The corrosion resistance of nitrogen-alloyed austenitic stainless steel to pitting processes under conditions of erosion corrosion

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Abstract

This work is concerned with the effect of interstitially absorbed nitrogen on pitting corrosion if erosion corrosion is also present at the same time. The results of the investigations have shown that nitrogen, in the form of negatively charged N^{3-} ions, which make possible the formation of NH_4^+ ions, slows down the initiation and growth of pits due to the rise in the pH value in the pit, from initial acidic value to basic value. This process is also possible in the presence of Cl^- ions. As a consequence the activation energy, which is needed for the initiation of pits, is high. Under the conditions of erosion corrosion the repassivation potential is equal to the pitting potential, and in certain conditions is higher than the latter. In the case of stainless steels and alloys, which do not contain added nitrogen, this effect is not noticeable.

Key words: nitrogen-alloyed stainless steel, pitting resistance, erosion corrosion

1. Introduction

This work is connected with the management of SO_2 emissions from the smoke gasses, which occur when burning fossil fuels in thermo-electric power plants. In devices for the removal of sulphur from smoke gasses, SO_2 can be removed. Desulphurizing is performed in the wet way, with the absorption of hot gasses into water to which finely ground $CaCO_3$ has been added, resulting in a rise of the resulting suspension to a pH of between 4.5 and 6.5. Without this additive this would be a very corrosive solution, which could damage different parts of the equipment. However, if $CaCO_3$ is added to water, gypsum is formed, whose particles make up an abrasive substance. Such a suspension contains about 25 000 to 80 000 ppm of aggressive Cl^- ions. The corrosion resistance of different stainless steels or nickel-alloys, from which different vital parts of the absorber are made, is mainly dependent on the content of SO_2, SO_3, and Cl^- ions, on the pH value, on the temperature, and on the abrasivity of the hard particles in the fluid. Since several factors are acting at the same time, the corrosion resistance of some types of stainless steels is weak, and the use of strongly nickel-alloyed alloys for different parts is too expensive. However, the new generation of stainless steels, which are alloyed with nitrogen, could represent a realistic alternative due to the favourable effect of interstitially dissolved nitrogen on the hardening processes of the austenitic matrix and the corrosion processes [1–3].

Pitting corrosion and stress corrosion cracking belong to the typical and most frequent types of damage to stainless steels, and the control of the initiation and growth of pits and of cracks due to stress corrosion cracking, which are the result of sharply-shaped corrosion pits, represents the most important preoccupation of all those who are concerned with the life-time of metal structures.

The following factors have a significant effect on the initiation and growth of pits:

– The corrosion resistance of steel and its ability to form adequate passive films;

– The high repassivation capability of steel which enables the rapid healing of damage in any given medium;

– The ability of material to resist mechanical degradation during the operation of solid particles,

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which change the nature of the surface (damage to the passive film) and to the peripheral layer of the matrix (cold work strengthening) in those cases when erosive corrosion is involved;

– An environment with aggressive ions, among which chlorides dominate. As opposed to oxygen, chloride ions make easier the hydration of metal ions, i.e. the formation of $M^{n+} \cdot H_2O$. In this way the speed of the anodic reaction is increased. In the presence of high enough concentrations of Cl^- ions this reaction is so fast that, for example in the case of iron and stainless steels, they cannot be passivated [4].

2. The initiation and growth of pits in metals, which are passivated

The initiation and growth of pits depends on local damage of the passive film, which represents a large cathode, whereas the bottom of the damage represents a small anode. According to the basic principles of electro-chemical corrosion, the sum of the speed of the cathodic reactions, which is expressed by the partial cathodic current (I_c), is equal to the sum of the rates of the reactions taking place on the anodic surface, expressed by the partial anodic current (I_a), without respect to whether uniform reduction of thickness is taking place, or local corrosion:

$$\sum I_a = -\sum I_c. \tag{1}$$

If the corrosion attack is uniform and if it is assumed that the anodic and cathodic surfaces are the same in size ($A_a = A_c$), then we can write that the current densities are:

$$\frac{I_a}{A_a} = \frac{I_c}{A_c}; \text{ or } i_a = i_c = i_{cor.} \tag{2}$$

However, in the case of local attacks it is characteristic that the anodic surface is much smaller than the cathodic surface ($A_a \ll A_c$), which means that the anodic current density is very high ($i_a \gg i_c$, or $i_a/i_c > 1$). The larger the ratio between i_a and i_c is, the stronger is the local corrosion attack.

The stability of a pit depends on the drop ΔE (i.e. the difference in potentials between the pitting potential E_p and the corrosion potential $E_{cor.}$). The wider the field of potentials, the larger the value of E_p, which means that the corrosion damage can be more easily repassivated, which depends on the electrolyte in the pit and its pH value. If the drop ΔE is a drastic one due to an aggressive medium with a low pH, then the possibility of repassivation is eliminated, and this is the condition for the growth of a pit due to corrosion. The shift in pH towards lower values in the acidic region can serve as an estimate of the stability of a pit in which the corrosion process is taking place. This is particularly evident in the case of non-buffered solutions, where, due to the process of hydrolysis, H^+ ions are released, as bearers of acidity:

$$M^{n+} + H_2O \leftrightarrow MOH^{(n-1)} + H^+. \tag{3}$$

In stainless steel, where the reactions of the hydrolysis of different compounds of the basic element are present, i.e. Fe, as well as of the alloyed elements, the production of H^+ ions is further increased. In the case of steel alloyed with Cr and Mo, it can be written:

$$Fe \rightarrow Fe^{2+} \rightarrow FeOOH + 3H^+$$

$$Cr \rightarrow Cr^{3+} \rightarrow CrO_4^{2-} + 8H^+$$

$$Mo \rightarrow Mo^{3+} \rightarrow MoO_4^{2-} + 8H^+.$$

Such a production of H^+ ions results in a reduction of the pH value of the neutral or even basic solution below pH 3.

