

BRAKE OPERATION OF INTERSTITIALLY DISSOLVED NITROGEN ON THE CORROSION OF AUSTENITIC STAINLESS STEEL

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The effect of alloying by nitrogen was investigated on the corrosion behavior of austenitic stainless steel modified with molybdenum. The influence of the nitrogen can manifest itself either through its action in passive film, or by changing the nature of the electrolyte in the vicinity of the electrode surface. Anodic polarization curves clearly indicated that investigated nitrogen-alloyed stainless steel, and the AISI 316L steel used as a comparison, are in passive state, however, the passivation current density is much lower for the nitrogen enriched stainless steel. The occurrence of NH_4^+ ions at the interface between the passive layer and the electrolyte, causes a locally increased pH value of the electrolyte close to the electrode surface, which makes for easier passivation of the steel. The presence of NH_4^+ ions mainly favors the repassivation of pits or stress-corrosion cracks.

Key words: austenitic stainless steel, nitrogen alloyed, formation of passive film, corrosion resistance

BRZDIACI ÚČINOK INTERSTICIÁLNE ROZPUSTENÉHO DUSÍKA NA KORÓZIU AUSTENITICKEJ NEHRDZAVEJÚCEJ OCELE

Študovali sme vplyv dusíka na koróznú odolnosť austenitickej nehrdzavejúcej ocele modifikovanej molybdénom. Vplyv dusíka sa prejavuje jeho pôsobením v pasivačnej vrstve alebo zmenou podstaty elektrolytu v okolí povrchu elektródy. Anodické polarizačné krivky ukázali, že v skúmanej nehrdzavejúcej oceli legovanej dusíkom a v porovnávannej oceli AISI 316L sa dosiahol pasivačný stav, pričom pasivačný prúd bol výrazne nižší v oceli obohatenej dusíkom. Výskyt iónov NH_4^+ na rozhraní medzi pasivačnou vrstvou a elektrolytom zapríčiňuje lokálne zvýšenie hodnoty pH elektrolytu v blízkosti povrchu elektródy, čo uľahčuje pasiváciu ocele. Prítomnosť iónov NH_4^+ pôsobí priaznivo najmä na opätovnú pasiváciu jamiek alebo napäťovo-korózných trhlín.

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1. Introduction

Nitrogen alloying has been found to have beneficial effects for stainless steels modified with molybdenum. However, the interstitial dissolution of the nitrogen and the homogeneous distribution of all the alloying elements are of decisive importance for virtually all the significant properties of these steels: structural, mechanical and corrosion. Today, nitrogen is the key to a new generation of high quality steels.

In recent years a number of new, austenitic stainless steels that are alloyed with nitrogen have been developed to meet the increasing demands placed on the corrosion resistance of such materials. Nitrogen alloying, particularly in combination with molybdenum, was found to have a remarkable beneficial effect on a wide range of corrosion properties [1]. The most notable effect relates to pitting corrosion resistance [2], although favourable effects are also observed for general corrosion and intergranular corrosion [3]. Research that focused on stress-corrosion cracking also showed that nitrogen plays an important role in the resistance to this type of corrosion attack [4].

This study deals with corrosion. We have focused on the passivation and re-passivation processes, the formation of a passive film, the enrichment of the electrode surface with nitrogen compounds, and the reaction of these compounds with the corrosive medium, where such species, acting as inhibitors, can occur.

2. Materials and experimental details

In this study we compare the nitrogen bearing NTR 50 austenitic stainless steel with AISI 316L steel. The solubility of nitrogen in the steels can be increased by introducing alloying elements such as Ti, Zr, Cr, Mn, or Mo to the melt. However, Ti and Zr form undesirable nitrides as they reduce the corrosion resistance and take nitrogen out of solid solution. Only a few elements increase the solubility of nitrogen without forming nitrides during the austenitization process. The most important element in this group is Mn. This is the reason why we alloyed the NTR 50 steel with Cr and Mo, and particularly with large amount of Mn. The chemical compositions of both steels are shown in Table 1.

