

LOW TEMPERATURE GAS NITRIDING OF STAINLESS STEEL – TECHNOLOGICAL AND UTILITY ASPECTS

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Summary

The paper presents the results of an investigation into gas nitrated austenitic stainless steel. The layers were obtained at a range of temperature 400-570°C and in the atmosphere containing between 20 and 100% NH₃. A particular stress is put on the layers produced below 500°C when the layers are predominantly composed of S-phase ("expanded austenite"). The properties of the layers were characterized by stationary potential tests, wear and friction studies and hardness measurements. The morphology of the layers was investigated by X-ray diffraction, scanning and light microscopy and elemental microanalysis. Potential technological problems, which have to be considered to practically apply this technology as well as main limitations concerning layer's properties, are discussed.

Keywords: Gas nitriding, austenitic stainless steel, expanded austenite

Niskotemperaturowe azotowanie stali austenitycznej – aspekty użytkowe i technologiczne

Streszczenie

Warstwy azotowane wytworzono w zakresie temperatury 400-570°C, w atmosferze o zawartości od 20 do 100% amoniaku. Szczególny nacisk w badaniach położono na wytwarzanie warstwy w temperaturze poniżej 500°C. Warstwy uzyskane w takich warunkach są zbudowane przede wszystkim z fazy S. Właściwości użytkowe warstw określono w badaniach galwanostatycznych, tribologicznych i twardości. Ustalono skład fazowy warstw metodą dyfrakcji rentgenowskiej i zawartość azotu metodą mikroanalizy. Przeprowadzono analizę możliwości praktycznego wdrożenia tej technologii do obróbki stali austenitycznej, uwzględniając ograniczenia technologiczne i właściwości użytkowe.

Słowa kluczowe: azotowanie gazowe, stal austenityczna, „expanded austenite”

1. Introduction

Austenitic stainless steel is widely applied in industrial practice thanks to its very good corrosion resistance. The main areas of its application encompass chemical industry, food processing and medicine. At the same time it is a material with relatively low mechanical properties (hardness and wear resistance) which reduces its further potential applications. Both hardness

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and wear resistance can be enhanced by surface treatment e.g nitriding. However, application of this treatment to austenitic stainless steel is very limited mainly due to following facts:

a) The presence of oxide passive layer on chromium containing steel prevents it from nitriding. In such a case it is necessary to conduct surface activation prior to nitriding. Therefore, most of the work done on nitriding austenitic stainless steel are based on ion treatment, where passive layer is removed by sputtering.

b) Much lower nitrogen diffusion coefficient in austenite than that in ferrite was the reason that mainly high temperature treatment was investigated (above 530°C). At this temperature nitrided layers are mostly composed of chromium and/or iron nitrides which negatively affect corrosion resistance.

The study published by Ichii et al [1] was a milestone in nitriding of austenitic steel. They demonstrated that if nitriding was conducted below 500°C then layers composed of a new phase were obtained. They turned out to be very hard and wear resistance maintaining at the same time corrosion resistance comparable with those of austenitic stainless steel. The S-phase was thought to be a supersaturated nitrogen solution in austenite [2-4] and its formation was explained by a high energy of nitrogen ions bombarding the surface [5, 6]. However, the layers containing S-phase can also be obtained by gas nitriding [7-9]. A detailed investigation on this technology led to a formulation of a new theory on S-phase formation and growth [7]. At the same time nitriding process conducted in thermodynamically stable conditions allowed to gain many insights concerning practical applications of this technology. A part of them is a subject of this paper. Moreover, utility aspects of these layers are discussed in terms of technological parameters.

2. Experimental

The investigations were conducted at laboratory set-up composed of quartz tube reactor. Such a construction enables nitriding atmosphere with a very low ammonia dissociation rate to be applied. The reactor volume was 0.012 m³. When pure ammonia was introduced into the chamber with linear rate around 1cm/s the volume of dissociate ammonia on the sample's surface (ca 7 cm²) measure in the outlet was below 0.05 vol.% thanks to avoiding ammonia dissociation on the reactor walls. To obtain atmospheres with a higher dissociation rate a necessary mixture of NH₃ and H₂ and N₂ was prepared in external reactor and introduced into the chamber. The parameters of gas treatment used in the experiments are presented in Table 1. To remove chromium oxides various treatments before gas nitriding were applied to activate samples' surface.

Table 1. Parameters of gas nitriding used in the experiments

Activation	Gas nitriding		
Ion sputtering: U = 1,35 kV, j = 3,5 mA/cm ² Time = 1200 s Gases: hydrogen, nitrogen	Temperature, °C	Time, h	Atmosphere
Phosphating	400-570	2-12	20-100% NH ₃ +NH _{3diss}
Chemical etching			

Samples made of AISI 321 steel 20 mm x 10 mm x 5 mm in size were mechanically and electrochemically polished prior to the treatment.