Neutral chloride media increase the acidity in the pit due to the formation of the metallic chloride M^+Cl^-, and through the hydrolysis of the latter the acid

$$M^+Cl^- + H_2O \rightarrow MOH + H^+Cl^- \tag{4}$$

is formed. On the basis of these reactions the question

Table 1. Chemical composition of the investigated steels and Ni-Cr alloys [wt.%]

Material	C	Mn	Si	Cr	Ni	Mo	N	Ti	Cu	Fe
Cronifer 1925 hMo	0.011	0.92	0.42	20.80	24.30	6.32	0.225	–	0.61	bal.
AISI 316L	0.015	1.29	0.39	16.87	10.58	2.14	0.044	0.004	0.353	bal.
Nicrofer 4221 hMo	0.030	0.45	0.30	19.68	38.54	3.89	–	0.96	1.66	35.53
Nicrofer 6020 hMo	0.053	0.18	0.20	21.62	64.75	8.65	–	0.12	–	0.45
Prokron 2 spec.	0.20	0.69	0.48	16.22	2.12	0.14	–	–	0.17	bal.
FeCr22Ni7Mo3N	0.043	0.157	0.152	21.97	7.063	3.09	0.196	–	0.083	bal.
Ni63Cr20Mo8Fe8	0.020	0.074	0.124	20.14	63.29	7.81	–	–	0.190	8.51

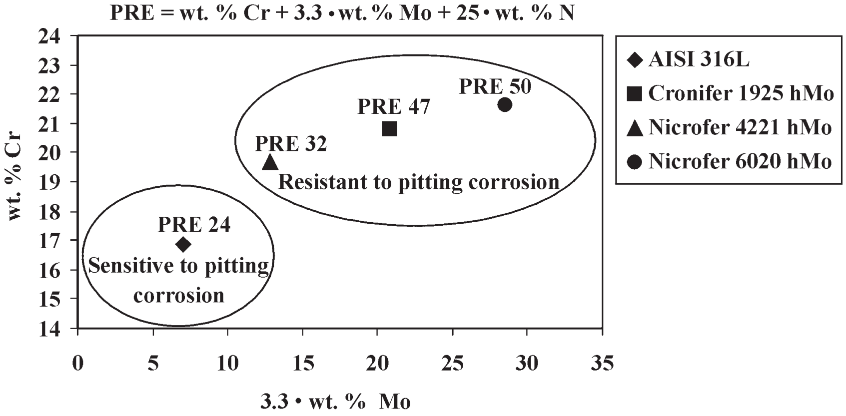

Fig. 1. Depending on the *PRE* value, in certain media the investigated steels are subject to pitting corrosion, or else they demonstrate high resistance to this kind of corrosion.

arises as to what the role of nitrogen in stainless steels of the austenitic type is. Is nitrogen able to change the nature of the electrolyte, which is rich in depassivators, i.e. Cl^- ions, for which it is characteristic that after the reaction (4) acidity is increased?

3. Materials

The following types of materials were investigated:

– nitrogen-alloyed austenitic stainless steel Cronifer 1925 hMo

– austenitic stainless steel AISI 316L

– austenitic Ni-Cr alloy Nicrofer 4221 hMo

– austenitic Ni-Cr alloy Nicrofer 6020 hMo

– nitrogen-alloyed duplex ferritic-austenitic cast steel, FeCr22Ni7Mo3N

– nickel austenitic cast steel Ni63Cr20Mo8Fe8

– martensitic stainless steel Prokron 2 spec.

Chemical compositions of the investigated materials are in Table 1.

4. Results and discussion

4.1. Determination of the pitting resistance equivalent

In the case of austenitic stainless steels and Ni-alloys the *PRE*, or pitting resistance equivalent, can be determined on the basis of Eq. (5), which takes into account the chromium and molybdenum content, as well as the effect of nitrogen, if the latter is added. Experience has shown that the resistance of steels of this type to crevice and pitting corrosion can be improved if a factor of 25 times the wt.% of N is applied, whereas in the case of duplex stainless steels a factor of 16 times the wt.% needs to be taken into account [5].

$$PRE = \text{wt.\% Cr} + 3.3 \cdot \text{wt.\% Mo} + 25 \cdot \text{wt.\% N}. \quad (5)$$

Equation (5) is an empirical one, and the value 30 is a limit value; below a value of 30 pitting occurs, and above a value of 30 pitting corrosion is not possible. However, in what environment, at what quantities of depassivators (e.g. aggressive Cl^- ions), and at what temperature?

In the case of the investigated materials, the *PRE* values are shown in Fig. 1, where, depending on this value, pitting corrosion is likely or, to the contrary, pitting corrosion need not be expected.

Viewed with respect to the nitrogen, which is used to alloy the Cronifer 1925 hMo steel, which has a *PRE* value of 47, and in comparison with the high-alloyed Ni-alloys Nicrofer 4221 hMo, with a *PRE* value of 32, and Nicrofer 6020 hMo, with a *PRE* value of 50, Cronifer 1925 hMo steel is clearly located in the region where these types of materials have a relatively high resistance to pitting corrosion. Is this the consequence of the operation of nitrogen which, in this process, supports passivation, extends the time for initiation of the pit, and, if the pit is formed, slows down its growth? It is quite clear that corrosion resistance can be increased, in the absence of interstitially dissolved nitrogen, only by increasing the content of chromium, which is the basis for passivation, as well as molybdenum, whereas, in reducing media the nickel content is important.

4.2. Determination of the critical pitting temperature

Determination of the critical pitting temperature (*CPT*) was performed using the electrochemical galvanostatic method, which, due to its high sensitivity, makes it possible to detect pits with sufficient accuracy at their initial stages and during their growth. In this method, which is based on galvanostatic anodic polarization, the potential on the surfaces of the electrodes changes at a constant value of the current, and at the same time the temperature of the medium is

