Surface modification of austenitic stainless steel by means of low pressure glow-discharge treatments with nitrogen

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Introduction

<u>Low temperature nitriding of austenitic stainless steels</u>:
formation of modified surface layers consisting mainly of **S phase** (supersaturated interstitial solid solution of nitrogen in the expanded and distorted γ-Fe f.c.c. lattice)
$\rightarrow$ **increase** of the **surface hardness** and **corrosion resistance** in Cl^- containing solutions

<u>Key step</u> in the nitriding treatment for obtaining a homogenous incorporation of N: removal of the passive oxide layer

Possible pre-treatment for achieving this goal: cathodic sputtering
$\rightarrow$ it allows surface cleaning and heating of the samples thanks to ion bombardment

Introduction

Aims of the research:

Preliminary investigation regarding the possibility of producing modified surface layers on austenitic stainless steels by means of **low pressure glow-discharge treatments with nitrogen**, **similar to cathodic sputtering**, so that **surface activation**, **heating** and **nitrogen incorporation** **can occur in a single step** having a **short duration (up to about 10 min)**.

The characteristics of the modified layers obtained with these treatments (microstructure, surface roughness, water wettability, surface microhardness, corrosion resistance) were compared to those of untreated and low temperature nitrided samples.

Materials and Methods

Materials

AISI 202 (chemical composition in wt.%: 0.065 C, 17.0 Cr, 4.1 Ni, 7.7 Mn, 0.40 Si, 0.15 N, bal. Fe)

Samples (40 mm x 17 mm x 0.7 mm) were obtained from cold rolled, annealed and pickled plates by cutting, grinding and polishing up to 6-μm diamond suspension.

Treatment equipment and conditions

Glow-discharge treatments were carried out in a laboratory plasma equipment. The samples were fastened on a prismatic sample holder, working as cathode and placed in the centre of the treatment chamber, which has an axial symmetry. The treatment temperature was controlled varying the discharge current supplied by a DC power supply and it was measured by a chromel-alumel thermocouple inserted into the sample holder.

Low pressure treatments (Type A and B): the discharge current density was fixed and increased with two constant steps (2.2 and 2.6 mA cm^{-2}), while the voltage drop between the electrodes and the treatment temperature were allowed to increase freely. When a prefixed voltage drop was reached, the power supply was turned off, the treatment chamber was evacuated and the samples were allowed to cool down to room temperature under vacuum.

Nitriding treatment (Type C): after a pre-treatment (Type A), nitriding parameters were changed to their nominal values and the treatment was carried out.

