

## The influence of temperature on the corrosion behaviour of high nitrogen austenitic stainless steel in chloride media

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The electrochemical behaviour of high nitrogen SS in comparison of conventional grade 304 SS was examined in aqueous 3.5% chloride solution at 20-80 °C using open circuit potential vs. time, potentiodynamic and galvanostatic tests. The raising of the temperature was found to have no important influence on the corrosion potential, but destabilise the passive film formation on both steels. At the critical value of anodic polarisation the passive films were damaged and pitting corrosion occurs at lower potential with the increasing of temperature. The high nitrogen steel demonstrates faster formation of passive films, but pitting potential of this steel is more sensitive to temperature changes in comparison with those of chromium-nickel one. The temperature has slight influence on repassivation process, which is generally steel composition dependent. At all experimental conditions the nitrogen steel has greater difficulty to repassivate.

**Keywords:** corrosion resistance; pitting; stainless steel; temperature; sodium chloride; anodic polarisation.

### INTRODUCTION

The establishment of the behaviour of new steel grades in different corrosive conditions is critical for determination of the areas of their practical application. Typically stainless steels are used in environments where they are resistant to general corrosion, but may be affected by local forms of corrosion such as pitting. For example, the stainless steels have found widespread marine and industrial applications, wherein the presence of aggressive chloride ions is frequently combined with a change of the operating temperature. That is why the characterisation of corrosion resistance of a new steel grade is usually performed in chloride media and aims to assess the impact of the factors that can affect the rate of penetration of chloride ions in the passive layer to provoke development of pitting, as well as those factors affecting the contents and the pH of the solution inside growing pits. Such parameters are the temperature and the degree of the anodic polarisation.

The spontaneous or applied anodic polarisation of the steel in concrete corrosive environment provides the possibility of occurrence and development of pitting. To maintain a stable passive state of stainless steel, the potential should not exceed certain critical value called pitting initiation potential. Its value depends on a number of internal and external factors, among which is the

temperature of the system [1-3]. Generally the raising of temperature accelerates the rate of kinetic limitation reactions as well as the diffusion processes in the electrolyte. Furthermore the temperature directly affects the content of oxygen dissolved in the corrosion environment, and hence the rate of formation and stability of the protective layer of stainless steels. It is well known that the rate of transport and chemisorption processes in the passive layer is accelerated at elevated temperature [4]. The result is thinning of the passive layer in some electrochemically active sites which causes local rupture. On the other hand, the high temperature increases desorption of chloride ions and accelerates diffusion processes between the solutions inside and outside the pit. These processes impede respectively the reaching a critical surface chloride concentration needed for breakdown of the passive film and make difficult maintaining of favourable conditions for the stable pit growth. Consequently, interpretations of the influence of temperature on the corrosion resistance of the steels are complex and often occasional [3, 5]. This necessitates the effect of temperature on the corrosion behaviour to be defined only experimentally.

This paper presents research on the influence of the temperature on the corrosion behaviour of high nitrogen austenitic chromium steel Cr23Ni12, developed at Institute of Metal Science - BAS in 3.5% NaCl. As a reference steel the conventional SS 304 (Cr18Ni9) was used.

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### EXPERIMENTAL PART

Two types of austenitic stainless steels have been investigated in this work: high nitrogen chromium steel Cr23N1.2 (22.35% Cr, 1.23% N, 1.10% Mn, 0.04% C, 0.36% Si, balance Fe) and conventional steel Cr18Ni9 (17.49% Cr, 9.37% Ni, 1.29% Mn, 0.05% C, 0.52% Si, balance Fe). The experimental specimens were disk shaped with a working area of 0.5 cm<sup>2</sup>. The preliminary treatment of the specimens included subsequently grinding by abrasive papers to a 600 grit finishing, rinsing with water and drying. Just before the start of the experiment the specimens were polished to an 800 grit finish, followed by rinsing with distilled water and degreasing with an alcohol-ether mixture. The 3.5 wt. % NaCl test solution was prepared using analytical grade reagent and distilled water. The electrochemical tests were performed under open air conditions at temperatures 20, 40, 60 and 80 °C.

