Krzysztof ROKOSZ[1], Jerzy CHOJNACKI[1], Tadeusz HRYNIEWICZ[1], Zbyszek ZBYTEK[2]
[1] Politechnika Koszalińska, Wydział Mechaniczny, ul. Racławicka 15-17, 75-620 Koszalin, Poland
[2] Przemysłowy Instytut Maszyn Rolniczych, ul. Starołęcka 31, 60-963 Poznań, Poland
e-mail: krzysztof.rokosz@wp.pl; jerzy.chojnacki@tu.koszalin.pl; Tadeusz.Hryniewicz@tu.koszalin.pl; zbytek@pimr.poznan.pl

CORROSION OF AISI 304L (EN 1.4307) STAINLESS STEEL IN ANIMAL SLURRY

Summary

The stainless steels are used to build parts of machinery for agriculture. These components should have adequate corrosion resistance because they contact with aggressive environments, such as natural and artificial fertilizers, or e.g. during the biogas production. In such environments austenitic AISI 304L (EN 1.4301) and AISI 316L (EN 1.4571) stainless steels are mostly used. In the available literature authors found no information on the corrosion potentiodynamic tests in manure. That was the reason to undertake the studies on one of the austenitic stainless steels to perform corrosion tests in the environment of animal slurry. The article presents the analysis of general and pitting corrosion of AISI 304L (EN 1.4307) steel in the environment which is the cattle slurry. Potentiodynamic measurements were made on the potentiostat ATLAS 98 with a scan rate of 0.1 $mV \cdot s^{-1}$ in the anodic direction and with scan rate of 1 $mV \cdot s^{-1}$ in the return cathodic direction. The measurement was started in the anodic direction from potential of minus 600 mV against the saturated calomel electrode (SCE) to achieve a current density of 1000 $\mu A \cdot cm^{-2}$. After that the cathodic scan was done back to the potential of -600 mV vs. SCE. The general corrosion in animal slurry is higher than in 3% water solution of sodium chloride. The corrosion potential measured in the animal slurry was equal to -525 mV vs. SCE. That clearly indicates a higher tendency to general corrosion in comparison with the results obtained in 3% sodium chloride solution (-200 mV vs. SCE). The passive current density ratio measured in the animal slurry to that one in 3% NaCl aqueous solution is equal approximately 8.5.
***Key words**: corrosion, stainless steel, animal slurry*

KOROZJA STALI AISI 304L (EN 1.4307) W GNOJOWICY

Streszczenie

Maszyny oraz urządzenia używane w rolnictwie budowane są najczęściej z elementów stalowych. Takie komponenty są narażone na korozję ze względu na to, że pracują w środowiskach korozyjnie agresywnych, takich jak nawozy sztuczne, czy też naturalne, jak i w produkcji biogazu. Najczęściej używanymi austenitycznymi stalami stopowymi są AISI 304 (EN 1.4301) oraz AISI 316Ti (EN 1.4571). W dostępnej literaturze autorzy nie znaleźli informacji na temat badań potencjodynamicznych w gnojowicy, czego wynikiem jest przedstawione opracowanie. W artykule przedstawiono analizę korozji ogólnej i wżerowej stali AISI 304L (EN 1.4307) w środowisku jakim jest gnojowica bydlęca. Pomiary polaryzacyjne wykonano na potencjostacie ATLAS 98 z szybkością skanowania 0.1 $mV \cdot s^{-1}$ w kierunku anodowym oraz 1 $mV \cdot s^{-1}$ w przypadku skanu powrotnego w kierunku katodowym. Pomiar rozpoczęto w kierunku anodowym od potencjału –600 mV względem nasyconej elektrody kalomelowej (NEK) do osiągnięcia gęstości prądu 1000 $\mu A \cdot cm^{-2}$, po czym następował pomiar w stronę katodową do potencjału -600 mV względem NEK. Jako elektrody prądowej użyto elektrodę platynową EPtP-301 oraz elektrody odniesienia NEK: EK 101 (0,244 V w temperaturze 25°C). Pomiary SEM/EDX przeprowadzono w Hochschule Wismar (Niemcy) na FEI Quanta 250 FEG z EDS-System NS7 oraz QuasOr EBSD-System. Chropowatość powierzchni oraz wżery były przedmiotem studiów na Taylor-Hobson Precision Talysurf CCI 6000 w Katedrze Mechaniki Precyzyjnej na Wydziale Mechanicznym Politechniki Koszalińskiej. Wyniki wykazały, że gnojowica bydlęca jest środowiskiem bardziej agresywnym niż 3% wodny roztwór chlorku sodu ze względu na potencjał korozji oraz prąd pasywacji. Potencjał korozji stali AISI 304L (EN 1.4307) w gnojowicy wskazywał na większą tendencję powierzchni do korozji (E_{corr} = –525 mV vs. NEK) niż w 3% wodnym roztworze NaCl (E_{corr} = –200 mV vs. NEK). Różnice są również widoczne w prądach pasywacji dla E_{corr} = 0 mV vs. NEK. Stosunek prądu pasywacji w gnojowicy do tego w 3% NaCl wynosi około 8,5. W przypadku korozji wżerowej zauważono odwrotną sytuację, to znaczy lepszą odporność na korozję wżerową w gnojowicy niż w roztworze 3% NaCl. Można to wstępnie tłumaczyć zaklejeniem powierzchni stali przez cząstki stałe gnojowicy, co będzie również podstawą dalszych badań.
***Słowa kluczowe**: korozja, stal odporna na korozję, gnojowica*

