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Protective Nitrided Layers on Ferrite-Austenite Chromium Steel

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High chromium ferritic-austenitic steel is widely applied as a constructional material due to its good corrosion resistance. The possibility to obtain nitrided layers on this steel could widen these applications thanks to producing hard and wear resistance protective coatings. However, this process is not well known and investigated. The paper presents results of investigations on the nitrided layer growth on ferritic-austenitic steel during gas nitriding. Particular attention is paid to importance of technological parameters such as temperature and activation treatment for layer formation. Process was conducted in ammonia atmosphere with 100 % of ammonia in temperature range 350 °C – 550 °C.

Keywords: expanded austenite, gas nitriding, duplex steel.

1. INTRODUCTION

Duplex stainless steels are a family of grades combining good corrosion resistance with high strength and easy fabrication. Their physical properties are between those of the austenitic and ferritic stainless steels but tend to be closer to those of ferritic and carbon steel. They have good mechanical and corrosion properties compared with austenitic stainless steel and are often used in chemical industries, chemical tankers, in energetic and offshore installations. The ferritic-austenitic stainless steel has a relatively low hardness and wear resistance. Nitriding seems to be a reasonable method to improve the wear resistance but unfortunately it affects negatively the corrosion resistance of chromium steel due to nitrides precipitation. It was found [1] that in case of austenitic steel when plasma nitriding was conducted at temperature below 500 °C it was possible to maintain high corrosion resistance thanks to formation so called "expanded austenite" (named also γN , *S*- or *m*-phase). The few works on plasma nitrided duplex steel [2 – 5] confirmed the formation of this phase also in case of ferritic-austenitic steel. For austenitic steel the formation of "expanded austenite" is also possible during gas treatment [6 – 7]. Moreover it was stated that applying ion sputtering as activation treatment it is possible to obtain layers with various morphology at the same gas nitriding conditions [6].

The main objective of the present work is to investigate the formation of nitrided layers on duplex steel during gas nitriding. The influence of gas used for activation and the nitriding temperature is analysed.

2. EXPERIMENTAL

The investigations were carried out on the samples made of austenitic-ferritic steel (see Table 1).

The size of the samples was $10 \times 20 \times 5$ mm. They were polished to a 3 μm diamond solution and electropolished as the ultimate method and afterward cleaned in the ultrasonic alcohol bath. Samples were treated according to the process parameters presented in Table 2.

Table 1. Chemical composition of ferritic-austenitic steel

C	Cr	Ni	Mo	Mn	Si
0.03	22.09	5.22	2.72	1.83	0.34

Table 2. Treatment parameters applied during experiments

Activation technique – ion sputtering	Treatment – gas nitriding
Atmosphere: hydrogen or nitrogen Current density : 3mA/cm^2 Voltage : 1.35 kV Time: 15 min	Atmosphere: 100 % ammonia Time: 3 hours Temperature: 350 °C, 400 °C, 450 °C, 500 °C, 550 °C

The gas nitriding experiments were conducted in the temperature range 350 °C to 550 °C for 3 hours in the ammonia atmosphere (100 % NH_3). To make the gas treatment possible before nitriding, the samples were activated by ion sputtering in the nitrogen or hydrogen atmosphere (see Table 2).

The morphology of the nitrided layers was investigated using light microscopy analysis – LMA (Nikon Epiphot 200) and electron scanning microscope (Jeol 6100). The composition of the layers was evaluated by X-ray diffraction (CuKα, X'Pert Philips) and by EBSD (Oxford Instruments). The phase identification was also done by Magnetic Force Microscopy (DI). Moreover, the layers microhardness was measured using Knoop technique (Boehler Microhardness Tester 2000) with load varying 10 to 100 gf and on cross-section with load 5 gf. Changes in the surface roughness after the treatment were measured with Mitutoya Surftest Profilometer.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

The ferritic and austenitic phases in duplex steel were identified using Magnetic Force Microscopy (MFM) and Electron Back Scattering Diffraction (EBSD). In Fig. 1 an example of MFM and AFM pictures obtained for duplex steel are presented.