Three electrochemical techniques were used in the corrosion measurements. The *open circuit potential (OCP)*-time dependence was measured in the test solutions for an hour at room temperature. Just after OCP record the specimen surface was anodically charged under constant current density 60 µA cm<sup>-2</sup> and the potential change with time was recorded (*galvanostatic tests*). The *cyclic potentiodynamic polarisation* measurements were

performed with potential scan rate 1mV s<sup>-1</sup>. The specimen was kept for 5 min at initial potential 0.7 V vs. SCE and followed by anodic polarisation (in positive direction). After passing through the passive state and when the current density exceeded 10<sup>-4</sup> A cm<sup>-2</sup>, the polarisation in reverse direction was carried out down to the point where the curve intersected the anodic one.

The electrochemical measurements were carried out in a conventional three-electrode cell with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The measurements were performed using PAR 263 potentiostat-galvanostat and Power Suite corrosion measurement and analysis software.

### RESULTS

#### Open circuit potential

Figure 1 shows the change of free potential of Cr23N1.2 and Cr18Ni9 steels as function of time at temperatures 20, 40, 60 and 80 °C in 3.5% NaCl solution. The ennoblement of potential is indication about the formation of passive film and self-protection from corrosion. Although both steels tend to become passive, dependences OCP-time show significant differences in its shapes.

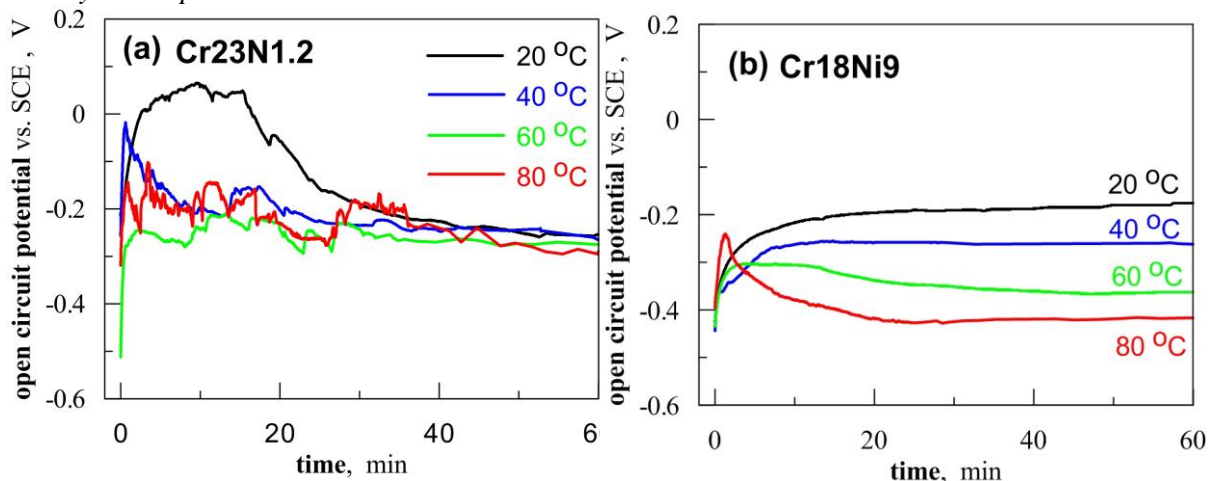


Fig. 1. Open circuit potential of Cr23N1.2 (a) and Cr18Ni9 (b) in 3.5% NaCl; 20÷80°C.

Table 1. Rate of passive film formation, mV s<sup>-1</sup>.

steel	method	temperature, °C			
		20	40	60	80
Cr23N1.2	open circuit potential	1.8	8.0	7.0	4.5
	galvanostatic polarisation	42.1	12.8	11.2	10.3
Cr18Ni9	open circuit potential	1.2	3.8	3.4	2.7
	galvanostatic polarisation	8.5	6.4	3.8	3.0

For chromium-nitrogen steel a sharp initial increase about 400 mV of the potential is typical. This behaviour presents rapid spontaneous passivation even at high temperatures. The slope of the dependence OCP-time in first seconds of the contact of the metal surface with the corrosive solution may be used as a criterion for rate of passive film formation. Thus determined values of the slope in mV per second for two stainless steels are presented in Table 1. The slopes of Cr18Ni9 steel are about two times smaller than Cr23Ni1.2 steel ones. The higher slope is found at 40°C for both steels. The further temperature raising leads to delay of the passivation.