1. Introduction

Machinery and equipment used in environmental technology are made mainly from metallic elements. These components are subjected to damages caused by corrosion, especially when these things are used in a corrosive environment. Such environments are inside buildings and containers with organic agriculture waste – animal slurry. One of the animal manure utilization method is a controlled process of anaerobic decomposition where biogas [20] and organic fertilizer are obtained [11]. This method can be also utilized to industrial waste, municipal solid waste and sewage sludge [10]. Mass of biogas production from the anaerobic treatment of cow manure can be a raw material for significant electrical current production [12].

Steel products are suitable for many types of agricultural chemical equipment provided it is adequately selected or secured [18]. Depending on composition of the feedstock to biogas production the type of steel has an impact on the corrosion resistance. Animal slurry contains hydrogen and oxygen in the form of water and also as a free compounds and the chemical elements: nitrogen, phosphorus, potassium, calcium, magnesium, sodium, trace elements of boron, copper, manganese, zinc, molybdenum, cobalt, sulfur. Number of chemical compounds and elements occurring in the biomass during the anaerobic process in biogas plants is very high. For the manure and biogas installations, austenitic stainless steels are recommended. These types of stainless steels are very often used in engineering [2-9, 13-17]. In biogas plants installations stainless steel can be used as a material for tanks, digesters, pumps and valves, agitators, pipes and fittings and purification applications. For instance, the AISI 316Ti (EN 1.4571) stainless steel has been used for the brackets, to build mixers, and for the handling equipment [7, 14-16, 21-24]. The digester tanks are made of stainless steel grade AISI 304 (EN 1.4301), and AISI 316Ti (EN 1.4571), dehumidifier systems are made of stainless steel grade AISI 316L (EN 1.4404) because these components of biogas installations come into contact with wet biogas and must withstand the corrosive action of the hydrogen sulfide contained in it [14, 23].

The effectiveness of sacrificial protection against corrosion with the use of magnesium electrodes as anode 10 HA and 10 HAV steel were examined under natural exploitation conditions of slurry tanks. The steels have been used for the container walls of the tank capacity of 500 m^3 filled up with the pig slurry [19].

Bietresato, and Sartori in their paper [1] describe the electrical measurements of manure conductivity and the main slurry composition. On the basis of the two electrodes and alternating signal ±5 V with a frequency of 1 kHz they managed to develop mathematical formulae to predict the amount of nitrogen, potassium and phosphorus which were measured in their studies.

In the available literature Authors found no information and/or report on polarization studies of austenitic stainless steels in animal slurry solution. Iron-chromium-nickel-molybdenum-magnesium compact com-pounds were found in the passive layers on stainless steels used. Many of them are present in the natural environment, but some others, like nickel and chromium on the sixth level of oxidation could be dangerous in higher doses for the human being.