The nitrided layers were investigated using the following techniques:

- Elemental composition: electron probe microanalysis (EPMS-EDS).
- Thickness of the layers: light and scanning microscopy.
- Phase composition: X-ray diffraction, Cu K α and Co K α ; Bragg-Brentano (XRD).
- Hardness measurements: Vickers indenter, 5g, on the cross-sections of the layers.
- Stationary chemical potentials were measured using potentiostatic tests using 3% NaCl at temperature 19°C against Ag/AgCl electrode during 1 and 24 h.
- Wear and friction tests: the specific wear rate was measured using pin-on-disk method consisting of alumina (99.6% Al₂O₃, hardness 1800 HV, roughness 0.025 Ra) ball of diameter 6 mm sliding against flat nitrided samples. For each conditions, three to four tests were carried out with fresh alumina ball. The normal force was 1 N and sliding speed 30 mm/s. The wear was measured using mechanical stylus profilometer Dektak 6M.

3. Discussion of the results

3.1. Properties of the layers vs. the nitriding parameters

Mechanical characteristics of the layers are very high and only slightly affected by nitriding process parameters (Fig. 1 and 2) within the temperature range below 515°C. The layers obtained in these conditions are mostly composed of S-phase (Fig. 3). Above this temperature nitrides dominate in the layers which can be the reason for lower hardness and higher wear rate of these layers. It was found that S-phase can contain between ca. 7.5-19 wt% of nitrogen and its lattice parameter can be higher than that of austenite by 5-13% [7]. The latter is responsible for very high stresses, which become evident when the phase formation in nitrided austenite takes place, and make the layer's hardness less sensitive to process parameters. The controlling the layer's hardness in this way is, therefore, rather limited. The hardness distribution on the layer's cross-

section is different from that obtained in typical nitrided layers (Fig. 4). A sudden drop of hardness close to matrix is observed which corresponds to a similar sudden change in nitrogen content measured in this area. No typical diffusion zone is observed in low-temperature nitrided austenitic stainless steel. This zone produced in other nitrided steel usually is many times thicker than a compound layer. In austenitic stainless steel this is due to limited diffusion of nitrogen in austenite at such a low temperature. The layer growth in these conditions is determined by S-phase formation rather than nitrogen diffusion. Therefore, when nitriding stainless steel is conducted, then it has to be considered that as a result a very hard layer on very soft substrate is obtained which can affect its behavior in potential applications.

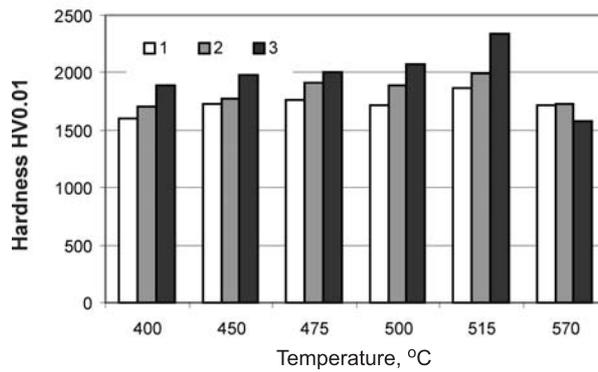


Fig. 1. Hardness of nitrided layers obtained in various conditions of gas treatment: 1 – 20% NH₃, 2 – 50% NH₃, 3 – 100% NH₃

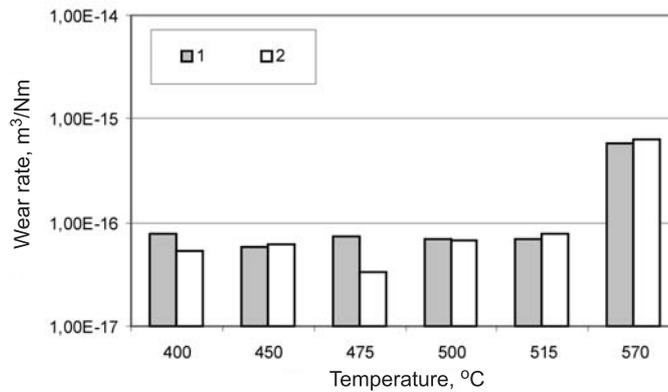


Fig. 2. Wear rate of nitrided layers obtained in various conditions of gas treatment: 1 – 20% NH₃, 2 – 100% NH₃ [7]