Materials and Methods

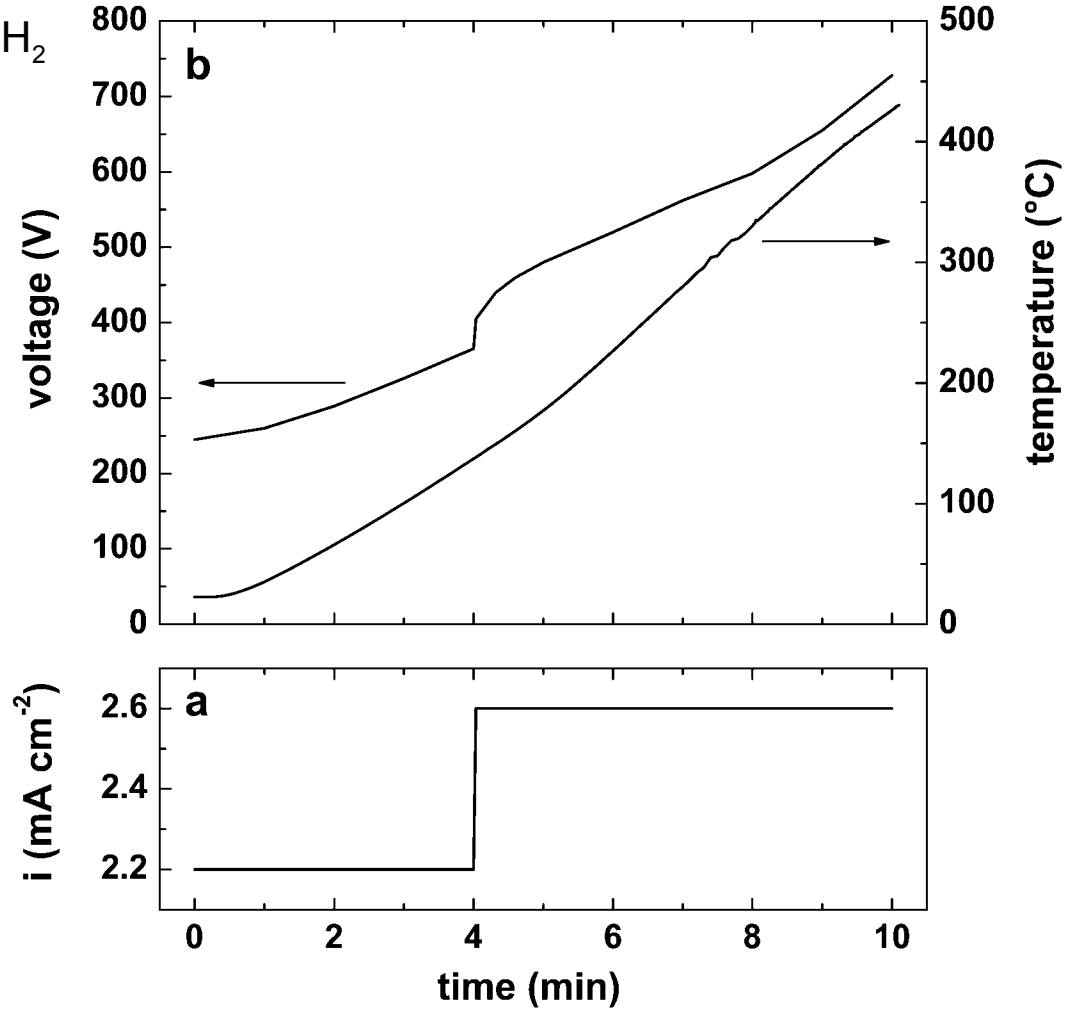
Treatments

Gas composition: 80 vol.% N_2 + 20 vol. % H_2

Type A
pressure: 130 Pa
max. voltage drop: 595 ± 5 V
max. bulk temperature: 330 °C
duration: 8 min

Type B
pressure: 130 Pa
max. voltage drop: 730 ± 5 V
max. bulk temperature: 430 °C
duration: 10 min

Type C
Type A + nitriding
Nitriding conditions:
pressure: 500 Pa
voltage drop: 150 ± 10 V
current density: 1.6 ± 0.1 mA cm^{-2}
bulk temperature: 380 °C
duration: 5 h



Current density (**a**), voltage drop and bulk temperature (**b**) vs. time for Type-A and -B treatments.

Materials and Methods

Characterization

Microstructure: light and scanning electron microscopies (etchant for the cross-sections: acetic glyceregia).

Phases: X-ray diffraction analysis (Bragg-Brentano configuration; Cu-Kα radiation).

Semiquantitative evaluation of alloy elements and N: X-ray fluorescence (XRF).

Roughness: Ra, Rz, Rc evaluation by means of a stylus profilometer (2-μm radius stylus with a 1-mN contact force; cut-off length: 0.25 mm).

Apparent static contact angle: sessile drop method (liquid: bi-distilled water; drop size: 0.5 μL; ambient laboratory conditions).

Surface microhardness: Knoop indenter (load: 10 and 25 gf).