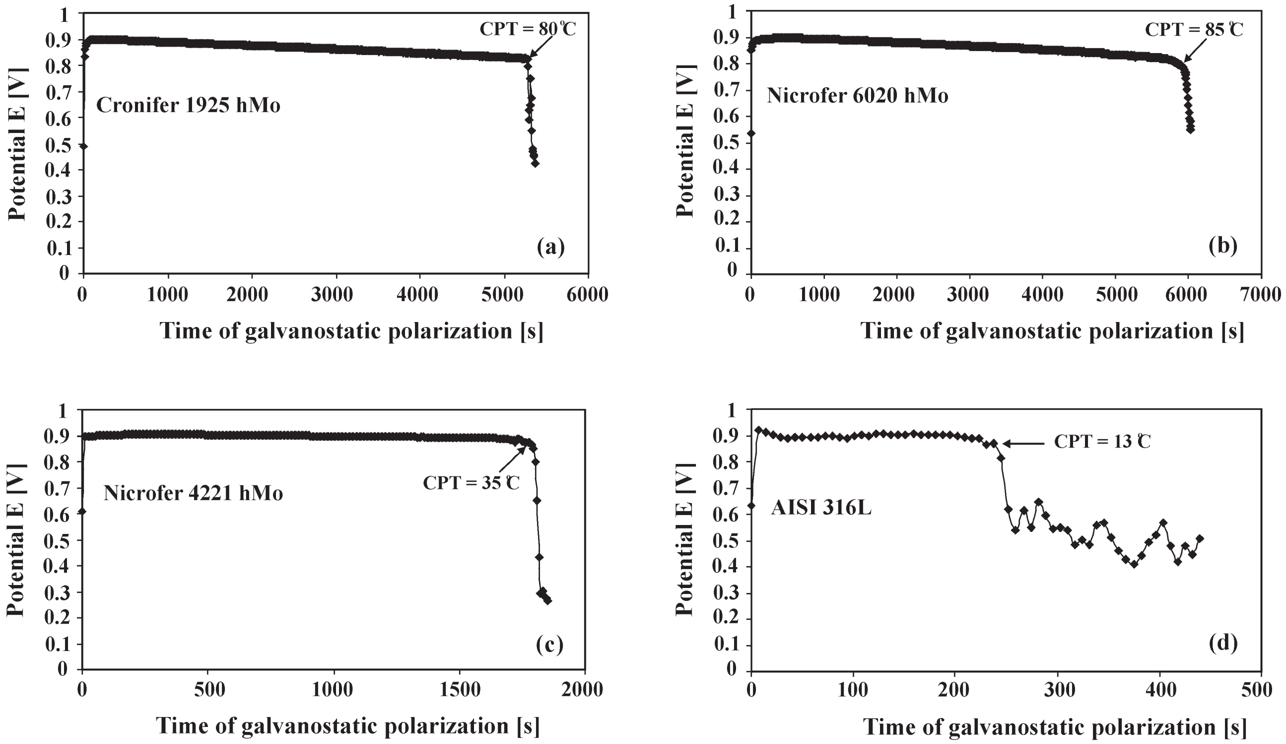

Fig. 2. *CPT* determined by means of galvanostatic polarization: a) Cronifer 1925 hMo, b) Nicrofer 6020 hMo, c) Nicrofer 4221 hMo, d) AISI 316L.

increased. When the potential achieves the value of the pitting potential (corresponding to a shift to the transpassive region), at a certain temperature a sharp drop in the potential of the material being tested occurs. This temperature is the *CPT*.

The testing parameters are the following:

– a medium consisting of 100 g $FeCl_3 \cdot 6\ H_2O$ and 900 ml of distilled water (6% $FeCl_3$)

– preparation of the samples with SiC grinding paper of grade 600

– surface area of the samples 1 cm^2

– pre-passivation of the samples in 20% HNO_3, for 10 minutes, at 50℃

– anodic polarization of the samples at a current density of 80 $\mu A/cm^2$

– uniform increase of the temperature of the medium in the corrosion cell at a rate of 3.5℃/min.

The results of the tests are shown in Figs. 2 and 3.

From Fig. 3 it can be concluded that the nitrogen-alloyed stainless steel Cronifer 1925 hMo dominates strongly over the stainless steel AISI 316L and over the alloy Nicrofer 4221 hMo which has a high content of chromium and nickel, to which molybdenum has been added. In the case of the nitrogen steel the critical pitting temperature is just below the value corresponding to the highly-alloyed Ni-Cr alloy Nicrofer 6020 hMo, which means that even with a much lower content of chromium, nickel and molybdenum, nitrogen has an important role in the behaviour of the Cronifer 1925 hMo. This is because in this case it is not a more stable film which is involved, which would be achieved with the increasing of the content of alloying elements, but a greater capability for passivation and repassivation in the case of damage to the passive layer can be achieved through the other effects of ni-

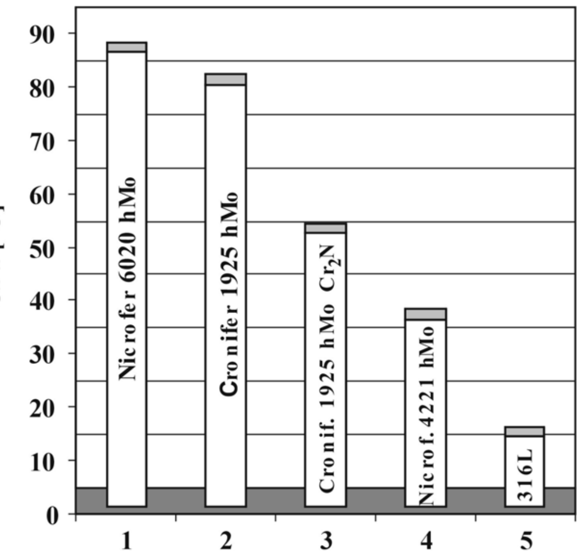

Fig. 3. *CPT* values for the investigated steels and Ni-Cr alloys.