The aim of this study was to reveal the general and pitting corrosion action of the animal slurry, with some detailed view on the pits formed on AISI 304L stainless steel surface. The electrochemical potentiodynamic study was performed to realize that task.

2. Experimental Procedure

The polarization scan rate was performed on potentiostat ATLAS 98 (Fig. 1a) at the scan rate of 0.1 $mV \cdot s^{-1}$ in the direction of anode and 1 $mV \cdot s^{-1}$ in case of reverse scan using SCE. Start of the scanning was done starting from –600 mV vs. SCE to the limit of current density at 1000 $\mu A \cdot cm^{-2}$ and a reverse scan back to the intersection with the plateau range of anodic curve was performed. All the polarization measurements were made after a one-hour samples keeping immersed in the animal slurry solution. The potentiodynamic studies were performed on AISI 304L (EN 1.4307) stainless steel without additional treatment (as received sheets of the material from ironworks). The composition of the stainless steel used is shown in Table 1.

Table 1. Chemical composition of AISI 304L (EN 1.4307) stainless steel provided by AK Steel Corporation database (wt%) [25]
Tab. 1. Skład chemiczny stali AISI 304L (EN 1.4307) na podstawie danych firmy AK Steel Corporation (% wag.) [25]

Element	wt%
Carbon	0.08
Manganese	2
Phosphorus	0.045
Sulfur	0.03
Silicon	0.75
Chromium	18.00 - 20.00
Nickel	8.00 - 12.00
Nitrogen	0.1
Iron	Balance

The platinum electrode EPtP-301 (the plate of dimensions: 4×5 mm) was used as a counter electrode (CE), a saturated calomel electrode EK 101 (+0.244 V in 25 °C) was used for a reference (RE), and the studied stainless steel plate (Fig. 1b) was the working one (WE). The cell was placed perpendicularly to the sample surface (see Fig. 1).

The SEM/EDX studies were performed at Hochschule Wismar (Germany) on the ESEM FEI Quanta 250 FEG with EDS-System NS7 and QuasOr EBSD-System. The surface roughness of AISI 304L (EN 1.4307) stainless steel as received, as well as pits formed after the potentiodynamic measurements in the animal slurry, were studied by interferometric method with Taylor-Hobson Precision Talysurf CCI 6000 (Coherent Correlation Interferometry).

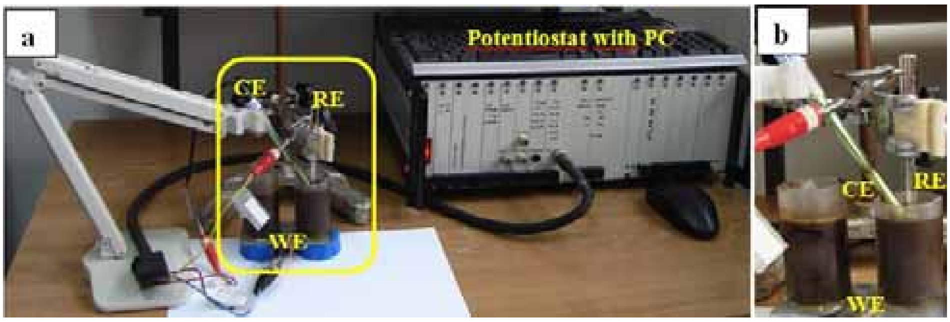

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Fig. 1. Set up for potentiodynamic measurements of AISI 304L (EN 1.4307) in animal slurry (a), zoom of the electrochemical cell with counter (CE), reference (RE) and working (WE) electrodes (b)
Rys. 1. Stanowisko pomiarowe do badań potencjodynamicznych na stali AISI 304L (EN 1.4307) w gnojowicy (s), powiększenie naczynka elektrochemicznego z elektroda prądową (CE), odniesienia (RE) oraz pracującą (WE) (b)

