

## Investigation of pitting corrosion by potentiostatic polarization measurements

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In the present study, two austenitic stainless steels (conventional Cr18Ni9 and high nitrogen Cr18Mn12N) are examined with the purpose of demonstrate applicability and sensibility of potentiostatic polarization method to pitting corrosion investigation. The experiments were conducted in 0.1 M Na<sub>2</sub>HPO<sub>4</sub> + 0.5 M NaCl at room temperature and open air conditions.

According to cyclic potentiodynamic polarization method for stable pits development on the surface of nitrogen bearing steel lower anodic polarization is necessary in comparison with the nickel containing steel. The latter is acriterion for lower pitting corrosion resistance. However, the pitting potential values obtained potentiostatically are by 0.2 V more positive and what is more, the potentiostatic method reveals metastable pits on Cr 18Mn12N steel with longer incubation time. The combination of results from the both used methods revises the final conclusion for the pitting corrosion resistance in nitrogen bearing steel favour.

**Key words:** pitting corrosion, potentiostatic polarization, steel.

### INTRODUCTION

The investigation of pitting corrosion is really important for evaluation of corrosion behaviour of stainless steels. The most used method of pitting corrosion studies is the cyclic potentiodynamic polarization method (CPPM). However, some of the corrosion parameters determined by it strongly depend from scan rate of potential even the experiments were performed at very low values of it [1, 2]. The other conditions influencing the pitting corrosion parameters obtained potentiodynamically are the surface state, i.e. the surface finishing, treatment and metallurgical factors [2]. Therefore, the use of additional electrochemical methods for proving and clarification of pits nucleation kinetic is recommendable.

One of these rarely used electrochemical methods is the potentiostatic polarization method (PPM) which serves as a basis of other investigation methods namely Potentiostatic scratch method, Pulse potentiostatic method, etc. [3]. However, Schwenk et al. [4] show that it is the most reliable way of evaluating susceptibility to pitting corrosion. The PPM could surmount the disadvantages of CPPM and obtain more real evaluation of pitting potential ( $E_{\text{pitt}}$ ). The method consists in continuous polarization of the examined samples at potentials before and after the pitting and repassivation ( $E_{\text{rp}}$ ) potentials previously

defined by CPPM. Some of the authors [5] accepted that pits start to appear when the resulting current exceeds 10  $\mu\text{A cm}^{-2}$ . The time in which the current suddenly rise is called incubation or induction time ( $t_i$ ). This is another important index which might be obtained only by PPM.

Potentiostatic polarization method was used and for assessment of the critical pitting temperature [6] applying fixed potential and continuously increasing the temperature until stable pits appearance.

In the present study, two austenitic stainless steels (conventional Cr18Ni9 and high nitrogen Cr18Mn12N) are examined with the purpose to demonstrate the applicability and the sensibility of PPM to pitting corrosion investigation.

### EXPERIMENTAL

Two austenitic stainless steels: the conventional Cr18Ni9 and the high nitrogen steel, (HNS) Cr18Mn12N were investigated in 0.1 M Na<sub>2</sub>HPO<sub>4</sub> solutions containing 0.5 M NaCl. All tests were carried out in a conventional three electrodes cell in open air conditions at room temperature with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode. All potentials were reported with respect to the SCE. Two electrochemical methods were used: (i) Cyclic potentiodynamic polarization method and (ii) Potentiostatic polarization method.

The electrochemical results were obtained with a Galvanostat/potentiostat (Princeton Applied

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Research Model 263) and computer software Power Suite.

## RESULTS

In order to determine the characteristic pitting potentials by CPPM, experiments with scan rate  $1 \text{ mV}\cdot\text{s}^{-1}$  were carried out. The obtained dependencies are presented on Fig. 1. From these dependencies the values of pitting potentials ( $E_{\text{pitt}}$ ) for both steels were established and pointed out on the figure. It is well expressed that the  $E_{\text{pitt}}$  of nickel containing steel is more than 0.2 V higher than the nitrogen steel one. Regarding these  $E_{\text{pitt}}$  values the Cr18Mn12N steel is more susceptible to pitting corrosion in this corrosion environment. If the pitting corrosion susceptibility is evaluated only by CPPM the Cr18Ni9 steel would be reported as the more stable one.

