%) giving rise to high compressive residual stresses. For 550 °C nitriding treatments a greater nitride precipitation leads to lower nitrogen contents in the matrix, a lower volume fraction of expanded austenite and a lower distortion of the austenitic lattice. The structure of the austenitic phase remains face centered cubic.

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