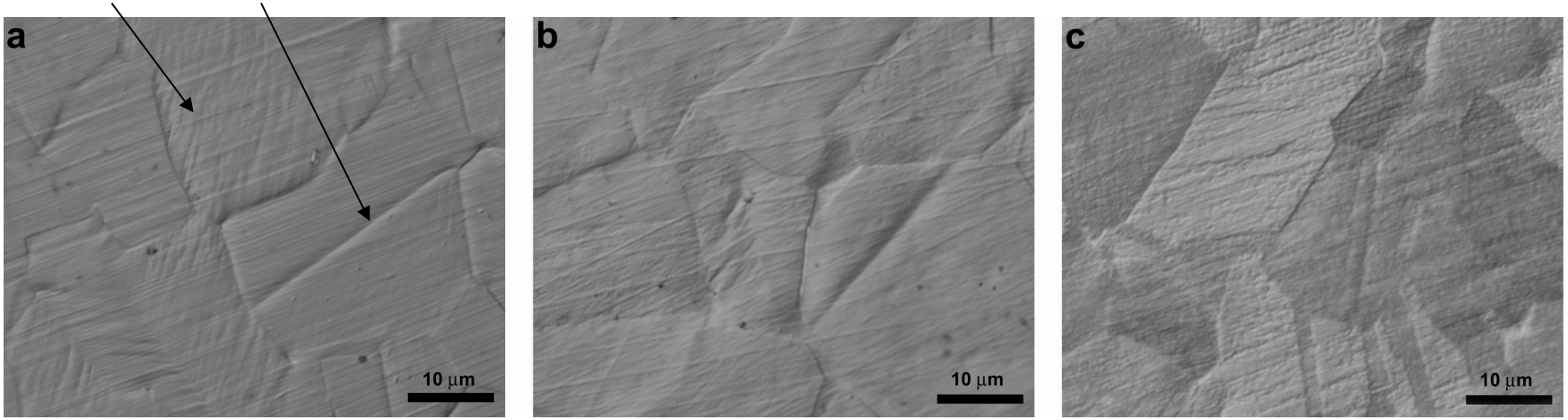
Corrosion behaviour: potentiodynamic method, coulometric analysis (integration of current density from corrosion potential to +1000 mV (Ag/AgCl)) (solution: 5 % NaCl, aerated; delay: 18 h; potential scan rate: 0.3 mV s^{-1}; exposed surface area: 1 cm^2; reference electrode: Ag/AgCl (3.5 M KCl); counterelectrode: platinum).

Results and discussion

Morphology and microstructure

Surface morphology and roughness

Relevant features: etching due to sputtering, and local plastic deformations (shear lines) due to the formation of the modifed layers.



Type A	Type B	Type C
Ra = 0.011 ± 0.002 μm	Ra = 0.042 ± 0.002 μm	Ra = 0.045 ± 0.005 μm
Rz = 0.09 ± 0.02 μm	Rz = 0.32 ± 0.04 μm	Rz = 0.32 ± 0.07 μm
Rc = 0.06 ± 0.01 μm	Rc = 0.20 ± 0.02 μm	Rc = 0.21 ± 0.05 μm