3. Results

Austenitic AISI 304L (EN 1.4307) stainless steel samples were used for the potentiodynamic studies. The SEM micrograph and chemical composition from EDS measurement of the studied material are presented in Fig. 2 (a) and (b), respectively. Based on the EDS results obtained, the chromium to iron ratio was calculated to be 0.26 (wt%). Except from iron, chromium and nickel in the steel matrix, there were also manganese and silicon as well as carbon and oxygen detected, mostly as contamination. In Figure 3, there are shown pictures from 3D roughness analysis. The first one (Fig. 3a) was obtained by filling non-measured points using a smooth shape calculated from the neighbouring points and after removing form with the use of polynomial of the second order:

$$-333 \cdot 10^{-6} + 1.18 \cdot 10^{-6} \cdot x - 3.03 \cdot 10^{-10} x^2 - 1.88 \cdot 10^{-7} \cdot y - 5.31 \cdot 10^{-10} \cdot x \cdot y + 1.99 \cdot 10^{-7} \cdot y^2$$

where x, y are the two dimensional axes of measured surface.

The 3D roughness parameters were measured according to the standard ISO 25187. In Figure 3b there is shown the photo simulation to illustrate the measured surface. On the basis of the performed analyses there were calculated 3D surface roughness parameters:

*S*a = 0.349 μm (Arithmetic Mean Deviation of the Surface),
*S*q = 0.49 μm (Root-Mean-Square Deviation of the Surface),
*S*p = 2.17 μm (Maximum height of summits),
*S*v = 4.26 μm (Maximum depth of valleys),
*S*t = 6.43 μm (Total height of the surface).

In Figures 4 and 5 there are presented polarization results from potentiodynamic corrosion measurements.

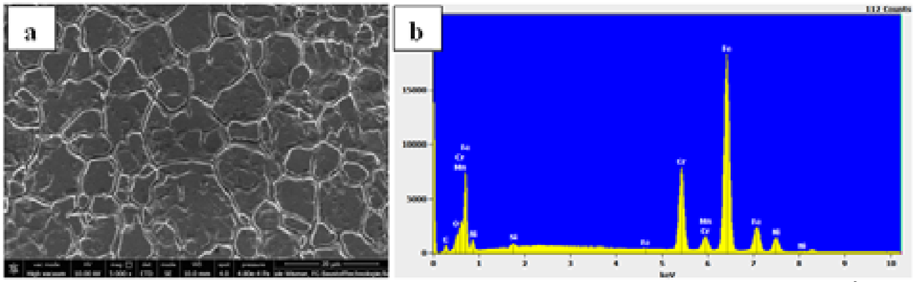

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Fig. 2. SEM (a) and EDS (b) results of AISI 304L (EN 1.4307) surface used for the studies
Rys. 2. Wyniki z badań SEM (a) oraz EDX (b) wykonanych na stali AISI 304L (EN 1.4307) użytej do badań

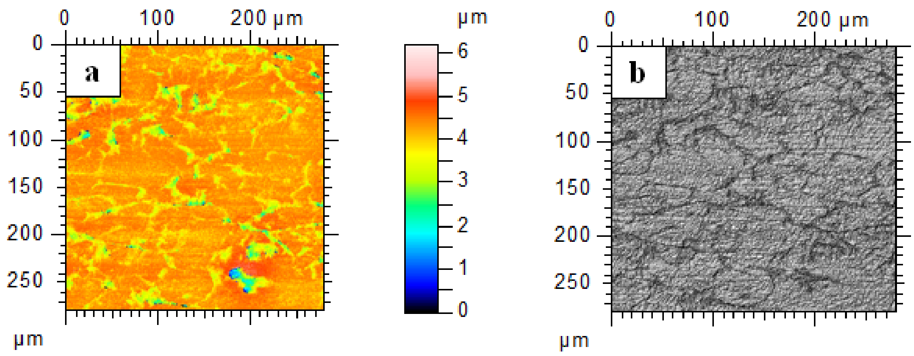

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Fig. 3. 3D surface analysis of AISI 304L (EN 1.4307) as received, colour image (a), photo simulation (b)
Rys. 3. Wyniki badań chropowatości powierzchni 3D stali AISI 304L (EN 1.4307) w stanie dostarczonym od producenta, obraz barwny (a), symulacja fotografii (b)