These potentials values were used to determine the potential range in which the potentiostatic polarization experiments to be performed as well as to compare the  $E_{\text{pitt}}$  values obtained by both used methods.

The typical potentiostatic dependencies obtained at the applied potentials around the previously determined by CPPM  $E_{\text{pitt}}$  are given in Fig. 2 and Fig. 3.

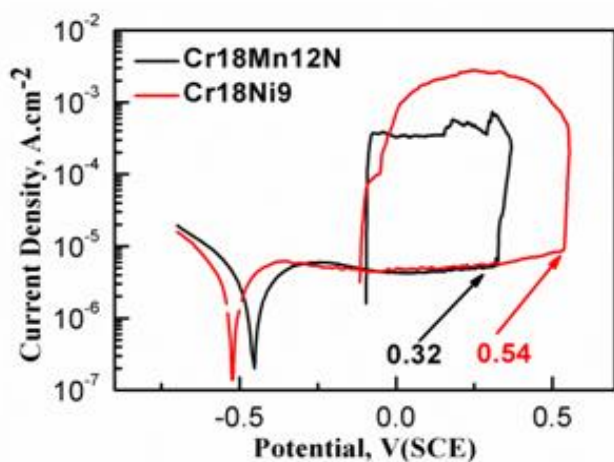


Fig. 1. Cyclic potentiodynamic polarization dependencies,  $1 \text{ mV}\cdot\text{s}^{-1}$ ,  $25^\circ\text{C}$ .

From the dependencies at applied potentials more negative than pitting potential information about the passive films thickness and its stability could be drawn [7]. It is accepted that the lower current density means more stable (thicker) passive layer as the time necessary for passive film breakdown depends from the film thickness [8]. From Fig. 2 it is obvious that both steels are in passive state and what is more there are not significant differences between the reached steady current densities. However, the nitrogen steel has slightly lower steady current densities which might

be sign for more stable passive layer contrary to the results from cyclic potentiodynamic experiments.

The results obtained at more positive than  $E_{\text{pitt}}$  potentials reveal that the current densities differ for both investigated steels. Here, it is well distinguished that the nitrogen containing steel has lower current density than the nickel one at the same applied potential (i.e. 0.36 or 0.38 V(SCE)). Additionally, it is clear that the pitting potentials determined by potentiostatic method (about 0.36 V(SCE) for both steels) are not the same as these