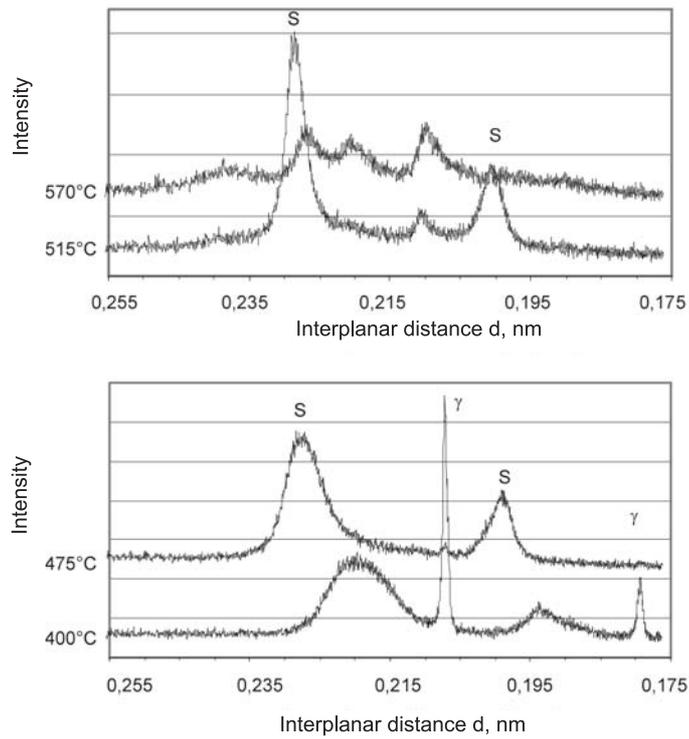


Fig. 3. Diffraction patterns of the layers obtained at various temperatures in atmosphere of 100% NH₃; treatment time – 2h [7]

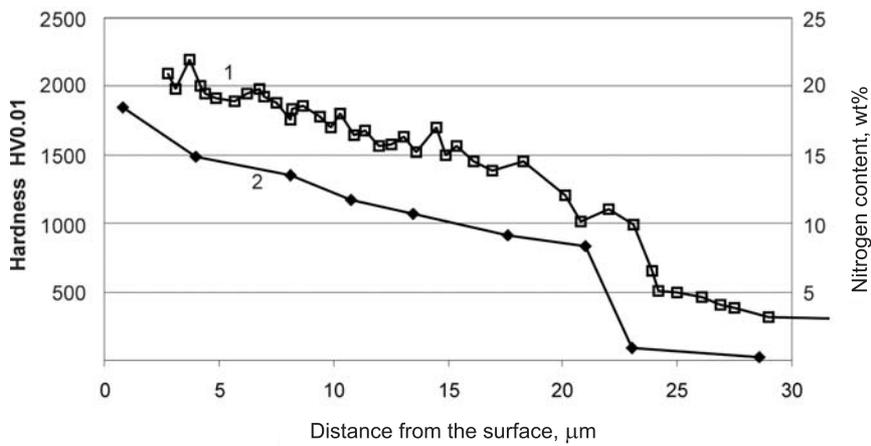


Fig. 4. Comparison of hardness and nitrogen profiles on the cross-section of nitrided layers; 100% NH₃, treatment time – 2h, temperature – 475°C, 1 – hardness, 2 – nitrogen content

A comparative study of the layers obtained by low temperature gas nitriding and ion treatment presented in the work [7] proved that they have the same morphology, composition and properties.

Wear resistance of the layers estimated in dry tests is insensitive to the process parameters. Only when the layer is mostly composed of nitrides, then accelerated wear is observed. However, the stainless steel is applied in many various areas where contact with aggressive environments is expected. Therefore, to evaluate a practical value of these layers it is necessary to test the wear in conditions simulating real conditions. Such tests done in liquids containing sulfuric and phosphoric acids demonstrated that tribological behavior of the layers can be strongly deteriorated if accompanied by corrosive interactions [10].