untreated AISI 202

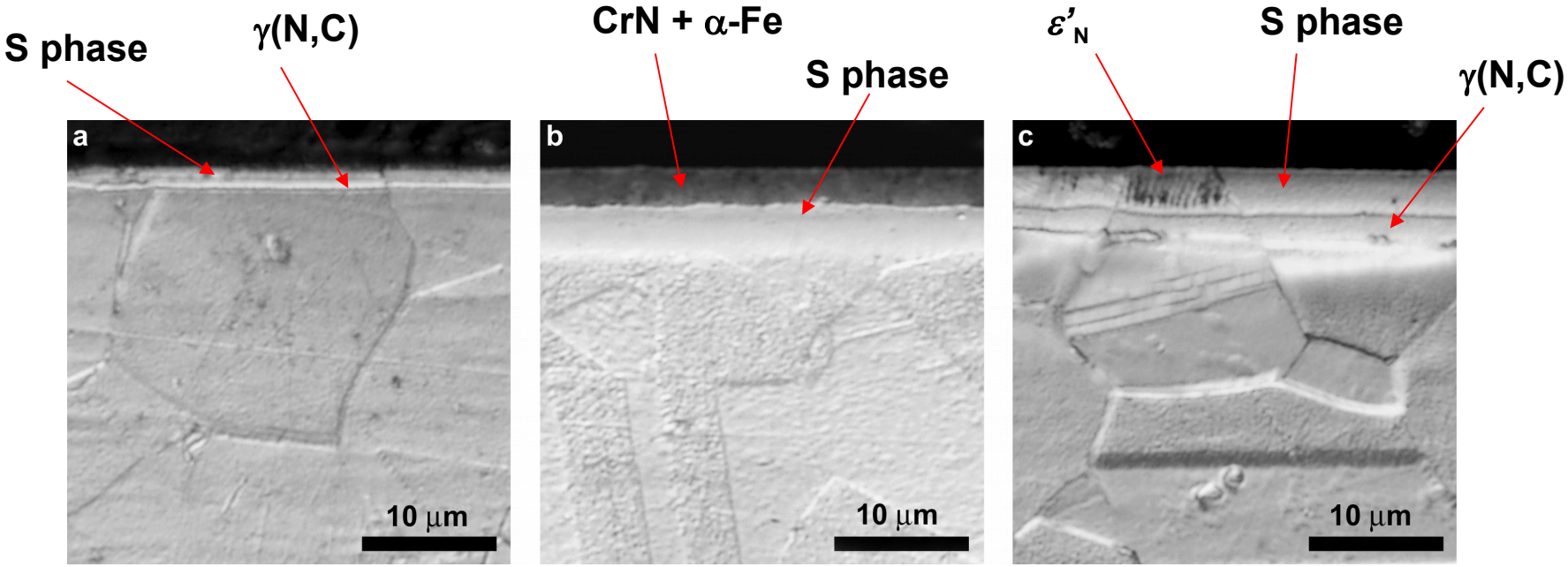
Ra = 0.007 ± 0.002 μm; Rz = 0.046 ± 0.008 μm; Rc = 0.029 ± 0.006 μm

Results and discussion

Morphology and microstructure

Cross-section microstructure

Formation of modified surface layers having a double layer microstructure.



Type A
thickness: 1.8 ± 0.2 μm
N content: ~22 at. %

Type B
thickness: 6.5 ± 0.3 μm
N content: ~25 at. %

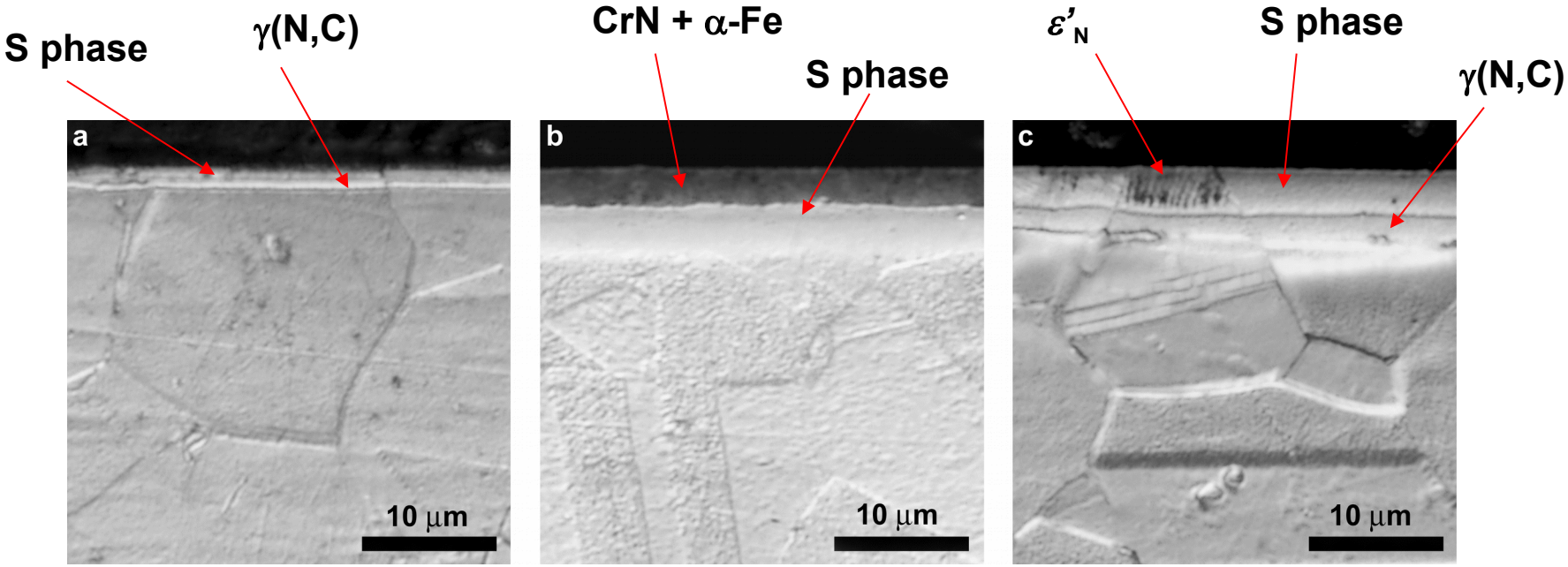
Type C
thickness: 4.8 ± 0.3 μm
N content: ~25 at. %