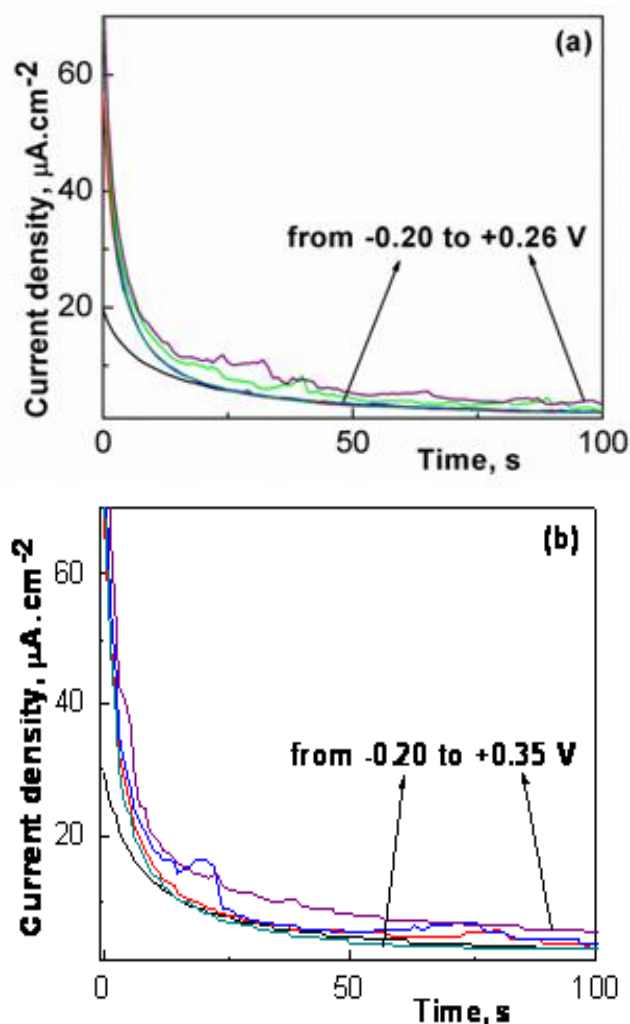


Fig. 2. Current density vs. time dependencies at  $E_{\text{ap}} < E_{\text{pitt}}$ : (a) Cr18Mn12N and (b) Cr18Ni9.

obtained by potentiodynamically polarization method (0.32 V(SCE) for Cr18Mn12N and 0.54 V(SCE) for Cr18Ni9). Thus, the both steels could have similar susceptibility to pitting corrosion in contrary to results presented on Fig. 1.

In addition, the dependencies for nitrogen steel at applied potentials 0.30 and 0.34 V(SCE) show that there is a metastable pits nucleation on the surface. It is expressed by small picks in the curve but the current density keeps its low value. Each

small fluctuation replies to pit initiation and repassivation [9-11]. These appeared and repassivated pits cannot be always registered by potentiodynamic measurements due to the limited resolution of the potentiostat. So, they must grow to a certain size before they can be registered. This growing needs time, and that is why they appear at more positive potentials in potentiodynamic measurements or the last registered only stable pits growing.

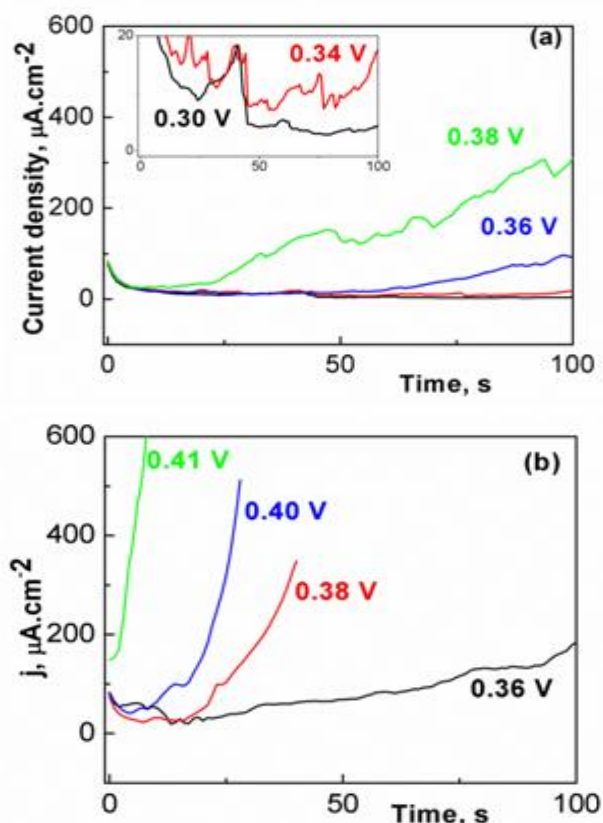


Fig. 3. Current density vs. time dependencies  $E_{ap} > E_{pitt}$ : (a) Cr18Mn12N and (b) Cr18Ni9.

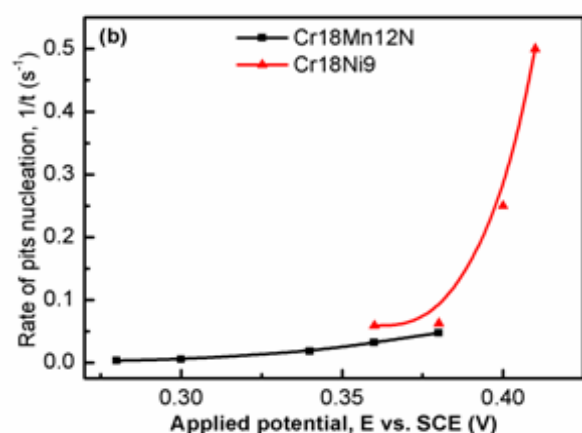


Fig. 4. Velocity of pits nucleation vs. applied potentials

An useful information which can be drawn from the potentiostatic results concerns the incubation time ( $t_i$ ). This is the time at which after the initial decrease the current density suddenly rises, hence this is the time required for pits growth to start [12]. Comparing the dependencies obtained for both steels it is well expressed that the incubation time of Cr18Ni9 steel is significantly shorter than that of the Cr18Mn12N. This fact gives additional information about the stability of the passive films and cannot be established by the cyclic potentiodynamic method.