For nitrogen steel the initial stage of a passive film formation is followed by a prolonged period of potential fluctuations and after some time the potential reaches to stationary value (Fig. 1-a). These fluctuations are associated with local damages of the surface layer. With increasing temperature, the intensity of the oscillation becomes larger and the establishment of the steady values of the potential takes increasingly long time (more than 1 hour at 80°C). The observed behaviour indicates that the high temperature

destabilize the passive film. Nevertheless, the influence of temperature on stationary values of OCP can be considered negligible, since after 40 minutes they are very close.

In the OCP-time dependences obtained for chromium-nickel steel (Fig. 1-b), the oscillations are not observed, which displays a greater stability and electrochemical homogeneity of its passive layer. However, the increased temperature leads to a shift of the stationary potential of nickel steel in a negative direction and his establishment to values typical for an active state (about -0.4 V vs. SCE).

*Potentiodynamic polarisation dependences*

According to the cyclic potentiodynamic dependences presented in Fig. 2, examined steels are in passive state in 3,5% NaCl. At anodic polarisation above critical potential value (pitting initiation potential  $E_{pit}$ ), the passivity is breached by pitting corrosion, which can be seen from the hysteresis loop. The increase of current density at decreasing anodic polarisation shows the presence of active points (pits) on the steel surface.

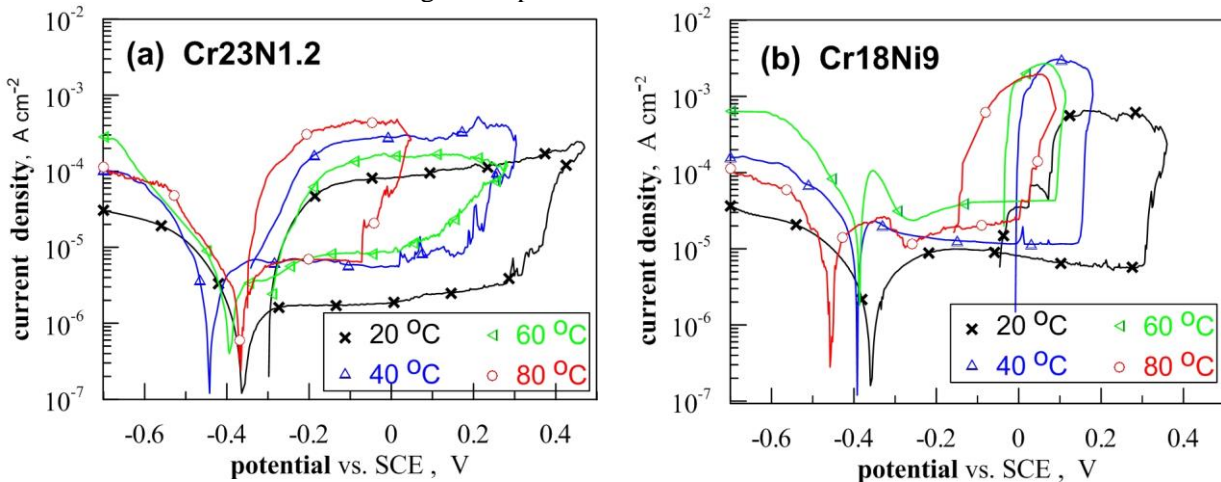


Fig. 2. Cyclic polarisation curves of steels Cr23Ni1.2 (a) and Cr18Ni9 (b) in 3.5% NaCl; 20÷80 °C.