All our investigations were performed on heat-treated samples. The NTR 50 steel was solution heat treated at 1150°C, 2 h, after which the nitrogen was interstitially dissolved in the austenite, in contrast, the 316L steel was stress-relieved at 900°C, 2 h.

Table 1. Chemical composition of the tested steels [wt.%]

Steel	C	Mn	Cr	Ni	Mo	N
NTR 50	0.030	4.60	21.15	12.72	2.22	0.247
AISI 316L	0.021	1.80	16.99	10.62	2.16	0.050

The electrochemical corrosion tests were performed using an EG&G – PAR Model 273 potentiostat and Softcorr 352 software; a saturated calomel electrode (SCE) was used as the reference electrode.

Analysis of the passive films was performed using a VG – Scientific Microlab 310F analyser, which was used for X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

3.1 Anodic polarization tests

The problem with stainless steels is not general corrosion but pitting corrosion that occurs in the pits generated at stress-corrosion cracks. For this reason our corrosion investigations were aimed at explaining the occurrence of the passive films, their stability and the capability of the material to repassivate after local damage. This can occur in a corrosion pit, which is the result of damage to the passive film, or at a crack tip due to stress-corrosion cracking, in which the wall of the crack is passivated, and anodic dissolving can occur in the thermodynamically unstable crack tip.

In our research into the corrosion resistance of the nitrogen-alloyed NTR 50 stainless steel, we used both anodic and cyclic potentiodynamic polarizations. Anodic polarization curves provide a good insight into corrosion resistance, because the kinetics of the corrosion reactions and the different mechanisms are a direct function of the events taking place on the surfaces of the corroding material (electrode surfaces). From the shape of the curve we can decide whether the metal is moving into the passive or active corrosion state, and additional important information is provided by certain electrochemical parameters that are characteristic of the passive state. These parameters are the pitting (breakdown) potential E_p , the critical passivation current density i_{cr} , and the current density i_{pas} in passive state. The passivation processes play an important role in pitting corrosion or in stress-corrosion cracking, because all three parameters provide a clear insight into the key controlling parameter, i.e. the possibility of passivation of the wall of pits, or the wall on stress corrosion cracks, while the crack tip remains active.

The values of the electrochemical parameters obtained in 1N H₂SO₄, at 30 °C are shown in Table 2, and in the graphs in Fig. 1.

The anodic polarization curves provide us with the surprising result that the nitrogen-alloyed NTR 50 stainless steel has a lower E_p than the AISI 316L stainless

Table 2. The values of E_p , i_{cr} and i_{pas}

Material	E_p [mV]	i_{cr} [$\mu\text{A}/\text{cm}^2$]	i_{pas} [$\mu\text{A}/\text{cm}^2$]
NTR 50	879	6	4 to 5
AISI 316L	932	290	50 to 165

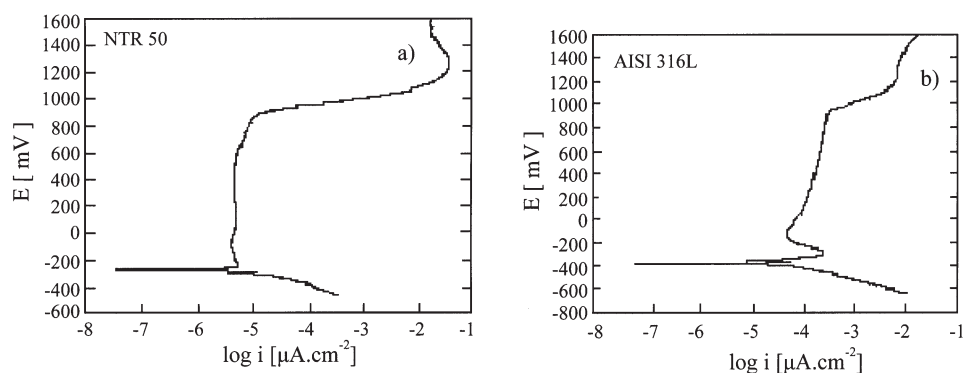


Fig. 1. Anodic polarization curves for both the investigated stainless steels: a) NTR 50, b) AISI 316L.

