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INFLUENCE OF PLASTIC DEFORMATION ON ELECTROCHEMICAL PROPERTIES OF X5CrNi18-10 STEEL

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Abstract
The purpose of the work was to determine the effect of plastic deformation on the electrochemical properties of X5CrNi18-10 steel. The tested material belongs to the group of stainless steels with low carbon content and is used in many industries due to high corrosion resistance. In most applications of the tested material, it is formed into complicated shapes and exposed to aggressive environments. An example can be applications in medicine (implants) as well as in civil engineering and nuclear energy. The literature on the subject shows a different impact of deformation on anti-corrosion properties. Samples with 5 different deformations were obtained. Electrochemical direct electrical current and alternating electrical current tests were performed for the obtained materials. The tests were carried out in a 1 molar sodium chloride solution. Studies have shown an increase in corrosion resistance of samples with increasing strain in the tested strain ranges.

Keywords: corrosion, electrochemistry, stainless steel, impedance spectroscopy, Tafel plots

Introduction
Steel 1.4301 is in the group of corrosion-resistant steels (EN 10088-1:2014) and has wide range of applications. In the automotive industry, it is used, among others as a construction material for the production of: exhaust system, catalyst and turbocharger housings, fuel tanks, truck and bus chassis, external and internal decorative elements, suspension elements, safety cages, road tankers. Various types of stainless steel are widely used due to corrosion resistance and the possibility of producing complex and visually attractive shapes (Kulakowski, Rokosz 2017). Stainless steel is also used in the production of cookware. It is estimated that about 43% of the kitchen utensils are made from this material (Bernstein 1977; Santonen et al. 2010). Most of the stainless steel used in cookware contains approximately 18% chromium, which ensures optimal corrosion resistance. Apart from chromium, it also contains nickel in the amount of 8-10% (Bassioni et al. 2015). Stainless steel is also widely used in construction. The most popular applications include the construction of glazed roofs and facades, as well as elevators and escalators. It is used for the construction of barriers and balustrades (Wciślik 2017). Austenitic stainless steels are also used in medicine. They are often used in the production of orthopedic implants due to properties such as resistance to corrosion and fatigue, as well as high resistance to fracture. These properties are important in the selection and modification of material for biomedical applications (Ryan et al. 2006; Alvarez et al. 2008). Another branch of industry in which stainless steels are used is nuclear power generation. Nuclear power plants construction materials should preserve the integrity of the fuel rods and prevent the release of radioactive
materials from the fuel into the coolant. The materials are also exposed to an aggressive environment. The aggressiveness of the environment is caused by the neutron flux velocity combined with the high temperature. Neutron radiation causes the displacement of atoms in the nodes of the crystal lattice (Stress Corrosion Cracking... 2011). This effect causes void swelling, phase instability and creep that increases with the intensity of the neutron radiation. To meet these conditions, the chemical composition / microstructure of stainless steels must be changed, for example by introducing smaller amounts of alloying elements such as Ti, Si and P. Recent research into the use of stainless steels as lining for nuclear fuel rods and fuel assembly components has shown that yttrium and oxide precipitates act as stable obstacles to the movement of atoms displacement and help to stop irradiation. Stainless steels have also been used as a replacement for copper alloys in tube bundles for feedwater heaters. Products from copper alloys cause galvanic corrosion and thus disturb the heat transfer (Venkatraman 2013). Austenitic steels are characterized by high corrosion resistance in acidic environment, which, however, changes with plastic deformation. Samples deformed by cold rolling have lower corrosion resistance than non-deformed samples. The corrosion resistance changes in the case of using an environment rich in chloride ions, which cause pitting corrosion (Freirea et al. 2011). It is concluded that plastic deformation produced in the cold and at high speeds causes the formation of local micro-cells (Rutkowska – Gorczyca et al. 2009). The increase in corrosion resistance was observed when crushing samples of AISI 321 steel to the level of 0.86. The steel used in the research had a crystallographic system of regular face centered. Additionally, by using heat treatment, samples of different morphology were obtained. Only in the case of samples with the smallest grain sizes, a reduction in corrosion resistance as a result of deformation was observed. In the case of samples with larger grain sizes, higher corrosion resistance of the deformed samples was observed. It is assumed that this effect is caused by the development of austenite crystallographic planes, which reduces the influence of the martensitic phase formation (Tiamiyu 2019). In the case of tests showing an increase in the corrosion potential, the applied deformations were single-fold and carried out at a constant rate. The reduction of the corrosion potential was observed in the case of small plastic deformations in the compression cycles resulting in an increase in the hardness of stainless steel. In addition, several rolling cycles (strains greater than 0.2) were required to achieve higher levels of deformation in the rolling process. The electrochemical parameters of the samples may be influenced by the size of the deformation and the related changes in the structure of the material. In the case of the breaking test, the electrochemical and structural parameters of AISI 304 steel in the range of elastic and plastic strains were examined. Comprehensive research, including
electrochemical and structural tests, showed a different influence of the type of deformation on the electrochemical parameters of the material. According to the research, elastic deformations do not affect the material's susceptibility to corrosion. Plastic deformations caused a significant reduction of the corrosion potential. The tests were carried out during stretching. The decrease in corrosion potential during deformation was attributed to the formation of cracks in the passive oxide layer. The disturbance of the layer structure probably resulted in the creation of new active surfaces enabling faster electrochemical processes to take place (Nazarov et al. 2019). The object of research is to determine the influence of plastic deformation in the tensile cycle on the electrochemical properties of X5CrNi18-10 steel (1.4301 or AISI 304). The tests will be carried out 48 hours after grinding the sample in order to enable the formation of an oxide layer.