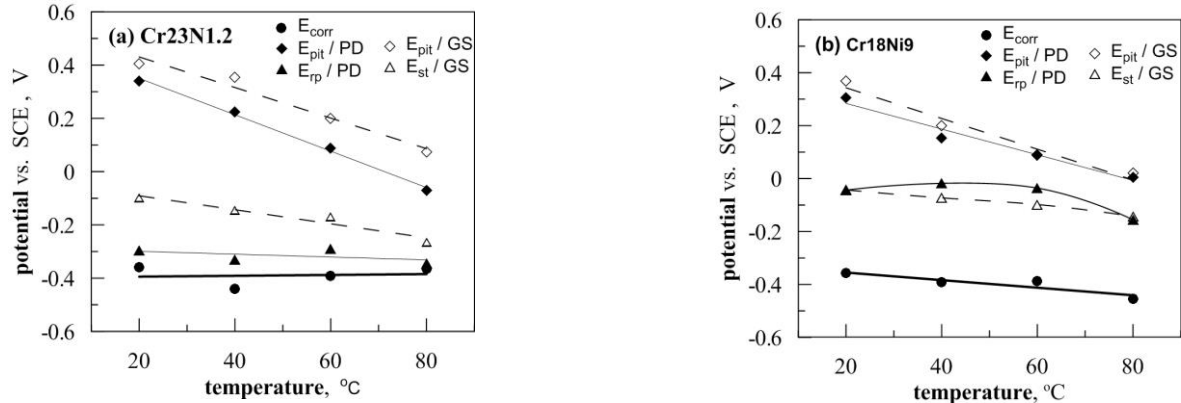


Fig. 3. Influence of temperature on the characteristic potentials obtained by potentiodynamic (black symbols and solid lines) and galvanostatic (blank symbols and dotted lines) tests for Cr23Ni1.2 (a) and Cr18Ni9 (b) stainless steels in 3.5% NaCl.

The characteristic electrochemical parameters vs. temperature determined from the potentiodynamic curves of the two steels are presented in Figs. 3 and 4. They show that the increasing of solution temperature from 20 to 80 °C has no significant effect on corrosion potential  $E_{corr}$ , but influences considerably the corrosion current density  $i_{corr}$ . The corrosion rate increases more than four times for Cr23Ni1.2 steel and about 10 times for steel Cr18Ni9 (Fig. 4).

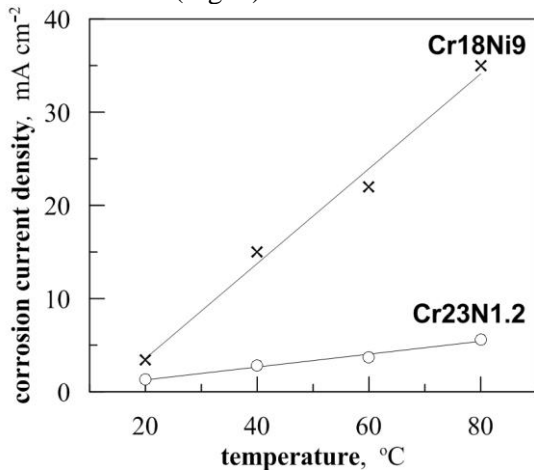
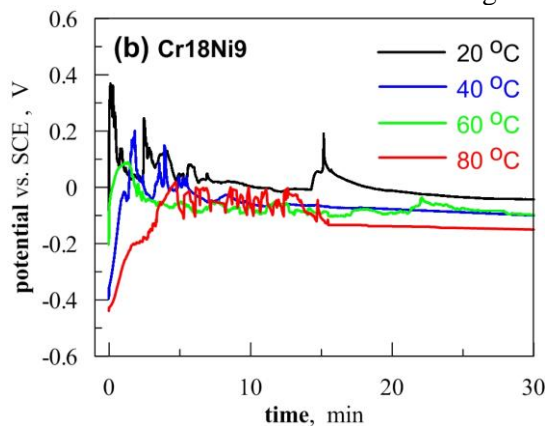


Fig. 4. Influence of temperature on corrosion current density of steels Cr23Ni1.2 and Cr18Ni9 in 3.5% NaCl.

All parameters, which characterise the stability of the passive state, become worse with the temperature increasing. For instance the passive current density  $i_{pass}$  increases the pitting initiation  $E_{pit}$  and repassivation  $E_{rp}$  potentials decrease. Hence the increased temperature deteriorates the protective properties of the passive film. Furthermore, this negative effect of the temperature is stronger for the nitrogen steel than for the conventional steel. In the temperature range 20-80°C, pitting potential  $E_{pit}$  decreases by more than 0.4 V for chromium-nitrogen steel and less (about 0.25 V) for chromium-nickel.