steel, a material that is well-known for its high resistance to pitting corrosion. However, the polarization curves show another surprising feature; i_{cr} and i_{pas} are much lower for the nitrogen-enriched steel than for the AISI 316L steel. This means that the occurrence of a passive film, or some sort of surface barrier that provides greater protection against corrosion, is accompanied by several other protective mechanisms in which nitrogen plays an active role. The influence of the nitrogen can manifest itself either through its operation in the passive film, i.e. in the film's external layer, which borders the electrolyte, or else by changing the nature of the electrolyte in the close vicinity of the electrode surfaces. Although it is characteristic of passive films that they raise the potential of the passivated metal into the nobler region, in the case of the nitrogen-alloyed NTR 50 steel, this effect is not clearly visible. This leads us to the hypothesis that, apart from passivity, the corrosive medium has an additional, specific influence in the vicinity of the electrode surfaces. The combined effect of these two factors has a strong influence on the kinetics of the corrosion processes taking place at the electrodes, which is most clearly seen in the significant shift of the passivation current density towards very low values. It can therefore be claimed that some nitrogen compounds act as an inhibitor.

3.2 Cyclic potentiodynamic polarization tests

The corrosion resistance of metals depends not only on the establishment of homogeneous passive films, but also on the individual material capacity to repassivate damaged locations. In this way pitting corrosion, which is the most characteristic type of corrosion damage that happens to metals that create a passive film, is prevented. The repassivation capability of damaged locations can be characterised by the repassivation potential E_{rp} . The larger it is, the greater is the power of

metal repassivation. Since the events in the pits or cracks caused by stress corrosion depend on the quality of the passive film and also on the speed of repassivation of the damaged locations, the results of measurements of this kind are important when determining the pitting or stress-corrosion mechanisms of nitrogen-enriched stainless steels.

The tests were performed in a saline medium according to ASTM G-61, which permits the destructive operation of the chlorides. The test conditions were as follows: a deaerated medium of 3.5 % NaCl at 20°C, a potential that increased at a rate of 3 mV/s. The results of the cyclic potentiodynamic polarization tests are shown in Table 3, and some characteristic records of the curves obtained in these tests are shown in Fig. 2.

Table 3. Experimentally obtained values of the repassivation potential

Material	E_{rp} [mV]
NTR 50	944, 921, 521
AISI 316L	-276

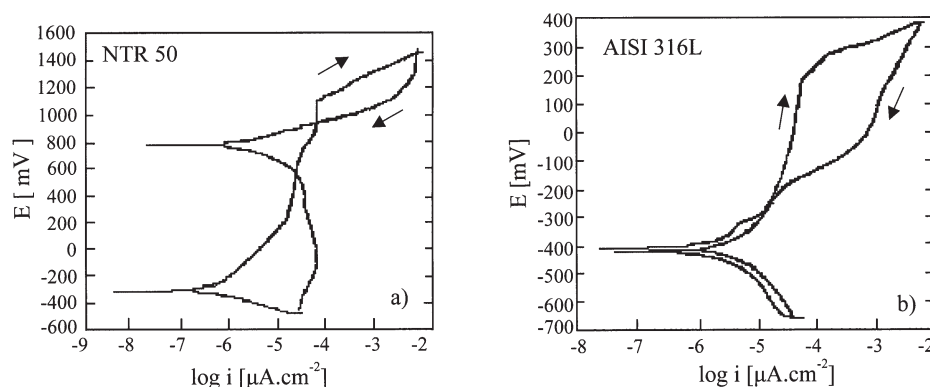


Fig. 2. Cyclic polarization curves: a) NTR 50, b) AISI 316L steel.