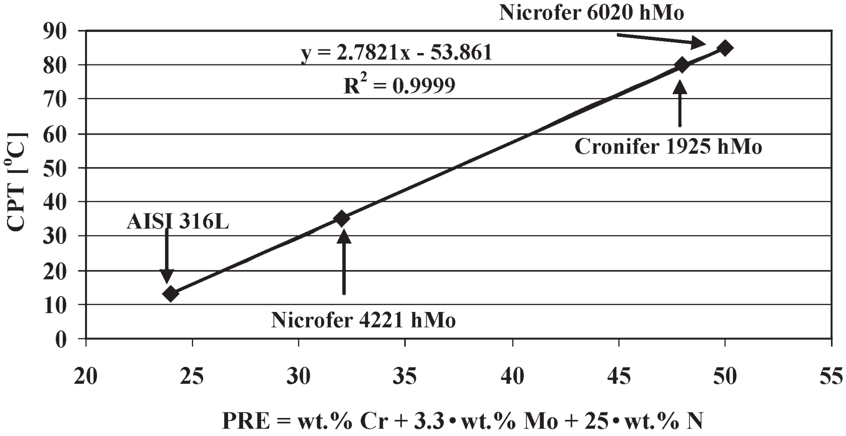

Fig. 4. Linear relationship between the *CPT* and *PRE* value for the tested materials. In the case of the Cronifer 1925 hMo steel the nitrogen is interstitially dissolved into the austenitic matrix.

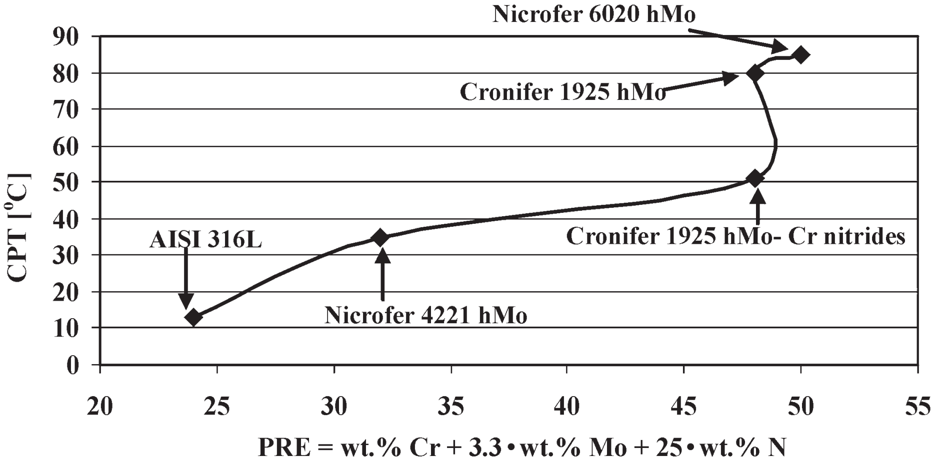

Fig. 5. With the appearance of Cr-nitrides in the Cronifer 1925 hMo steel the linearity ceases. At the same *PRE* value the *CPT* is lower than in the case when the nitrogen is interstitially dissolved in the matrix.

trogen. How therefore might it be possible to prevent the operation of the very large quantities of chlorides which so drastically increase the concentration of H^+ ions in the corrosion pit, crevice or stress corrosion crack, where the basic or slightly acidic medium relatively quickly changes into an aggressive and strongly acidic medium? Can the nitrogen reverse the tendency of increasing of acidity in the presence of chlorides into the opposite direction, i.e. so that the reaction given in Eq. (4) can be slowed down and the pH value can be raised? Grabke [6] has pointed out that nitrogen can have the effect on the initiation of pits if it is anodically segregated in the form of negatively charged nitrogen atom $N^{\delta-}$, but with the assumption that this negatively charged segregated nitrogen corresponds to N^{3-}. Together with H^+ ions from the electrolyte it reacts to form NH_4^+ ions:

$$N^{3-} + 4H^+ + 3e \rightarrow NH_4^+. \qquad (6)$$

It is assumed that the NH_4^+ ions bind with the water where, in a narrow region next to the electrode surfaces, they cause a local increase of the pH of the solution. This slows down the initiation of pits and has a particularly favourable effect on the processes of repassivation of the corrosion damage site. The ammonium ion NH_4^+ thus acts as a buffer. The increase of pH is the consequence of the consumption of H^+ ions anywhere in the direct vicinity of the electrode surfaces: in a pit, crevice or stress corrosion crack. Within this context it is necessary to find a relationship between the *CPT* and the *PRE* value. Such an attempt to find a relationship is shown in Figs. 4 and 5.

In this case the linear relationship means that the *CPT* increases with an increasing content of the alloying elements (Cr, Mo and N), and this is manifested in the *PRE* in such a way that this parameter, too, increases. However, the degree to which steel can be alloyed with nitrogen is not unlimited. Its solubility in the austenite is limited. In the case of increased quantities, exceeding 0.40 wt.%, embrittlement of the steel can occur or poor workability. Resistance to pitting corrosion, stress corrosion cracking and even erosion corrosion should be based on other principles; and the effect which is the consequence of increasing the content of chromium and molybdenum (a more stable passive film) could probably be achieved with the proper combination of all three, i.e. nitrogen, chromium and molybdenum. In this case not only the passive film would be critical but also the operation of NH_4^+ ions in the direct vicinity of the electrode surfaces. The chromium nitrides in the Cronifer 1925 hMo steel play a negative role in the pitting process, although they have a positive effect in the case of erosion corrosion. Since the Cr_2N contains 90.5 % Cr, 5 % Mo and approximately 3.5 % Fe (admixtures of Si and other elements in traces), it is quite clear that the matrix in the vicinity of the Cr-nitride is depleted with bearers of passivation (Cr and Mo). It means that some Cr atoms are substituted by Mo, Fe and other admixture atoms. Since the amount of both of these elements in the vicinity of the nitrides is small [7], the passivation of this depleted zone is incomplete, which provokes pitting corrosion. Thus, in research of erosion corrosion it is sensible to look for a compromise between the positive effect of the Cr-nitrides with regard to erosion corrosion, and the negative effect of the latter on the processes of depletion of their vicinity with Cr and Mo, and the occurrence of pitting corrosion. This is exactly the reason why the authors eliminated steel with Cr-nitrides from further investigations.

4.3. Determination of the activation energy needed for the initiation of pits

In electrochemical electrode processes the activation energy (Q_a), which is needed for the activation of a process, is usually calculated from the slowest reaction. It is quite clear that as Q_a increases so too does the corrosion resistance of the metal system involved. It was assumed that the quality of the passive film on the investigated steels varies, and additional effects were expected in the case of the nitrogen-alloyed steels, where the nitrogen can cause changes on the electrode surfaces with the appearance of NH_4^+ ions.