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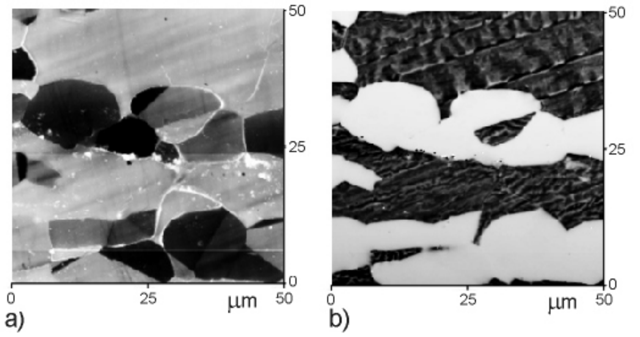

Fig. 1. AFM (a) and MFM (b) image of the surface of duplex steel. The darker regions in the right picture correspond to ferritic (magnetic) grains

3.1. Microstructure of the layers

Fig. 2 shows the diffraction patterns for all the samples investigated in these experiments.

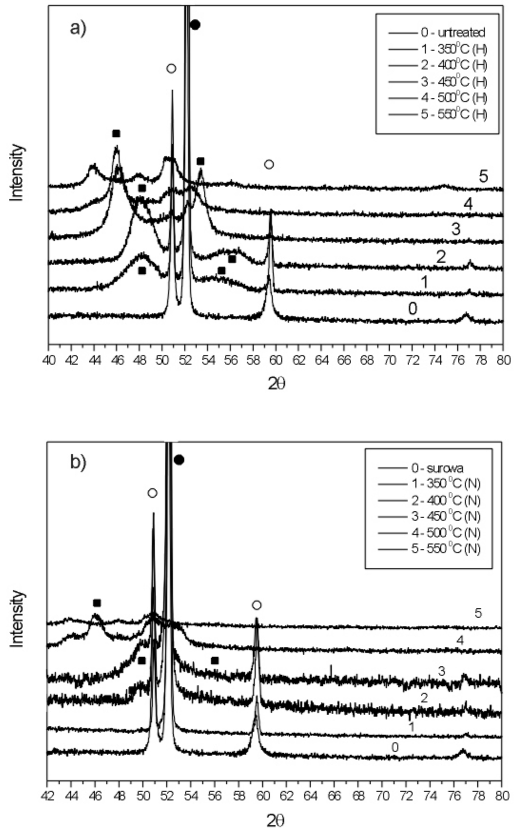

Fig. 2. Diffraction patterns for all the samples depending on the nitriding temperature and sputtering gas: a – sputtered in hydrogen (H); b – sputtered in nitrogen (N)

It can be seen that both sputtering gas and nitriding temperature have important influence on phase composition of the layers. In case of cleaning in hydrogen, "expanded austenite" is detected already in samples nitrided at 350 °C and its peaks are shifted much more in the direction of lower angles than it is observed for the samples sputtered in nitrogen. For those latter nitrided at 350 °C there are no visible peaks of γN phase. For higher nitriding temperatures only very weak peaks are observed. For both sputtering gases above 500 °C the presence of nitrides can be detected. The exact identification of them was impossible, because peaks were very broad and very weak. Cr_2N and Fe_2N were identified but some peaks could be also attributed to CrN and Fe_4N nitrides. Diffraction measurements confirmed the beneficial effect of hydrogen on formation of "expanded austenite" and nitriding kinetics, which was mentioned by others scientists, who observed better process kinetics when nitriding in plasma contained hydrogen [8 – 9]. In investigations presented here, however, this positive influence of hydrogen is observed when this gas is used for cleaning only. It could suggest, that this improvement results from better removing of chromium oxides thanks to reduction character of hydrogen.

The appearance of the surface after nitriding was similar for both sputtering gases but changed with temperature of the treatment. For samples nitrided at 350 °C – 450 °C the differences between ferritic and austenitic structures are clearly visible (Fig. 3). On the surface the characteristic relief [10] was observed which becomes even more clear with temperature (Fig. 3). For the samples nitrided at 500 °C and 550 °C it was no more differences between ferritic and austenitic grains, and the whole surfaces are uniformly rough.