Results and discussion

Morphology and microstructure

Cross-section microstructure

Formation of modified surface layers having a double layer microstructure.



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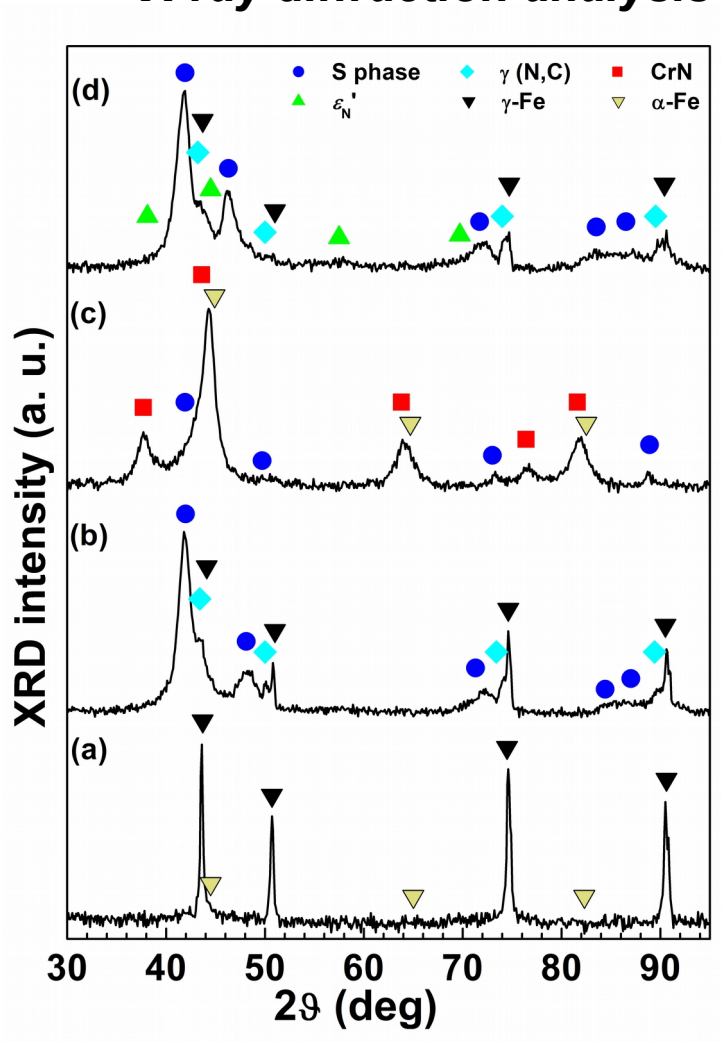
thickness: 4.8 ± 0.3 μm
N content: ~25 at. %