Corrosion resistance is then the most important parameter, which determines the practical application of nitrided layers. It was found that layers obtained below 430°C exhibit the best corrosion resistance, even better than austenite. An increase of temperature and ammonia content in the atmosphere reduces the anticorrosive properties of the layers due to the nitrides precipitation. This process is observed in the whole layer during the treatment above 500°C, but it starts also at a lower temperature. Nitrides (mainly Cr₂N and Fe₂N) start to form in an upper part of the layer. Their quantity increases with the temperature and time of the treatment. The S-phase is metastable and, as it was investigated by others [11, 12], it decomposes into nitrides. The stability time becomes shorter as temperature increase. Therefore, when the time of nitriding increases, then as a result in the upper part of the layers, which is formed at the beginning of the treatment, decomposition of S-phase is possible. The potentiostatic measurements of the layer potential confirmed that when nitriding time increased the electrochemical potential of the layer decreased (Fig. 5). This observation seems to be a principal factor, which can seriously limit a potential application of nitrided austenitic stainless steel. The kinetics of layer growth strongly depends on the temperature and ammonia content in the atmosphere (Fig. 6). The higher temperature and ammonia content the faster the layer growth. At the same time a reverse effect on corrosion properties is observed. Keeping the temperature of the treatment as low as possible to avoid nitrides formation leads to obtaining thin layers. To increase the layer thickness in these conditions a much longer treatment time is required which at the same time increases the risk of nitrides formation. From the experiments it can be concluded that the best corrosion resistance demonstrate layers obtained below 430°C and at this temperature it is possible to carry out the treatment even for 12 hours without a risk of much deterioration of corrosion resistance (Fig. 5). But at the same time only layers no thicker than 10 μm can be obtained. Conducting the treatment in the temperature range 430-475°C allows to obtain thicker layers (around 20-30 μm) but it is recommended to reduce the ammonia content.

Because the latter seems to have much more negative effect on corrosion resistance than the time of the treatment.

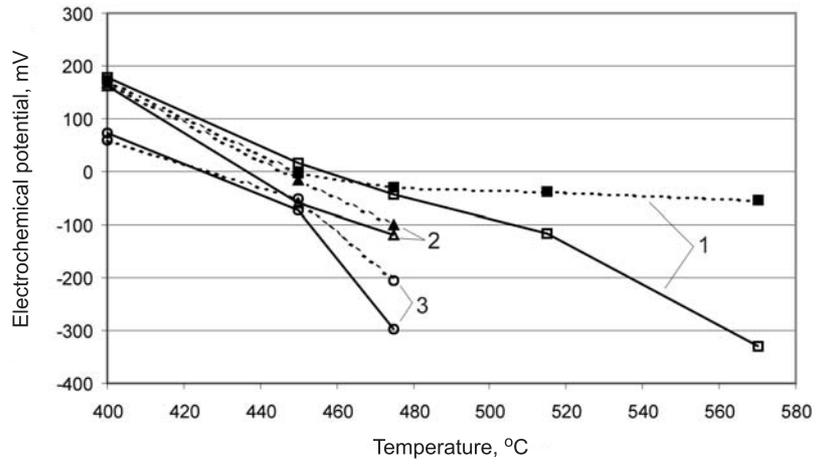


Fig. 5. Electrochemical potential measured against Ag/AgCl electrode for gas nitrided layers obtained in various conditions of the treatment; treatment time: 1 – 2h, 2 – 5h, 3 – 12h, solid line – 20% NH₃, dashed line – 100% NH₃

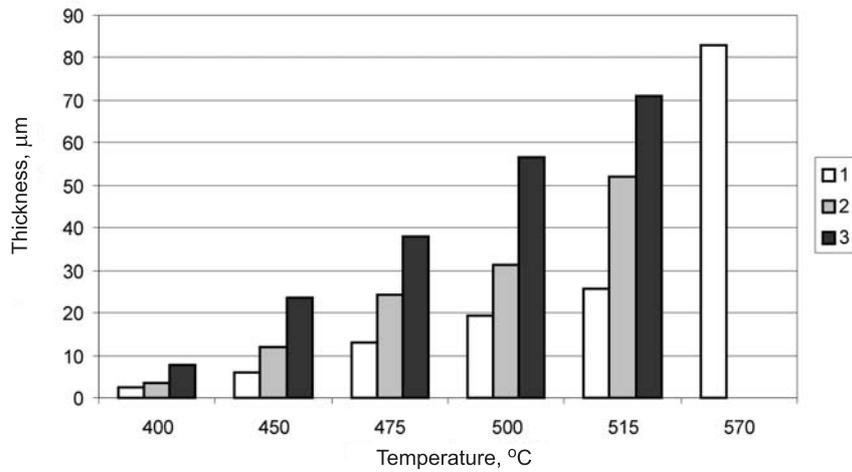


Fig. 6. Thickness of the gas nitrided layers obtained after treatment at various temperatures, nitriding atmosphere – 100% NH₃, treatment time: 1 – 2 h, 2 – 5 h, 3 – 12 h [7]