When turning the scan in cathodic direction, the current for steel Cr23Ni1.2 remains at high levels in



a large range of potentials and abruptly decreases near to the corrosion potential. Figure 3 shows that the repassivation potential is slightly dependent on the temperature (black triangle and solid lines). Therefore, at temperatures above 60 °C nitrogen steel has increased susceptibility to pit formation and lower repassivation ability than nickel steel.

### Galvanostatic results

Figure 5 shows typical galvanostatic polarisation curves for Cr23Ni1.2 and Cr18Ni9 steels in 3.5% NaCl in the temperature range 20-80 °C, obtained at the current density 60  $\mu\text{A cm}^{-2}$ . The density of the anodic polarisation current is experimentally chosen as the lowest value sufficient for a stable development of pits in the investigated temperature range.

The dependences potential-time demonstrates that initially the potential increases linearly with the time (Fig. 5). This part of the curve corresponds to the galvanostatic growth of passive layer. The raising of the temperature reduces the slope of the initial linear region ( $dE/dt$ ), which is an indication of delay in the rate of passive film formation (Table 1). The deviation of the curve from linearity is a result of destabilisation of the passive layer and the local breakdown in it. The maximum reached potential value corresponds to the pitting potential  $E_{pit}$ . After reaching this value, the potential decreases due to the metal dissolution in certain active surface areas. The initiation and repassivation of each pit is displayed on chronopotentiometric dependences as potential fluctuation respectively in negative and in positive direction. After some time, the potential is established on its stationary value  $E_{st}$ , which corresponds to the potential of the stable pits growth [6]. Several authors identify this potential  $E_{st}$  as the potential of repassivation determined

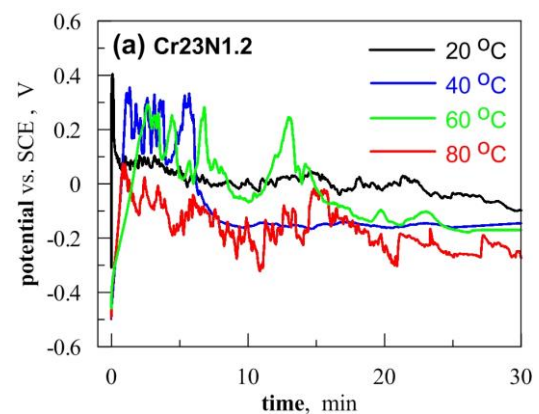


Fig. 5. Chronopotentiometric curves at applied anodic current 60  $\mu\text{A cm}^{-2}$  of steels Cr23Ni1.2 (a) and Cr18Ni9 (b) in 3.5% NaCl, 20-80 °C.

potentiodynamically  $E_{tp}$  [7]. Despite the completely different nature of these two potentials, as  $E_{st}$  values tend to reach those of the  $E_{tp}$ , the stationary potential can be used as a characteristic value for the minimum potential below which pitting does not develop. The increasing of the temperature leads to prolongation of the time required to reach a steady state.

On Fig. 3 the values of pitting potential ( $E_{pit}$ ) and stationary potential ( $E_{st}$ ) obtained from galvanostatic potential-time dependences are presented by dotted lines and blank symbols. When raising the temperature from 20 to 80 °C, the pitting potential  $E_{pit}$  decreases for both steel approximately with 0.35 V. Figure 3 shows a good correlation between the results obtained by galvanostatic and potentiodynamic methods for the conventional steel. Contrariwise the obtained galvanostatically  $E_{pit}$  values for Cr23N1.2 are more positive with 100-200 mV than the corresponding potentiodynamic values. These results can be explained by the longer induction time required for the appearance of pits on nitrogen steel. Due to delay in pits formation, the potential has time to reach more positive values at the abruptly imposed anodic polarisation.

## DISCUSSION

The results from OCP measurements and from potentiodynamic method, give information for general corrosion assessment, whereas the galvanostatic polarisation and the cycling potentiodynamic methods allow evaluation of the susceptibility of the steels to pitting corrosion at the experimental conditions.

The three electrochemical methods experimentally proved the expected relatively similar corrosion behaviour of the both steels in 3.5% NaCl solutions. In range of the temperature 20-80 °C similar values of the corrosion potential and the width of the passive zone were registered. Both steels are affected from pitting corrosion at close values of the anodic polarisation. Nevertheless, some important differences, related to the corrosion current density as well as the rate of formation and repassivation of the passive layers on two steels were found out.