Since the time needed for the failure of a passive film in a medium depends on the temperature (as the latter increases, so the time to failure shortens), such a relationship can be written using Arhenius' equation:

$$\frac{1}{t_{\text{init.}}} = A \cdot \exp\left(\frac{-Q_a}{RT}\right), \tag{7}$$

where $t_{\text{init.}}$ is the time needed for the initiation of a

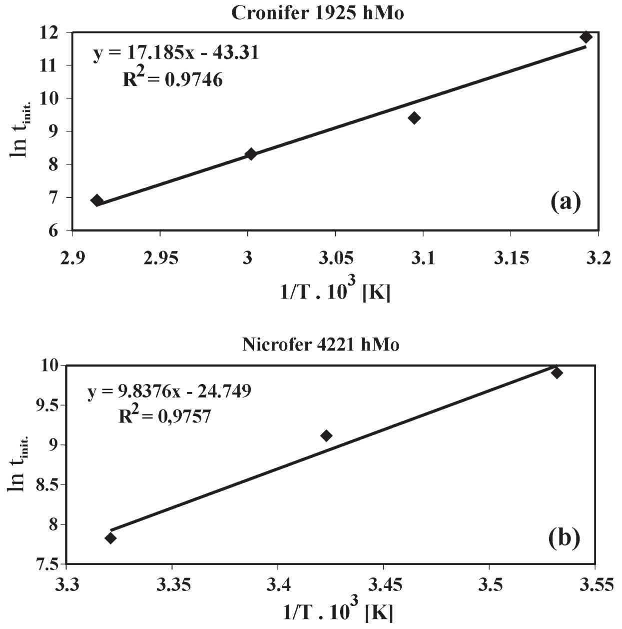

Fig. 6. Relationship between temperature and the time needed for the initiation of a pit, for the a) Cronifer 1925 hMo and b) Nicrofer 4221 hMo steels.

pit, defined with the drop in potential at a certain temperature, A is a constant, Q_a is the activation energy which is needed for the initiation of a pit in the case of local failure of the passive film, R is the gas constant, and T is the temperature [K].

Q_a is calculated from the slope of the straight line, which defines the relationship between $\ln t_{\text{init.}}$ and $1/T$ (see Fig. 6):

$$\begin{gathered} \operatorname{tg}\alpha = \frac{\Delta \ln t_{\text{init.}}}{\Delta 1/T}; \quad \frac{Q_a}{R} = \operatorname{tg}\alpha; \\ Q_a = R \cdot \operatorname{tg}\alpha \left(\text{kJ} \cdot \text{mol}^{-1}\right). \end{gathered} \tag{8}$$

Experimental conditions:

– Passivation of both materials in a solution of 20 vol.% HNO_3, at the temperature of 50 ℃, time: 10 minutes;

– The electrochemical measurements were performed at different temperatures in the 6% solution of $FeCl_3$. The time needed for the initiation of a pit was determined by means of galvanostatic polarization at a constant current density of 80 $\mu A/cm^2$.

In the case of Cronifer 1925 hMo a maximum testing temperature of 70 ℃ was selected, since its *CPT* is 80 ℃, and in the case of Nicrofer 4221 hMo which has a *CPT* of 35 ℃, this temperature was 28 ℃. It is a fact that in the case of Nicrofer steel Q_a cannot be determined in the same temperature range 70/ 60/ 50/ 40 ℃ as it was selected for the Cronifer steel, since under such experimental conditions the passive film

Table 2. Activation energies needed for the occurrence of a pit

Material	Temperature [°C]	$t_{\text{init.}}$ [s]	Q_{a} [$\text{kJ}\cdot\text{mol}^{-1}$]
Cronifer 1925 hMo	70	1000	142.9
	60	4090	
	50	12132	
	40	141050	
Nicrofer 4221 hMo	28	2500	81.8
	19	9081	
	10	20060	

would fail immediately. This means that the Nicrofer 4221 hMo steel, which contains no nitrogen, has a very low threshold of temperature sensitivity in comparison to the nitrogen-alloyed stainless steel. Thus, in the case of the high-alloyed Nicrofer 4221 hMo alloy, Q_{a} was found to occur in a much lower temperature range that is undoubtedly an expression of the poorer quality of the passive layer.

The calculated activation energies are shown in Table 2.

The calculated activation energies, which are necessary for the formation of a pit at some thermodynamically least stable location in the passive film, provide a good overview of the quality of the passive film and its resistance to pitting corrosion. Cronifer 1925 hMo steel forms a highly stable and resistant passive film which clearly has a high repassivation capability. The quality of the passive film must be exceptionally good, since a great deal of energy is needed for its local failure and the formation of a pit. It is clear that nitrogen has, in the sense of Eq. (6), an important role in the slowing down of the initiation and growth of pits. The measured activation energy, which is needed for the initiation and growth of a pit, is, in the case of Cronifer 1925 hMo, very large and cannot be compared with the energy which is needed for the same process in the case of the also high-alloyed Nicrofer 4221 hMo, which, however, does not contain nitrogen. There is no comparison since the threshold of sensitivity for the process of pitting is reached, in the case of Nicrofer, at very low temperatures. Such a conclusion is in accordance with the calculated *PRE* value and the measured *CPT* of this nickel alloy, for which these two parameters show a poorer corrosion resistance than that achieved by nitrogen-alloyed stainless steel.