The solid solution of austenite in which the nitrogen is interstitially dissolved makes it possible to establish a high-quality passive film, however, the E_{rp} is somewhat lower than the E_p . Such conditions can permit mild forms of pitting corrosion since pits are only prevented if $E_{rp} > E_p$. This indicates that the NTR 50 steel does not create completely homogeneous passive films. For the case of AISI 316L stainless steel, which is known to be a high-quality steel because of its added molybdenum and its increased resistance to pitting corrosion, the characteristic parameter

of cyclic polarization is less favourable. This means that the quality of the passive film and its capability to prevent the occurrence of pits cannot be compared with that of the NTR 50 steel, where the nitrogen is interstitially dissolved in the solid solution of austenite, i.e. without nitrides and therefore without a chrome depleted zone in its direct vicinity. From the results of our research, we found that nitrogen has a strongly positive effect in austenitic stainless steels, it increases the resistance to pitting corrosion and accelerates the processes of repassivation in the pit or in the crack during pitting or stress-corrosion cracking.

3.3 Repassivation process

Grabke [2] states that nitrogen can have an effect on the initiation of pits if it is anodically segregated in the form of negatively charged N^{3-} ions (the results of this research were based on the nitrogenation of pure iron, and the presence of N^{3-} ions in the form of $N^{\delta-}$ was proved by XPS analysis), which can cross the passive film and together with the H^+ ions from the corrosion medium react to form NH_x compounds, such as NH_3 , or be in the form of NH_4^+ ions.



The NH_4^+ ions bind themselves to water, and, within a narrow region next to the electrode surfaces, they cause a local increase in pH. The NH_4^+ ammonium ion acts as a buffer. The rise in pH is therefore the consequence of the consumption of H^+ ions from the corrosive medium.

Based on the 450 ml of electrolyte, the nitrogen ions were determined with the Kjeldahl or spectrophotometric methods. The NTR 50 steel was electrochemically dissolved (transpassive region at 1050 mV) in 1N H_2SO_4 . The results are shown in Table 4.

Table 4. The measured concentrations of nitrogen ions [$\mu g/ml$]

NH_4^+	NO_3^-	NO_2^-
4.0	3.09	<0.1

Apart from the ammonium ions, the strongly oxidising NO_3^- ions also help with the repassivation. The combined action of these two components has an effect, not only on the time of initiation of a pit or stress-corrosion crack, but also on the prevention of the stable growth of the pit (the size of the numerous repassivated pits remains small). It is quite clear that the NH_4^+ and NO_3^- ions operate in a similar way in pits or stress-corrosion cracks, where, using the mechanisms described above, they retard the initiation and growth of both. Within this context it is necessary to

mention that electrochemically dissolved NTR 50 steel was performed in an aerated solution of 1N H_2SO_4 , which means that oxygen makes possible the formation of NO_3^- ions. In pits, crevices and cracks, the oxygen (acting as a depolarizer on the cathode) is quickly consumed. Thus, the actual controlling force for repassivation is only provided by the NH_4^+ ions.

3.4 XPS analysis of the passive film

X-ray photo-electron spectroscopy (XPS) was mainly used to prove the presence of $\text{N}^{\delta-}$ ions, which pass through the surface of the metal into the passive film, as well as the NH_4^+ ions and other NH_x species. Other alloying elements are also important for the establishment of a passive film, and their role was determined in this analysis.

Passive films were created on the NTR 50 nitrogen-alloyed steel in 1N H_2SO_4 , at 30°C, with an exposure time of 12 hours. The thickness of the passive film in this solution was 8.5 nm. Fig. 3 shows the concentration profiles of the XPS analyses of the passive film, Fig. 4 shows a magnified view of the lower part of concentration profiles, and Fig. 5 shows the corresponding spectra.