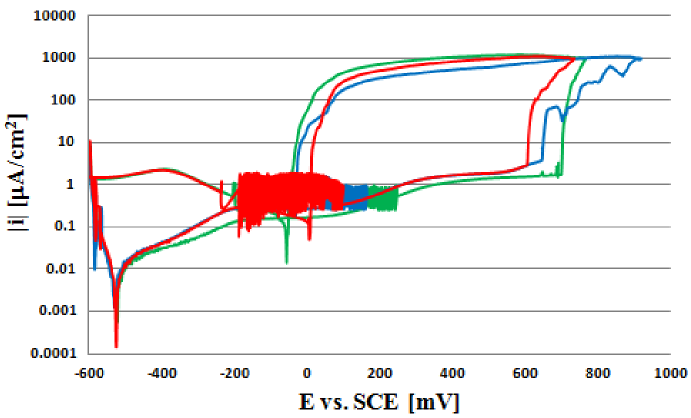

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Fig. 4. Potentiodynamic results of AISI 304L SS (EN 1.4307) austenitic stainless steel immersed in animal slurry solution
Rys. 4. Wyniki z badań potencjodynamicznych na stali stopowej austenitycznej AISI 304L SS (EN 1.4307) w gnojowicy

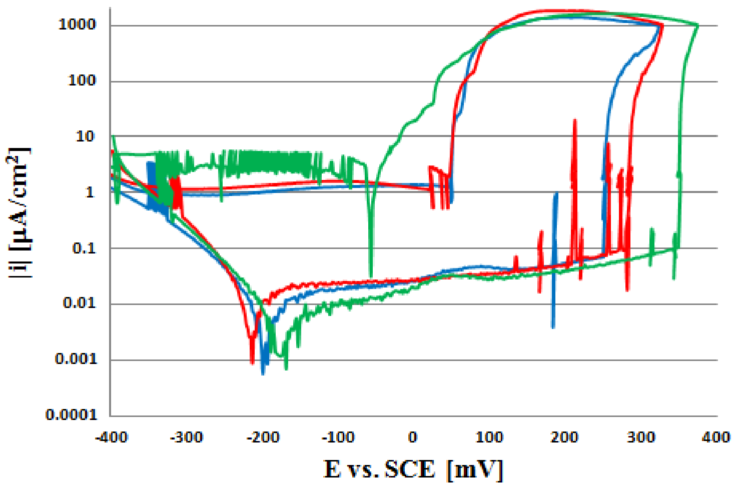

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Fig. 5. Potentiodynamic results of AISI 304L (EN 1.4307) austenitic stainless steel submerged in 3% NaCl water solution
Rys. 5. Wyniki z badań potencjodynamicznych na stali stopowej austenitycznej AISI 304L SS (EN 1.4307) w 3% wodnym roztworze chlorku sodu (NaCl)

It is clearly visible that the tendency to general corrosion is higher in case of the animal slurry than in 3% NaCl solution. Corrosion potential in the animal slurry is equal –525 mV vs. SCE and for measurements in 3% NaCl it is about –200 mV vs. SCE. On the other hand, the potential at plateau region, 0 mV vs. SCE for animal slurry amounts to the current density of about 0.17 $\mu A \cdot cm^{-2}$ and for 3% NaCl, about 0.02 $\mu A \cdot cm^{-2}$. Thus it appears, the corrosion rate of AISI 304L (EN 1.4307) in the animal slurry is about 8.5 times higher than that in 3% NaCl (the most aggressive aqueous sodium chloride solution). On the other hand, there is pitting potential which for the animal slurry is very high (average of about 700 mV vs. SCE) versus that one in 3% NaCl (on average of about 300 mV vs. SCE), what could suggest a higher pitting corrosion resistance.

Pits formed on the steel surface after polarization measurements could suggest that the sticky "film" coming from the solution/manure created of additional solid particles should slow down the pitting corrosion. The study results show it is not the case. In view of the phenomena occurring on the steel sample in the animal slurry, the Authors are going to perform additional studies with other electrochemical cell, in which there will be no possibility of "gluing" the steel surface.