4.4. The effect of nitrogen on the electrochemical processes in the corrosion pit and the change of pH

Determination of pH in an artificially created pit was made possible, together with the measuring of the potential of the medium in the pit, with a special antimony microelectrode. This electrode was located at a depth of 6 mm in the artificially created pit, which had a depth of 7.2 mm and a diameter of 1.6 mm. The test specimen with the artificially created pit was placed in the basic solution, which was subject to constant stirring by means of a magnetic mixer. The tempera-

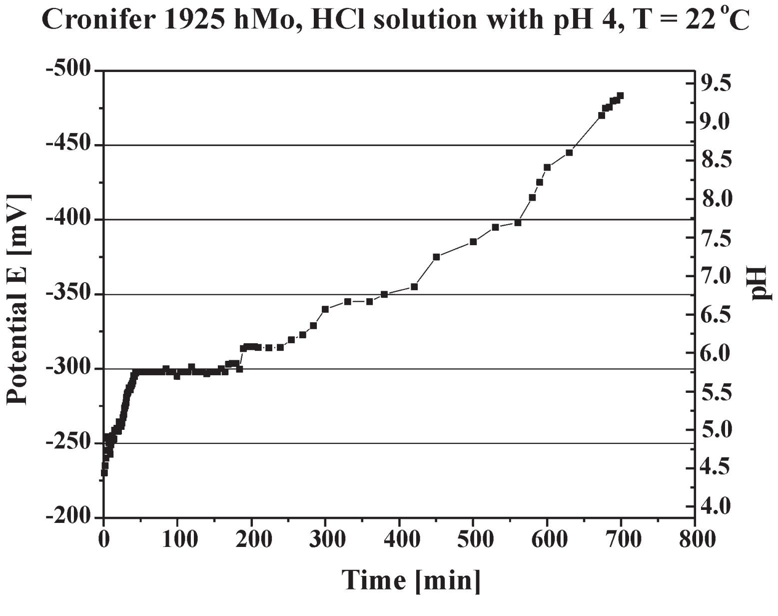

Fig. 7. Change in pH of the medium in the pit, from an initially acidic value to the basic region due to the effect of interstitially dissolved nitrogen, in the Cronifer 1925 hMo steel.

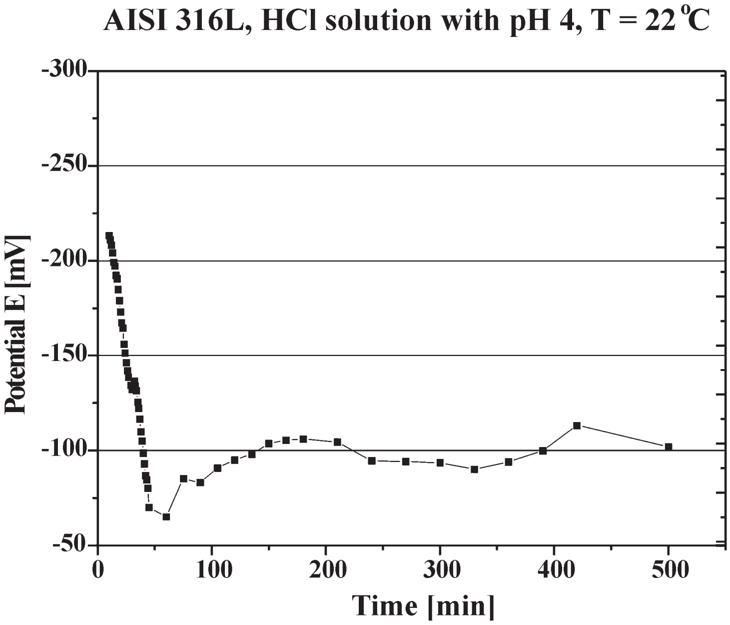

Fig. 8. In the stainless steel AISI 316L, which does not contain alloyed nitrogen, due to the specific electrochemical processes in the pit the local acidity of the medium increases further.

ture of both test media (the solution of HCl with pH of 4, and the 3.5% solution of NaCl with a pH of 6) was 22 °C. The nitrogen stainless steel Cronifer 1925 hMo was compared with the stainless steel AISI 316L, which does not contain alloyed nitrogen.

Initially the relationship between the pH value and the potential of the different buffered solutions was determined. It was found that there is a linear relationship between the pH value and the potential. The slope of the straight line was, depending on the Sb-microelectrode, within the limits −49.16 and −51.71 mV/pH, which is characteristic for such electrodes. In this way it was possible to perform later monitoring of the change in the pH value in the pit due to the specific electrochemical processes inside it. The results of the test are shown in the following diagrams.

Figure 7 provides a convincing demonstration of the effect of interstitially dissolved nitrogen in the stainless steel Cronifer 1925 hMo. The events in the pit and the increase in the pH due to the action of the NH_4^+ ions (Eq. 6) are completely in agreement with the authors' hypothesis that alloyed nitrogen is able to control corrosion mechanisms in the corrosion pit in such a way that the ammonium ions increase the pH of the solution inside the pit, from an aggressive acidic of pH 4 to a basic of pH about 9.5. In this basic region conditions exist for the repassivation of the electrode surfaces, which means that polarization of the corrosion process occurs. The shift of pH towards higher values thus represents a criterion for the stability of the pit, which due to the action of the ammonium ions will not continue to grow, and at the critical value will not permit the occurrence of, for example, stress corrosion cracking. The results of the measurements indicated that the production of NH_4^+ ions is immediately established on the electrode surfaces, and the quantity of these ions in the pit increases rapidly since there are large enough quantities of H^+ ions for the reaction with the N^{3-} ions. In the stainless steel AISI 316L, which does not contain nitrogen, the conditions are quite the opposite (see Fig. 8). Due to the specific electrochemical processes inside the pit acidity increases, and conditions for polarization of the corrosion process do not occur. The AISI 316L stainless steel cannot become passivated even though due to the alloyed molybdenum it shows certain resistance to pitting corrosion, although this is not comparable with the resistance of the stainless steel Cronifer 1925 hMo.

The above text provides a sufficiently well-based explanation as to why, in the case of the Cronifer 1925 hMo steel, such a high activation energy (amounting to 142.9 $\mathrm{kJ\cdot mol^{-1}}$) is necessary for local destruction and the initiation of pits in the passive film and what is the reason for such a high *CPT*, which is near that achieved by the Ni-Cr-Mo superalloy Nicrofer 6020 hMo. The reason for this is the production of NH_4^+ ions, which enable rapid passivation and the formation of a homogeneous passive film, and on the front surface of the passive film there are additionally some layers of NH_4^+ ions. Such a double barrier provides efficient protection against corrosion.