Results and discussion

Morphology and microstructure

X-ray diffraction analysis



Type C

Type B

Type A

untreated

Note:

- γ(N,C): solid solution of N, C in γ-Fe
- ε_N': solid solution of N in h.c.p. ε' martensite

Results and discussion

Morphology and microstructure

Effects of low pressure treatment:

- increase of mean free path of molecules, atoms and ions present in the plasma
- increase of discharge voltage between the electrodes

consequences:

- increase of ion and fast neutral energy → very efficient sputtering, deep etching
- increase of the number of active nitrogen atoms → possibility of large nitrogen incorporation and diffusion in the substrate

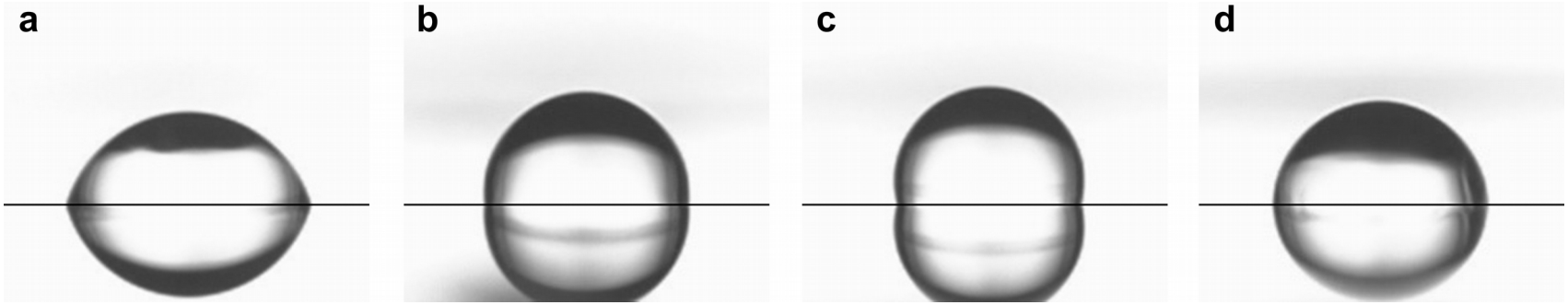
Low pressure treatments are very sensitive to process parameters:

- lower voltage drop and temperature (Type A): modified surface layers similar to those obtained with low temperature nitriding (nitriding duration for having similar thickness: 1 – 3 h);

- higher voltage drop and temperature (Type B): formation of large amount of CrN, which causes the subsequent transformation of austenite into b.c.c. α-Fe.