**Materials and methods**

In this work samples of X5CrNi18-10 steel as presented on Figure 1 were used. The samples were cut from a 5 mm thick metal sheet with the use of electro erosive cutter ZAP BP09d.

![Sample shapes](image)

The dimensions of the samples were as follows: \(L_0 = 30\) mm, \(L_1 = 45\) mm, \(L_2 = 60\) mm, \(L_3 = 125\) mm, \(b_1 = 5\) mm, \(b_2 = 10\) mm, \(h = 5\) mm. The tensile tests were performed in accordance with the PN-EN ISO 6892-1 standard. The samples were stretched at a speed of 2.5 mm / min on the Tira Test 27100 testing machine. The deformations obtained were: 0.07; 0.12; 0.16; 0.20; 0.23. Three samples were prepared for each level of deformation. In addition, three samples were left undistorted. The samples were ground on a laboratory grinder with the use of sandpaper graded from 200 to 800 to the resulting roughness Ra from 0.4 to 0.5 \(\mu\)m. The test samples were left in the desiccator for 48 h and then their roughness was measured again. The samples were cleansed with acetone and placed in an electrochemical vessel (Figure 2).
necking of the samples was the place isolated within electrochemical unit with the use of 5 mm diameter o-ring. Therefore the electrochemical data were obtained from 19.6 mm² area.

Fig. 2. Electrochemical vessel (www.atlas-sollich.pl)

A 1M NaCl solution was poured into the electrochemical vessel with the sample attached, which allows for linear changes in the conductivity of the solution without the participation of processes related to the change of the ion activity coefficient. A silver chloride electrode as reference electrode and a platinum electrode as counter electrode were placed in the vessel. The Lugin capillary was placed on the reference electrode and placed 0.5 mm above the sample. The electrodes and the sample were connected to a electrochemical unit - ATLAS 1131 EU&IA by Atlas-Solich. The system was then stabilized to steady-state potential for 6 hours. The LPR measurement was performed by lowering the potential of the working electrode by 50 mV below the stationary potential, and then increasing the potential to 50 mV above the stationary potential. Potential changes occurred at a rate of 1 mV / s. The study of impedance spectroscopy was carried out using the amplitude of the potential changes of 50 mV. Measurements were made in the frequency range of the alternating current 100 kHz to 1 mHz. Measurements were made using the AtlasCorr program, and the results analysis was performed using the AtlasLab program.

Results
The values of the corrosion potential and the polarization current density were obtained from the Tafel curves. An exemplary plot of the dependence of the sample potential on the logarithm of the absolute value of the polarization current density determined for an undistorted sample is shown in Figure 3.

![Figure 3](image)

**Fig. 3.** The dependence of the sample potential on the logarithm of the absolute value of the polarization current density for the undistorted sample.

Figure 4 shows the dependence of the corrosion potential on the amount of plastic deformation.