The change in the pH in the pit during the action of the chloride ions in the 3.5% solution of NaCl with an almost neutral pH of 6.4 takes place according to somewhat different rules. It was assumed that after

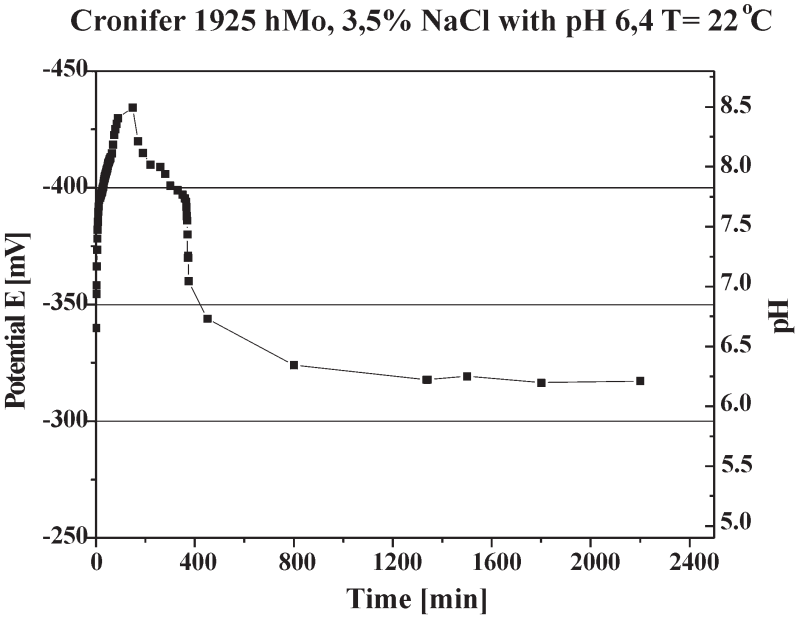

Fig. 9. Change of pH in a pit for Cronifer 1925 hMo steel, exposed to 3.5% NaCl.

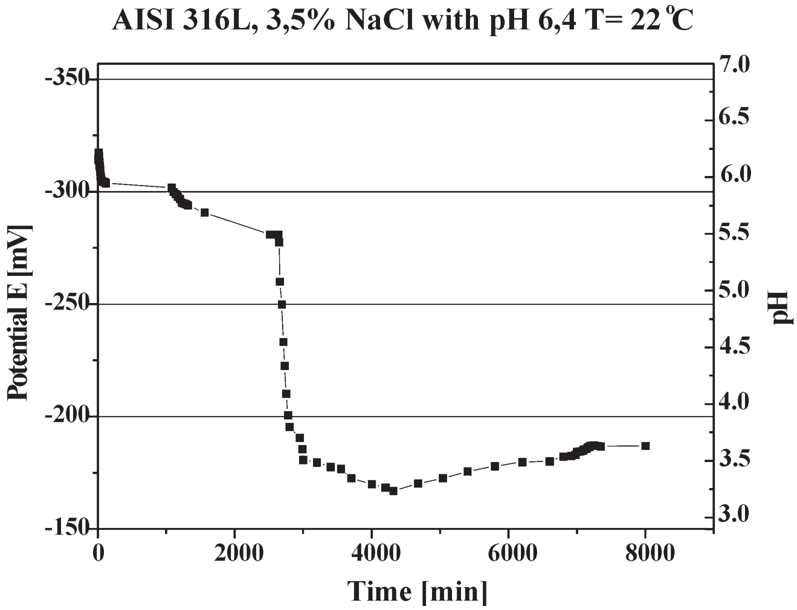

Fig. 10. Change of pH in a pit for AISI 316L steel, exposed to 3.5% NaCl.

the establishment of the corrosion process the interstitially dissolved nitrogen acts in the presence of Cl^- ions, as a negatively charged atom of nitrogen (N^{3-}), which is capable of changing the pH value on the electrode surfaces with the reaction according to Eq. (6), and secondly, that this ion repels the Cl^- ions, since both have a negative charge.

The results of tests in an artificially created pit with a diameter of 1.6 mm and a depth of 7.2 mm are shown, for the Cronifer 1925 hMo steel, in Fig. 9, and in Fig. 10 for the comparative steel AISI 316L, which does not contain alloyed nitrogen.

Investigations into the change in potential and pH of the medium in the pit in the case of the exposure of Cronifer 1925 hMo steel the 3.5% NaCl with pH of 6.4 (see Fig. 9), show quite different conditions than in the case of the same steel but in an acidic solution of HCl. In the 3.5% solution of NaCl the Cl^- ions become the dominant parameter and the driving force of the corrosion process, since the quantity of H^+ ions in this almost neutral solution is much smaller. Nevertheless, the quantity of H^+ ions present in the initial stage makes possible the production of NH_4^+ ions which is sufficient, after about 10 minutes, to in-

Table 3. Cyclic polarization with a rotating electrode in an abrasive suspension

Material	Working electrode	Medium	pH	T [℃]	Rotation rate of the working electrode [r.p.m.]	Pitting potential E_p [mV]	Repassivation potential E_{rp} [mV]
Cronifer 1925 hMo	rotating	bauxite + NaCl + H_2O	5	50	5000	from 1013 to 1056	$E_{rp} > E_p$ $E_{rp} = E_p$
AISI 316L	rotating	bauxite + NaCl + H_2O	5	50	5000	115	25
FeCr22Ni7Mo3N	rotating	bauxite + NaCl + H_2O	5	50	5000	1220	1051
Ni63Cr20Mo8Fe8	rotating	bauxite + NaCl + H_2O	5	50	5000	441	$E_{rp} > E_p$
Prokron 2 spec.	rotating	bauxite + NaCl + H_2O	5	50	5000	−176	−295

crease the pH of the medium in the pit from 6.4 to approximately 8.1, and after 100 minutes a maximum pH value of about 8.8 is achieved. This is sufficient for the walls of the pit to be passivated, which prevents the reaction according to Eq. (3) and thus prevents the anodic dissolving of the electrode surfaces within the pit. The anodic reaction is also prevented because the oxygen, as a depolarizer at the cathode, is quickly consumed, and the H^+ ions, which also act as depolarizers, are successfully consumed by the N^{3-} ions. With the occurrence of passivity the rate of diffusion of the N^{3-} ions through the passive film is partly reduced. Due to the mainly consumed H^+ ions and the lower rate of diffusion of N^{3-} ions at the boundary layer between the passive film and the electrolyte the concentration of ammonium ions is also reduced, which causes a rapid decrease in the pH to a value which corresponds to the main part of the medium, outside the pit. After approximately 600 minutes a sufficiently stable equilibrium is therefore established between the outside medium and the medium inside the pit.