The results of the XPS analyses provide a clear view of the nitrogen in the investigated austenitic stainless steel. It occurs in three forms in the passive film: as

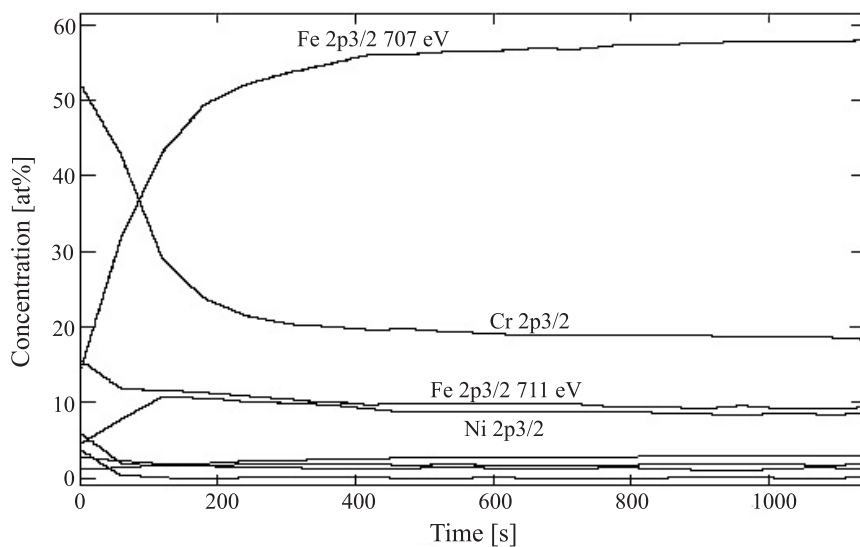


Fig. 3. XPS profile analysis of the passive film with concentration profiles.

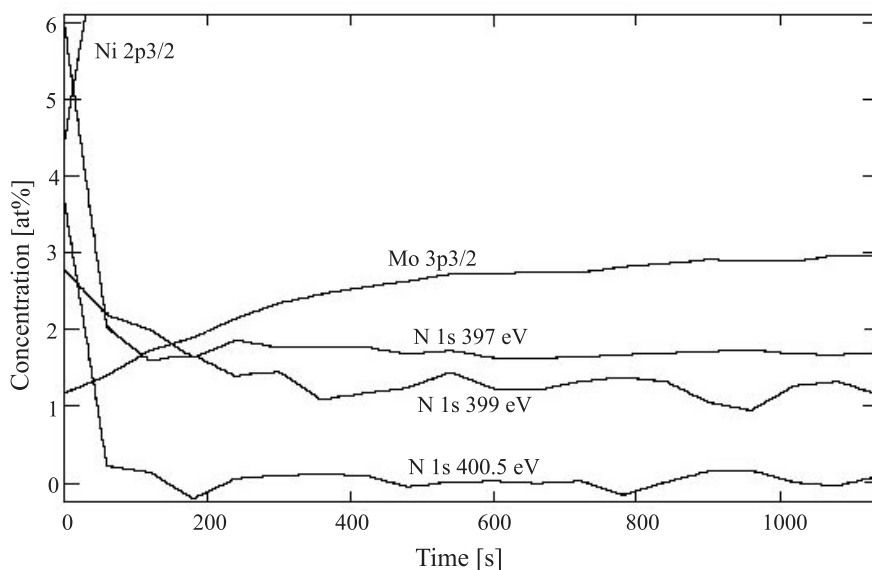


Fig. 4. Magnified view of the lower part of the concentration profiles from Fig. 3.

$N^{\delta-}$ ions (N^{3-}), bound in NH_3 , but mainly as NH_4^+ ions. Based on the values of the binding energies of the electrons in the nitrogen 1s orbital, we can conclude that the incorporation of this element in the passive film is possible in three energy states. These binding energies are characteristic for the following nitrogen components:

- N1s 397 eV corresponds to $N^{\delta-}$ (N^{3-}),
- N1s 399 eV corresponds to NH_3 ,
- N1s 400.5 eV corresponds to NH_4^+ .