The protective layer on the chromium-nitrogen steel forms faster, which is demonstrated by the precipitous slope of the initial linear growing of potential without and with applied anodic polarisation (Table 1, Figs.1 and 4). However the rapid spontaneous anodic polarisation leads to quick attainment of the free potential at which the dissolution of some anodic nonmetallic inclusions

begins and the adsorption of the aggressive ions is stimulated [8-11]. So the fluctuations on the dependencies OCP-time are observed only for Cr23N1.2 steel and they are related to activation and repassivation of the local areas on the surface, most probably dissolution of the nonmetallic inclusions, nascence and repassivation of metastable pits or crevice growth. Though the maximum reached values of OCP are found to be below the critical potential values  $E_{pit}$  established by the two others electrochemical methods. Consequently, despite the well-expressed maximum on the OCP-time curve, without external anodic polarisation, the pits would not be developed. The superposition of the stationary values of the open circuit potentials on the respective potentiodynamic dependencies allow to see that the free potentials of both steels are located in the passive region, but for the nitrogen steel they are between  $E_{pit}$  and  $E_{tp}$  (Fig. 2). Hence, if on the steel Cr23N1.2 surface temporary favourable conditions for pits formation are created, the pit development can be prolonged also at potentials under  $E_{pit}$ .

The sharp potential increase in anodic direction under galvanostatic polarisation of the nitrogen steel shows not only rapid formation of the passive layer, but also lower conductivity of the passive films.

The lower values of the corrosion and the passive currents, the fast passivation of steel Cr23N1.2 surface as well as the longer induction time for pits initiation can be explained with the bigger chromium content [12] and the nitrogen incorporation in the passive film and formation of more compact structure [13-15]. Nitrogen enrichment of the passive layer or the accumulation of N on the metal/oxide interface is proved in many investigations, which explain the difficulty in anodic dissolution of the bare metal [13, 15-18]. Furthermore Kumagai *et al.* [16] have established lowering of the thickness of the passive layers at high nitrogen content in the chromium steels. The smaller thickness of the passive layer on the studied nitrogen steel is the probable reason for their easier breakdown in strongly aggressive environments as 3.5% NaCl at 80 °C in comparison with the Cr18Ni9 steel.

## CONCLUSION

The temperature rising from 20 to 80 °C in 3.5% NaCl solution increases the corrosion rate of Cr22N1.2 stainless steel slighter that of Cr18Ni9 steel. The high nitrogen steel is characterised with faster formation of the protective passive film. The high temperature deteriorates the protective

properties of the passive film which results in increase of the passive current density and their destruction at smaller anodic polarisation. This negative effect of temperature is stronger for nitrogen steel in comparison with to conventional steel. The temperature has slight influence on repassivation process, which is generally steel composition dependent. At all experimental conditions the nitrogen steel has great difficulty to repassivate.

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## ВЛИЯНИЕ НА ТЕМПЕРАТУРАТА ВЪРХУ КОРОЗИОННОТО ПОВЕДЕНИЕ НА АУСТЕНИТНА НЕРЪЖДАЕМА СТОМАНА С ВИСОКО СЪДЪРЖАНИЕ НА АЗОТ В ХЛОРИДНИ СРЕДИ

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(Резюме)

Сравнено е електрохимичното поведение на стомана SS с високо съдържание на азот с това на стомана с конвенционалното качество 304 SS в 3.5% воден разтвор на хлориди при 20–80 °C, използвайки потенциала на отворена верига по отношение на времето, потенциодинамични и потенциостатични тестове. По отношение на температурата беше установено, че няма значително влияние върху корозионния потенциал, но дестабилизира образуването на пасивен филм и върху двете стомани. При критични стойности на анодната поляризация пасивните филми се повреждат и точкова корозия се наблюдава при по-нисък потенциал с повишаване на температурата. Високоазотната стомана показва по-бързо образуване на пасивни филми, но питинг потенциалът на тази стомана е по-чувствителен на температурни промени в сравнение с този на хром-никеловата. Температурата има слабо влияние върху процес на репасивиране, което зависи основно от състава на стоманата. При всички експериментални условия азотната стомана по-трудно се репасивира.