Results and discussion

Apparent water contact angle



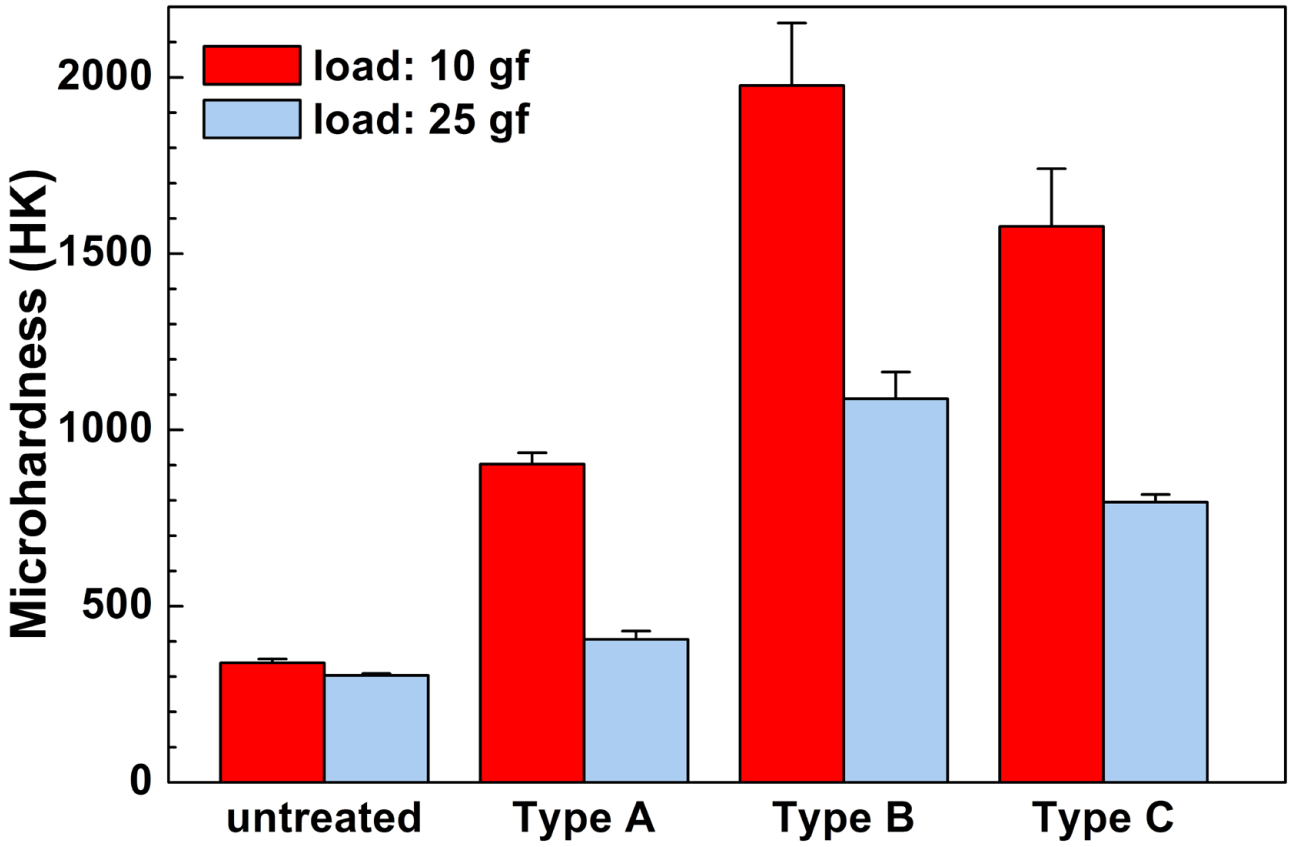
untreated	Type A	Type B	Type C
73° ± 3°	96° ± 2°	104° ± 2°	84° ± 6°

Images of 0.5-μl drops deposited on the surface. The black line is drawn as a guide to the eye to outline the surface and to separate the drop from its reflection.

The increase of the apparent contact angle suggests that fakir drop lies on a composite surface of solid and air pockets trapped underneath, according to the Cassie-Baxter model. The combination of strong etching at grain boundaries and plastic deformations inside the grains seems to promote the formation of many air pockets, so that a hydrophobic behaviour (contact angle > 90°) is observed.

Results and discussion

Microhardness



As the test load is increased, lower hardness values are detected, due to both the indentation size effect and the fact that layers having different characteristics are tested.

Results and discussion

Corrosion behaviour

• Untreated, and Type-A and -C treated samples: passive corrosion behaviour; solubilized nitrogen has a beneficial effect for increasing corrosion resistance;
• Type-B samples: active corrosion behaviour; large amount of CrN prevents the formation of a protective passive film.