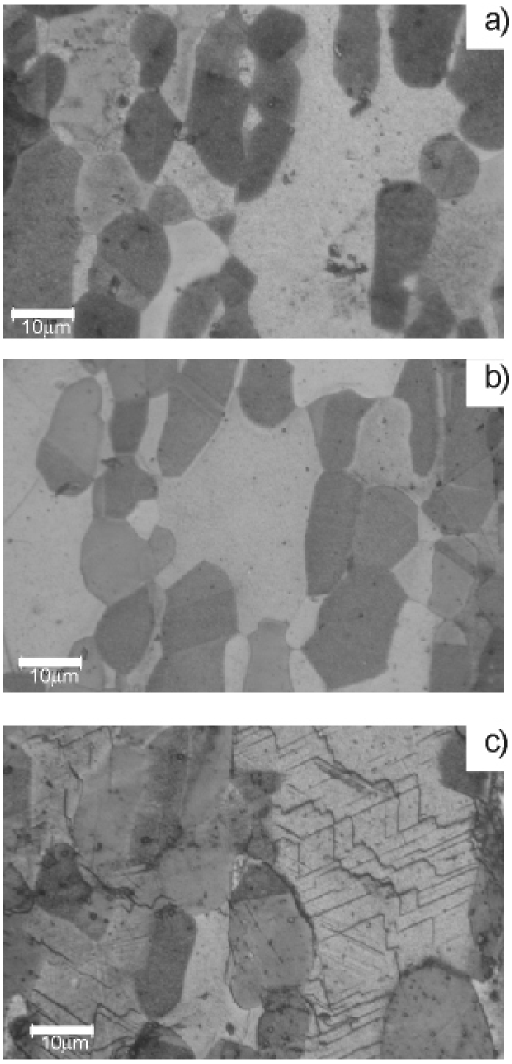

Fig. 3. Surface of the samples sputtered in nitrogen after nitriding at: a – 350 °C , b – 400 °C, c – 450 °C

The differences in morphology of the layers can be also observed on their cross-sections. The growth of the layers depends on the grain type. In the most of cases the layer on the austenite was thinner than that one on ferrite, which is shown in Fig. 4. The part of the layer produced on austenite has characteristic curvature being thicker in the near of the grain border and thinner in central part of the grain. Similar observation was made by Kliauga [11] on the plasma nitrided duplex steel. But he observed the opposite effect on gas nitrided samples. It means that thicker layer was detected on austenite. In these experiments such layers were also obtained in some sputtered in nitrogen samples. For the moment there is no plausible explanation of this phenomenon and it will be investigated in more depth.

The investigation of the layers by EBSD technique, have shown interesting relationship. The part of the layers produced on austenite was easily identified as austenite (Fig. 5) which is typical for "expanded austenite" produced on austenitic stainless steel [12]. The layer made on ferrite was not identified neither as austenite nor ferrite or nitrides. It is surprising taking into account that in these layers only γN phase is detected on diffraction pattern (Fig. 2). It could suggest that layer produced on ferrite has different nature from that produced on austenite.

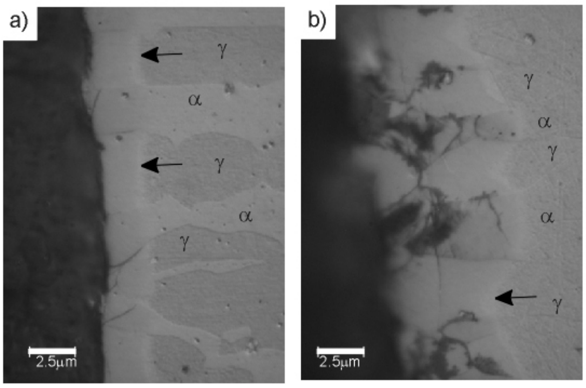

Fig. 4. Cross sections of the layers on duplex steel after nitriding at: a – 400 °C; b – 450 °C. The arrows shows the curvature of the layer on austenitic grains