In addition, the rate of pits nucleation (expressed by  $1/t_i$ ,  $s^{-1}$  [13]) vs. applied potential is shown in Fig. 4. The rate of pits initiation also gives valuable information. It is clear that the stable pits onto Cr18Ni9 steel surface appear at 0.36 V(SCE) and develop faster than pits on Cr18Mn12N steel surface which have rather metastable character.

Generalising the results obtained by potentiostatic polarization method it is well expressed that the Cr18Mn12N steel has similar corrosion resistance to pitting corrosion as Cr18Ni9 steel, which is completely opposite to the conclusion drawn from the results obtained by potentiodynamic method. Similar contradiction but in opposite direction was established and by Olefjord et al. [14] who studied Cr20Ni20Mo6N0.011 and Cr20Ni20Mo6N0.19 steels in HCl solutions. In the same way, they established that even the potentiodynamic dependencies do not show difference in the steel's behavior the potentiostatic dependencies at the same applied potential differ significantly. These inconsistencies of the results obtained by both methods suggest that the choice of method for pitting corrosion investigation must be made depending on the corrosion media on the one hand and the investigated material on the other hand. The choice of different study method has to depend on different properties of the formed in different corrosion environment passive films and on different surface conditions related to the pits nucleation. These surface conditions include different active sites for pits nucleation on materials (metallurgical defects, finishing, etc.). So, the potentiostatic results could be great supplement and verification to the results of potentiodynamic polarization method.

## CONCLUSIONS

Taking into consideration all written above it can be concluded that:

1. During electrochemical studies of pitting corrosion the using of potentiostatic experiments

after cyclic potentiodynamic polarization measurements will provide really important and useful information for the susceptibility of materials to pitting corrosion and the type of the appeared pits.

2. The use of only potentiodynamic polarization method for determining and comparing the behaviour of various materials in a given environment is not sufficient.

3. The evaluation of properties of the passive layers could be made using the potentiostatic polarization method.

4. The choice of appropriate method for evaluation of corrosion behaviour of materials strongly depends from the materials themselves and from the concrete corrosion environment.

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## ИЗСЛЕДВАНЕ НА ПИТИНГОВА КОРОЗИЯ ПОСРЕДСТВОМ ПОТЕНЦИОСТАТИЧНИ ПОЛЯРИЗАЦИОННИ ИЗСЛЕДВАНИЯ

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(Резюме)

В настоящата работа са изследвани две аустенитни неръждаеми стомани (конвенционалната Cr18Ni9 и високо азотната Cr18Mn12N) с цел да се демонстрира приложимостта и чувствителността на потенциостатичния поляризационен метод при изследване на питингова корозия. Експериментите са проведени в 0.1 MNa<sub>2</sub>HPO<sub>4</sub> + 0.5 MNaCl при стайна температура.

Според цикличния потенциодинамичен поляризационен метод за развитието на устойчиво нарастващи питинги на повърхността на азотната стомана е необходима по-ниска анодна поляризация в сравнение с тази при никеловата стомана. Последното е критерий за по-ниска устойчивост към питингова корозия. Обратно, потенциалите на питингообразуване получени чрез прилагане на потенциостатичния поляризационен метод са с 0.2 V по-положителни, нещо повече потенциостатичният метод открива метастабилни питинги върху стомана Cr18Mn12N, развиващи се след по-продължително инкубационно време. Съвместното разглеждане на резултатите от двата използвани метода променя крайното заключение за устойчивостта към питингова корозия в полза на азот-съдържащата стомана.