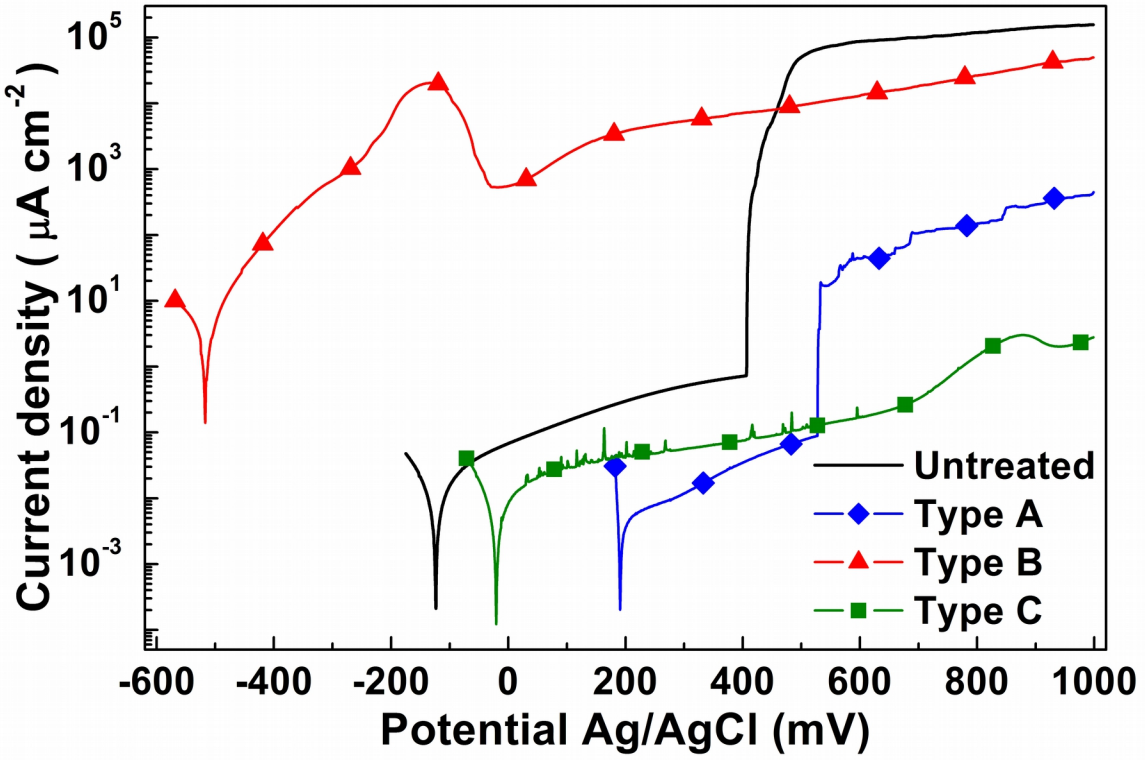
Coulometric analysis

untreated
Q: $(1.9 \pm 0.1)\ 10^5$ mC cm^{-2}

Type A
Q: $(2.8 \pm 0.3)\ 10^2$ mC cm^{-2}

Type B
Q: $(5.6 \pm 0.2)\ 10^4$ mC cm^{-2}

Type C
Q: 3 ± 1 mC cm^{-2}



Polarization curves of samples untreated and treated as indicated

Conclusions

Low pressure glow-discharge treatments, performed at 130 Pa in 80 vol. % N_2 + 20 vol. % H_2 gas mixture on AISI 202, allow surface activation, heating and nitrogen incorporation in a single step having a short duration (up to 10 min).

Low pressure treatments are very sensitive to process parameters:

• **lower voltage drop and temperature** (Type A): modified surface layers similar to those obtained with low temperature nitriding (nitriding duration for having similar thickness: 1 – 3 h), consisting mainly of S phase; improved surface hardness and corrosion resistance in comparison with untreated AISI 202;

• **higher voltage drop and temperature** (Type B): formation of large amount of CrN, which causes the subsequent transformation of austenite into b.c.c. α-Fe; very high surface hardness, poor corrosion resistance.

The treatments produce an increase of surface roughness, which affects water wetting properties, causing a hydrophobic behaviour.