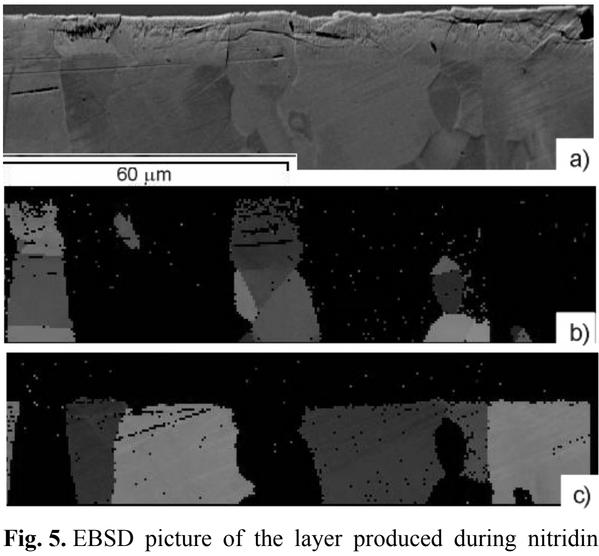

Fig. 5. EBSD picture of the layer produced during nitriding at 450 °C: a – SEM picture of the layer; b – austenite; c – ferrite identification

3.2. Properties of the layers

In Fig. 6 the thickness of the layers is presented in relation to the process parameters. The temperature of the nitriding is decisive for layer growth. Also some slight differences are observed between the samples sputtered in nitrogen and hydrogen, but they are rather ambiguous, and also need further investigations.

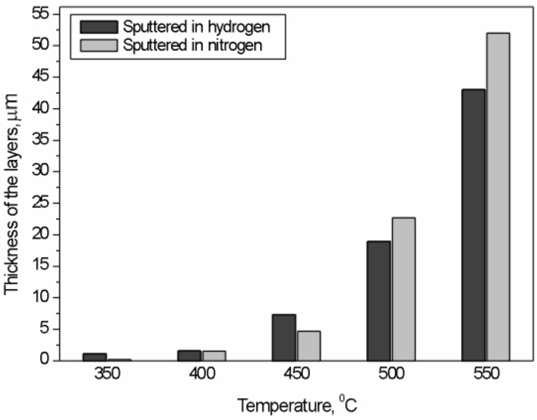

Fig. 6. Thickness of the layers depending on the sputtering and gas nitriding parameters.

The roughness measurements reflect very well the relief that was observed on the surface after nitriding. The changes of Ra parameters depending on the nitriding and sputtering conditions are presented in Fig. 7. Also in this case the strong influence of temperature is observed.

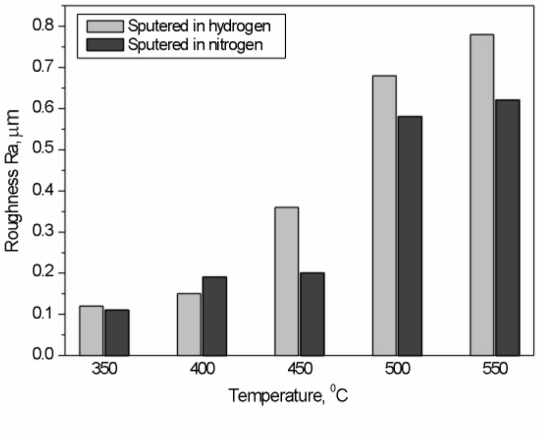

Fig. 7. Roughness of the samples after gas nitriding

The nitriding of the duplex steel has important influence on hardness of duplex steel, as it can be seen in Fig. 8. Due to very thin layer obtained at temperatures 350 °C and 400 °C it was impossible to measure the microhardness profiles for these samples, but for the samples nitrided at higher temperatures the measurements confirmed very high hardness of these layers both on the ferritic and austenitic grains.