From the profile analysis it follows that the surface layer of the passive film is mainly composed of chromium oxide, whose concentration on this surface exceeds 50 % (in the NTR 50 steel the proportion of chrome amounts to 21.15 %). Taking into account the quantity of nickel and molybdenum in this steel (12.7 % Ni and 2.22 % Mo), the activity of these two elements in the corrosion process is less than the activity of the chrome, which is the reason for their considerably smaller concentrations in the passive film. The surface layer also contains $N^{\delta-}$, which, in the form N^{3-} , reacts quickly with protons from the electrolyte to form the ammonium ion NH_4^+ , and NH_3 . The NH_4^+ ions build up in the vicinity of the electrode surfaces, i.e. on the interface between the passive film and the electrolyte, or else remain to some extent, together with the NH_3 in the numerous pores on the surface of the

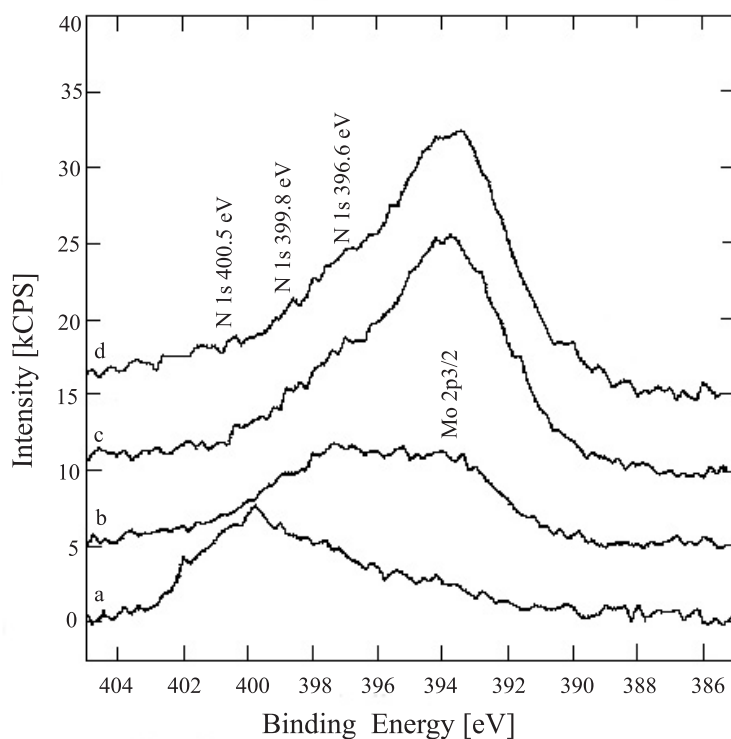


Fig. 5. XPS spectra for nitrogen in the passive film.

film. The concentrations of NH_4^+ and NH_3 fall as the depth is increased, which means that their presence is directly related to the reaction of the H^+ ions on the interface between the passive film and the electrolyte. This makes it clear why their accumulation is directly connected to this location.

4. Conclusion

Alloying of austenitic stainless steel by nitrogen enhances corrosion resistance. The influence of the nitrogen can manifest itself either through its action in the passive film, or by changing the nature of the electrolyte in the vicinity of the electrode surface.

Anodic polarization curves clearly indicated that nitrogen-alloyed NTR 50 steel, and the AISI 316L steel used as a comparison, are in a passive state, however, i_{cr} and i_{pas} are much lower for the nitrogen-enriched stainless steel. Cyclic potentiodynamic polarization tests showed that in such conditions there was only a

mild form of pitting corrosion in the case of NTR 50 steel. The same characteristic parameters for the AISI 316L steel were less favourable.

The occurrence of NH_4^+ ions at the interface between the passive layer and the electrolyte, causes a locally increased pH value of the electrolyte close to the electrode surfaces, which makes for easier passivation of the steel. The presence of ammonium ions mainly favours the repassivation of pit nuclei.

XPS analyses showed that the nitrogen in the passive film occurs in three forms: N^{3-} , NH_4^+ and NH_3 .

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