In Figure 6, there are shown the three examples of pits after potentiodynamic study in the cattle slurry. The smallest pit (Fig. 6a) area is equal 92797 μm^2 and the volume of 1797625 μm^3. For the biggest pit presented, the area is 0.755 mm^2 and the volume is 9205328 μm^3. In all stages of the pitting process, extensive pits formation was noted with some new, small ones created inside them (Fig. 4c).

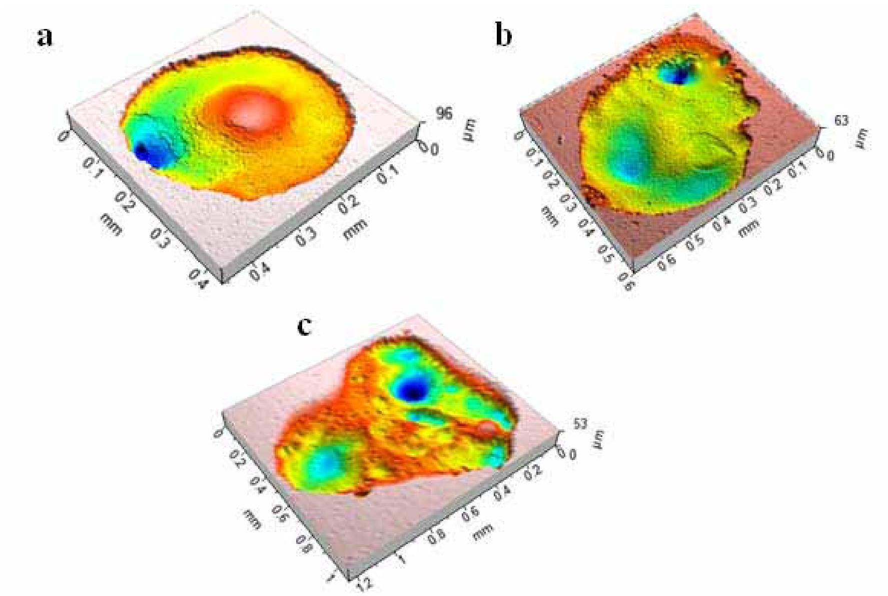

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Fig. 6. Pits development after potentiodynamic study in the cattle slurry: pit's area 92797 μm^2, pit's volume 1797625 μm^3(a); pit's area 0.264 mm^2, pit's volume 915990 μm^3(b); pit's area 0.755 mm^2, pit's volume 9205328 μm^3 (c)
Rys. 6. Rozwój wżerów po badaniach potencjodynamicznych w gnojowicy: powierzchnia wżeru 92797 μm^2, objętość wżeru 1797625 μm^3 (a); powierzchnia wżeru 0,264 mm^2, objętość wżeru 915990 μm^3 (b); powierzchnia wżeru 0,755 mm^2, objętość wżeru 9205328 μm^3 (c)

4. Conclusion

The results of the study have shown, that the cattle slurry is more corrosive environment than 3% water solution of sodium chloride. The corrosion potential of AISI 304L (EN 1.4307) stainless steel measured in the animal slurry (E_{corr} = –525 mV vs. SCE) clearly indicates a higher tendency to general corrosion in comparison with the results obtained in 3% sodium chloride solution (E_{corr} = –200 mV vs. SCE). The differences in passive current densities have also shown that the corrosion resistance in slurry is lower than that in 3% NaCl solution.

The ratio of passive current density measured in the animal slurry to that one obtained in 3% NaCl solution for E_{corr} = 0 mV vs. SCE is equal about 8.5. However, the pitting potential has shown the other situation, i.e. better pitting resistance in the animal slurry. Most probably it is due to creating an additional solid-particle solution layer which slow down the pitting corrosion. The following studies, using other set up, where the steel electrode will be placed at the top of the electrochemical cell, are needed. They are to reveal the role and influence of solid particles coming from the animal slurry on the general and pitting corrosion.

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