![Figure 4](image)

**Fig. 4.** Dependence of the corrosion potential on plastic deformation
In the tested material, the value of the corrosion potential measured against the silver chloride electrode increased with deformation. The measured values ranged from -0.24 to -0.075 V. The values of the corrosion potential increase with the value of deformation. The exception is a sample with a deformation value of 0.12. Except for the sample with a plastic deformation of 0.12, all other samples are significantly different from the non-deformed sample. We also observe a significant increase in potential between samples with a deformation of 0.07 and materials with deformations of 0.2 and 0.23. The corrosion potential is a measure of the energy required for the electrochemical oxidation process to occur. The higher the potential value, the greater the material resistance. In the case of the test subjects, it can be concluded that the deformation increases the resistance to corrosion processes in the test solution.

Another parameter obtained from the analysis of Tafel curves is the value of the corrosion current density. Corrosion current density values for materials with specific deformations are shown in Figure 5.

Corrosion current density is inversely proportional to deformation. The highest value of the corrosion current density was measured for the undeformed sample with the value of 17 nA/cm². The smallest corrosion current density value was measured for a sample with a strain of 0.23. The current density value for the most deformed sample is 5 nA/cm². The current density shows a clear decrease after exceeding the deformation of 0.16. The results of the measured current densities for strains greater than 0.12 differ significantly from the undistorted sample. It should be noted that the corrosion current densities are low in all cases and are in the

![Fig. 5. The dependence of the corrosion current density on the plastic deformation of the sample.](image-url)
nanoampere limits. The greater the value of the current density, the greater the exchange of electrons on a given surface. In the tested cases, the number of oxidation reactions decreases with increasing strain.

The next test carried out on deformed samples was to determine the behavior of the sample under the influence of alternating current using the EIS method. The impedance spectra presented in the form of Nyquist plots are presented in Figure 6.

The Nyquist plots for all tested samples have the same shape. Nyquist plots have the shape of straight lines, which means that the equivalent circuit that best approximates the tested sample is a series connection of a resistor and a variable phase element (Figure 7).

This means that no new chemical substances appear on the tested surfaces as a result of deformation, which makes it possible to meet the condition of low invasiveness of the study on the structure of the material. It can be concluded that as a result of deformation on the material surface, only the quantitative ratio of the substances already present changes. The highest real
impedance was determined for samples with a deformation of 0.16, and the lowest for samples with the greatest deformation. The second sample with the highest corrosion resistance is shown for non-deformed samples and samples with a deformation of 0.2. The lowest values of the real impedance show the samples with the highest deformation. By analyzing the slope of the curve to the axis of real impedance, we can assess the extent to which a given surface is covered with a non-conductive layer. In our case, metal oxides will be the non-conductive element. The sample that is most similar to an ideal capacitor and thus has the largest amount of metal on the surface is probably the most deformed sample. The slope of the curve in the direction of the x axis increases with the amount of deformation up to the level of 0.12. The following curves show Nyquist curves further away from the x axis. It can be assumed that as a result of further deformation, the percentage of surface covered with the oxide material decreases.

Discussion

The deformation of samples made of X5CrNi18-10 steel increases the corrosion resistance of the material in the scope of the tested deformations, if we only take into account the DC tests. The corrosion potential, which determines the activation energy of the corrosion process increases. The corrosion current density is reduced, which means less corrosion processes occur. The impedance spectra show that the surface does not have a metallic characteristic, but most likely an oxide one, which affects the electro-insulating properties. In the research conducted by Rybalka et. Al (2006) the stainless steel with the content of chromium of 12.4 % ratio exhibits different impedance spectra which have more metallic character. In presented research the greater chromium content leads to higher oxide character. The morphology of the oxide coating may have a greater influence on electrochemical processes taking place during the operation of alternating current. Probably, plastic deformation favors the process of chromium passivation in the presence of air. This mechanism is supported by research conducted by Nazarov et. al (2019). This effect may cause an increase in the amount of oxide and the observed decreases in the corrosion potential and the polarization current density. The EIS test results may prove the homogeneity of the oxide layer on the steel surface. For the tested samples, the homogeneity of the oxide layer probably increases to a deformation of 0.12. After exceeding this level, the amount of oxide continues to increase, but larger amounts of discontinuities appear, causing greater slopes of the impedance spectrum towards the OY axis (imaginary impedance). This effect may be caused by change of valance of chromium in oxide layers which may be supported by shift of potential, sharper decrease of current density and impedance spectra slope after strain of 0.12. This effects were reported as indicative of chromium oxide valance change by Marijan and Gojic (2002), but the effect was caused by
forced potential changes. From a electrochemical stand point the strain increase may cause similar effect by decreasing the potential for chromium oxide formation and increasing the amount of passive layer as presented by Zhang et al. (2018).

References