There are also two other microstructural aspects of the layers which should be taken into account in some applications. Layers containing S-phase are predominantly magnetic. This fact can limit their application in, for example, medicine, some sensitive instruments or simply in situation where wearing surfaces should be kept as clean as possible. It is possible to obtain non-magnetic layers on austenitic stainless steel for example when atmosphere with very low ammonia content is used or in case of insufficient surface activation [7]. Moreover, when carbonitriding is applied a non-magnetic layer is also produced [13]. But the layer growth rate is much smaller in these cases than for a magnetic S-phase. The second aspect is related to plasma pre-treatment. It was found that depending on the sputtering parameter and gas used it is possible to obtain layers with an additional sub-layer on the top [14]. This sub-layer is composed of a mixture of amorphous oxy-nitrides and demonstrates very good tribological performance. The friction coefficient of the range of 0.1-0.15 was measured for such a layer.

3.2. Technological aspects of the treatment

It is still an open question which treatment is better for austenitic stainless steel: gas or ion nitriding and to answer the question it is necessary to conduct more detailed comparative studies of both processes. However, some observations already mentioned in previous chapters as well as investigation where hybrid plasma-gas treatment was used for nitriding allow at least one opinion in favour of a gas treatment was presented. Layers containing S-phase are very sensitive to heating, which can lead to nitrides precipitation. During an ion treatment the exact temperature of the surface is not known and moreover, uneven plasma density distribution over the surface can lead to overheating of the edges. To avoid nitrides formation in such areas the temperature of the process is significantly reduced which affects kinetics of layer growth as mentioned earlier. Gas treatment enables the temperature of the surface to be precisely controlled and uniform. Thanks to that the treatment can be conducted at a higher temperature.

The surface activation is another problem, which frequently arises when gas nitriding of austenitic steel is discussed. Undoubtedly the necessity of additional treatment makes the whole process more complicated. The investigation carried out on the samples where activation other than ion sputtering was used (phosphating, etching and NH_4Cl addition to the atmosphere) demonstrated that ion treatment is not necessary to obtain layers composed of S-phase [7]. But it was also observed that in case of other activation treatment it was necessary to use atmospheres containing high ammonia content (Fig. 7). For example when phosphating was applied, layers containing S-phase were obtained only when the ammonia content in nitriding atmosphere was higher than 70 vol.%. Such an atmosphere is difficult to maintain in practical applications due to the ammonia dissociation on the chamber walls. At the same time sputtering with hydrogen

allows the S-phase to be formed even in atmosphere containing only 20 vol% of ammonia. Joining both processes seems to be economically justified, as it can allow ammonia use to be significantly reduced. Moreover, conducting both processes in the same reactor would allow to benefit from advantages of both techniques. Plasma treatment cleans and activates surface in the most effective way while gas treatment enables elements to be heated and nitrided in the most uniform and effective way.

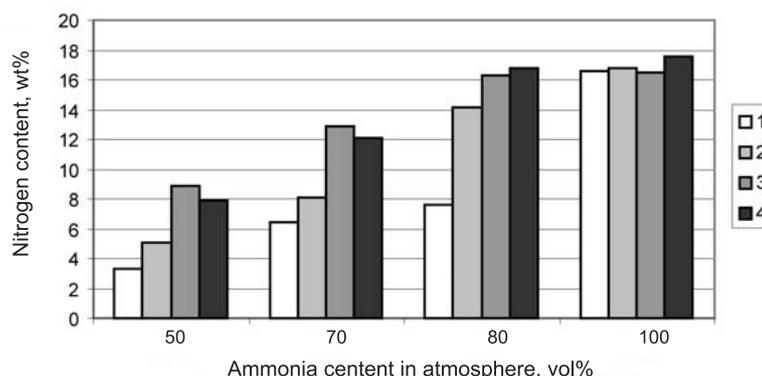


Fig. 7. Nitrogen content in the gas nitrided layers depending on the ammonia content in nitriding atmosphere and on type of activation treatment: 1 – phosphating, 2 – chemical etching, 3 – sputtering with hydrogen, 4 – sputtering with nitrogen [7]

4. Summary

Low temperature nitriding of austenitic stainless steel is a promising surface treatment, which can produce layers with very good mechanical characteristics and corrosion resistance. The main limitation concerns the layers' thickness. It is possible to obtain layers with a good corrosion resistance with maximum thickness of ca. 30 μm . A hybrid treatment: ion sputtering and gas nitriding of austenitic stainless steel can be a competitive process to ion nitriding. The characteristics of the layers obtained in both processes are comparable and gas nitriding allows avoiding the risk related to uneven phase composition of the layers, which deteriorates corrosion resistance. Moreover, depending on the combination of the parameter of both treatments it is possible to obtain layers with various morphology, which can have different potential applications.

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