It is clear that the N^{3-} and Cl^- ions are repelled, and this means that only a small number of chlorides can react with the cations of the iron and the alloying elements (the secondary reaction of the corrosion process). The consequence of this is that only a few chlorides penetrate the passive film. In this way, at a relatively high basicity of the medium in the pit, rapid passivation can occur. The growth of the pit is stopped since, due to the repelling effect of the N^{3-} ions, the reaction given in Eq. (4), according to which H^+ ions are formed, is prevented. The N^{3-} ions thus perform another important role; not just preventing an increase in the pH of the medium in the pit, but also, with their repelling action towards the chlorides, making possible the existence of a passive film at a time when a chemical equilibrium is being established between the main part of the medium outside the pit and the medium inside the pit. From Fig. 10, which shows what is happening inside the pit in the case of the stainless steel AISI 316L, it can be concluded that an autocatalytical process is established, which permits growth of the pit and different production of H^+ ions. Thus the characteristic reactions, which initiate the action of the interstitially dissolved nitrogen, cannot manifest themselves in the case of the AISI 316L stainless steel, which does not contain nitrogen.

4.5. Study of passive films by means of the polarization of a rotating electrode under conditions of erosion corrosion

Cyclic polarization can be used to study passive films, the quality of the latter being determined mainly by the pitting potential (E_p), which represents the first failure of passivity with a shift into the transpassive region, and the repassivation potential (E_{rp}), at which the loop is closed with reverse passivation. Higher values of E_p and E_{rp} represent passive films of greater stability, and the material shows a higher capacity for repassivation.

The media and electrochemical conditions of experimentation were the following:

– medium: an aqueous suspension with 20 % by mass of Al_2O_3 and the addition of 10 000 ppm of Cl^- ions/l of the suspension, with pH 5 and $T = 50$ ℃

– size of the particles of bauxite: from 0.015 to 0.045 mm

– limit current of reverse cyclic polarization: 5000 μA

– rotation rate of the working electrode: 5000 r.p.m.

The results of these experiments are shown in Table 3.

From the results it can be concluded that the nitrogen stainless steel Cronifer 1925 hMo, which has $E_{rp} > E_p$ or $E_{rp} = E_p$, shows a high resistance to pitting under conditions of erosion corrosion. Such values of the repassivation potential provide very few possibilities for the occurrence of pits, which can, for example, be the cause of stress corrosion cracking. This means that, under conditions of erosion corrosion, in the case of the duplex alloy with nitrogen or nitrogen stainless steel smaller corrosion pits can occur, but due to the steel's excellent repassivation capability, which is provided by the interstitially dissolved nitrogen, the pitting process and stress corrosion cracking is strongly hindered, and in certain situations even completely polarized. Clearly the electrostatic forces on the boundary surface between the steel and the corrosive medium are so large that they attract NH_4^+ ions (corrosion inhibitors) and that they successfully keep them there. For this reason the flow of the medium, i.e. the rate of rotation of the working electrode, does not have such a strong effect, and this provides effective inhibition of the steel surface. Later investigations contributed additional proof, which can be attributed to the nitrogen, i.e. that the surface of steel is hardened when bombarded with hard particles (nitrogen strengthens the austenite), thus increasing the abrasive resistance of such material.

In comparison with the nitrogen duplex cast steel FeCr22Ni7Mo3N, the nickel cast steel Ni63Cr20Mo8-Fe8 and the steel Cronifer 1925 hMo, the stainless steel AISI 316L is quite unusable under conditions of erosion corrosion. Its repassivation potential is very low, and the characteristically large loop in the reverse record of the corrosion current indicates a tendency for the occurrence of pitting corrosion under the given conditions of experimentation.

Such experiments with hard martensitic stainless steel Prokron 2 spec. have shown that, under conditions of erosion corrosion, the hardness of the material is important but rather its capacity, at those locations where damage has occurred to the passive film, to repassivate. In the opposite case, the joint operation of erosion and corrosion causes uninterrupted anodic dissolving of the metal and the carrying away of corrosion products which do not provide protectively. In this way, at damaged locations the metal is constantly exposed and subject to degradation.

5. Conclusions

The pitting resistance equivalent of the nitrogen stainless steel Cronifer 1925 hMo was found to be almost the same as that of the high-alloyed Nicrofer 6020 hMo, and this is also true of the critical pitting temperature, which is a good indicator of the resistance of the passive film in the case of the initiation and growth of pits. Calculations of the activation energy needed for the initiation of pits provide strong support for the above statements, and for the role of nitrogen in the case of the processes inside the pit. In the case of the Cronifer 1925 hMo steel this energy is very large, which means that nitrogen participates in the formation of very stable passive films. It is also considered that the operation of nitrogen in front of the electrode surface is manifested in the form of several layers of NH_4^+ ions.

When monitoring corrosion processes, measurements of pH values in pits indicate the nature of operation of nitrogen, which is manifested with a rapid rise of pH into the basic region, which accelerates the processes of passivation and repassivation. This is, however, possible only if NH_4^+ ions, which have an inhibiting effect, are formed next to the electrode surfaces.

A study of the quality of passive films, which are of decisive importance for pitting corrosion processes, has shown that NH_4^+ ions cause a very large rise in the repassivation potential, i.e. conditions in which $E_{\mathrm{pro}} = E_{\mathrm{p}}$ or even $E_{\mathrm{pro}} > E_{\mathrm{p}}$, which do not permit pitting corrosion. This means that processes of this kind are strongly inhibited.

Later investigations into the deformation hardening of Cronifer 1925 hMo steel due to the bombarding of the surface with hard particles from a dynamic fluid have shown, that deformation hardening, which is the consequence of the occurrence of a twin structure and a dislocation forest, represents, together with the formation of NH_4^+ ions, a combination which causes an exceptional rise in the sensitivity threshold of casts and steels containing nitrogen to the traditionally unfavourable degradation caused by erosion corrosion.

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