The second important parameter of nitrided layers is their corrosion resistance. Although in the presented experiments such measurements were not made, some information about corrosion behavior can be known

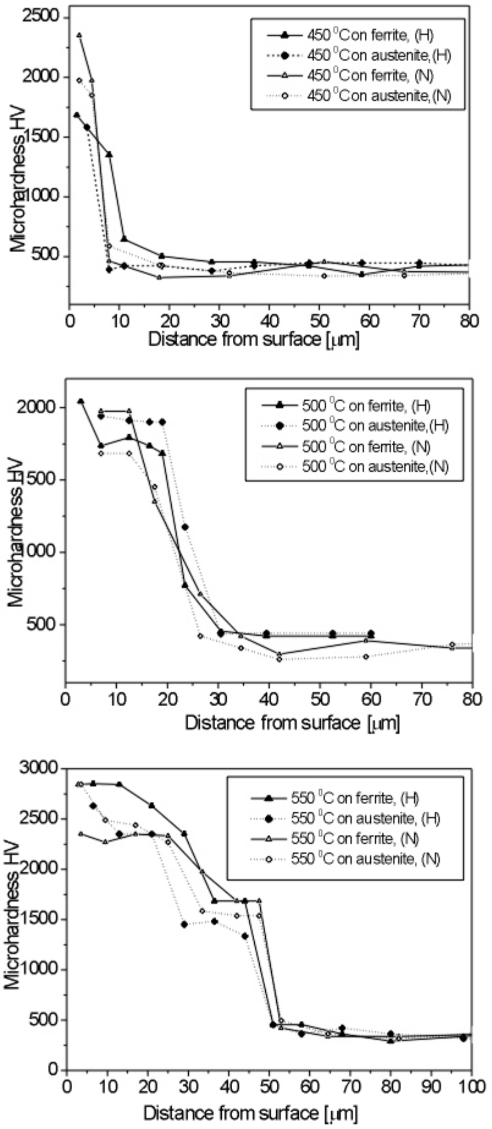

Fig. 8. Microhardness profiles of the samples nitrided in various treatment conditions

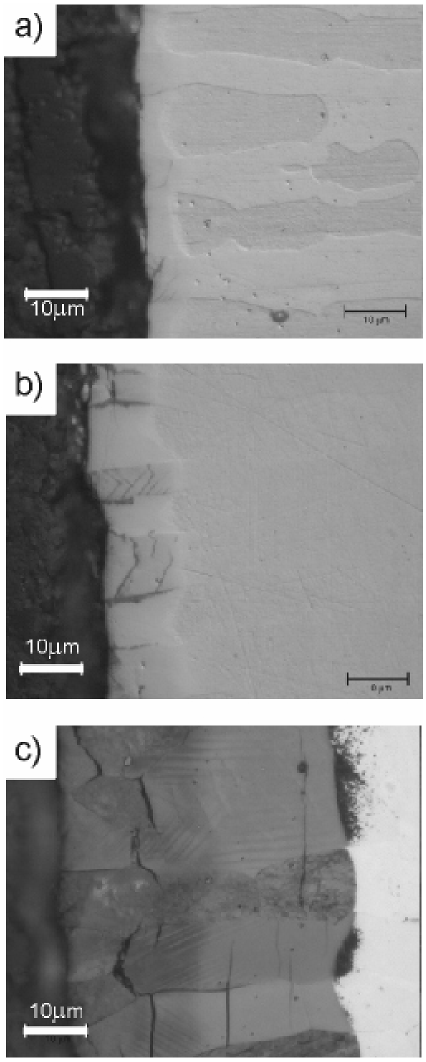

Fig. 9. Pictures of the cross-section of the layers obtained after nitriding at: a – 450 °C, b – 500 °C, c – 550 °C. Samples sputtered in hydrogen; LMA

looking at the cross-section of the layers after etching (Fig. 9). Layers, which were obtained after nitriding at 450 °C or below remain white after etching (Fig. 9, a), that could suggest their good corrosion resistance. For the sample nitrided at 500 °C the part of the layer produced on ferrite seems to be more attacked by etchant than that on austenite (Fig. 9, b). In case of the sample nitrided at 550 °C the whole layer is uniformly dark (Fig. 9, c).

4. CONCLUSIONS

1. During gas nitriding of duplex steel at low temperature (below 500 °C) it is possible to produce hard and corrosion resistant nitrided layer
2. The layers morphology and growth is mostly determined by nitriding temperature, however some influence of sputtering gas was also noticed. Cleaning in hydrogen has more positive effect on layer formation than in nitrogen.
3. The layers exhibit good uniformity on ferritic and austenitic grains, but the nature of the layer produced on ferrite seems to be different from that obtained on austenite, which was composed of γN phase.

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