Corrosion resistance of cementing steel X19NiCrMo4 in medium of 5 % NaOH and 5 % H2SO4

Brajčinović, Sandra; Begić Hadžipašić, Anita

CORROSION RESISTANCE OF CEMENTING STEEL X19NiCrMo4 IN MEDIUM OF 5% NaOH AND 5% H$_2$SO$_4$

Sandra Brajčinović[*], Anita Begić Hadžipašić

University of Zagreb Faculty of Metallurgy, Aleja narodnih heroja 3, 44000 Sisak, Croatia

Abstract

This paper presents the results of testing the corrosion behavior of X19NiCrMo4 cementing steel in 5% NaOH and 5% H$_2$SO$_4$ solution. Electrochemical measurements were performed by measuring the open circuit potential, determining the corrosion parameters using electrochemical impedance spectroscopy (EIS) and Tafel extrapolation. The corrosion rate, which was determined by Tafel extrapolation method, was lower in 5% NaOH solution than that in 5% H$_2$SO$_4$ solution. The obtained results were confirmed by the method of electrochemical impedance spectroscopy, which showed a higher value of charge transfer resistance of the tested steel in an alkaline medium, which proves higher corrosion resistance.
Metallographic analysis were performed on a sample previously etched in nital and on a sample after polarization measurements. Images of the electrode surface after polarization measurements in 5% H$_2$SO$_4$ medium showed a completely corroded steel surface indicating dissolution of the oxide layer due to acid exposure. No changes were observed on the sample surface in the alkaline medium.

Keywords: cementing steel, corrosion rate, impedance, charge transfer resistance, microstructure

Corresponding author *(e-mail address):* smitic@simet.unizg.hr

INTRODUCTION

Cementing steel marked X19NiCrMo4 (DIN 17350) is classified in the group of special steels, i.e. tool steels intended for cold work. For tool steels, it is necessary to meet certain requirements in their production. Top requirements are easy workability, good polishing and stability measures during the heat treatment, surface resistance to pressure and wear [1]. The primary use of X19NiCrMo4 steel is in the tool industry for the production of plastic molds and rollers for cold rolling of profiles. However, the application of tool steels is diverse and due to their mechanical properties they are also used for other purposes. Due to the above, cementing steel can come into contact with various aggressive agents and coolants, which due to their properties can act aggressively and gradually destroy the surface layer of the metal [2].
Due to the variety of applications, the aim is to achieve good corrosion resistance of the material in various conditions of production and use. For this purpose, anti-corrosion

protection methods are applied, such as: coating, electrochemical protection methods, use of corrosion inhibitors or alloying of steel with chromium and nickel. Studies based on testing the stability of metals in solutions of different pH values are important in selecting the appropriate inhibitor. Also, the influence of microstructure and selection of appropriate alloying elements greatly contributes to the quality of steel and thus to corrosion resistance in certain media [3].

The aim of this paper is to investigate the corrosion intensity of cementing steel in acidic and alkaline media. Sulfuric acid and sodium hydroxide were used for the study. Sulfuric acid is a strong acid. In aqueous solution, it completely dissociates into hydrogen ions (H^+) and sulfate ions (SO_4^{2-}). In extreme conditions, metals in contact with acids or alkalis are susceptible to corrosion. Sulfuric acid is used for the synthesis of various organic compounds, for the production of paints, in metal processing and is found in acid rains. It has multiple effects, in addition to acting as an acid, it can be an oxidizing, dehydrating or hygroscopic agent [4,5].

Sodium hydroxide is considered to be the most commonly used hydroxide in the chemical industry. Due to its alkalinity it is used as a pH regulator. It is used in the production of soap, in the textile industry, for aluminum processing or metal cleaning [6].

Tool materials are components of certain machines in industrial plants and can easily come into contact with acids and alkalis. The obtained corrosion parameters after testing in the mentioned media enable better recognition of the quality of materials, but also easier selection of anticorrosive agents and their application in industrial plants.

MATERIALS AND METHODS

A sample marked X19NiCrMo4 (DIN 17350) was used to test the influence of media and microstructure on the corrosion resistance of cementing steel. The chemical composition of the tested steel is shown in Table 1. Solutions of 5% NaOH and 5% H_2SO_4 were used as working medium during electrochemical tests.

Table 1. Chemical composition of X19NiCrMo4 steel (in weight percentage)

C	Si	Mn	P	S	Cr	Mo	Ni	Fe
0.170	0.27	0.41	0.009	0.002	1.18	0.19	3.90	balance

According to the table of chemical composition, it can be seen that the tested steel contains alloying elements chromium, manganese, molybdenum and nickel. In addition to nickel, all of the above alloying elements in combination with carbon form carbides. Nickel does not produce carbides, but it increases the corrosion resistance of steel. The content of phosphorus and sulfur is low, and the overall chemical composition meets the quality according to the prescribed production values. The addition of a controlled amount of selected alloying elements makes it possible to achieve stability of the surface oxide layers formed on the surface of the material. Improved corrosion resistance is most often achieved by adding chromium (up to 12% Cr) [7].

SAMPLE PREPARATION

Samples of X19NiCrMo4 cementing steel were cut into cubes and prepared by pressing into a conductive mass using a hot sample pressing device (SimpliMet® 1000). After that, they were machine sanded with waterproof sandpaper of grade No. 240, 400, 600 and 800 and polished (Al$_2$O$_3$ suspension in water) on an automatic grinding and polishing device (Büehler). They were washed in distilled water and degreased in ethanol. One prepared sample was set aside for etching in the nital to highlight the microstructure [8]. The second sample was prepared for the purpose of electrochemical tests.

ELECTROCHEMICAL TESTS (E$_{CORR}$, EIS, TAFEL)

To obtain data on the corrosion behavior of samples, the method for determining the corrosion potential E_{corr}, electrochemical impedance spectroscopy (EIS) and Tafel extrapolation method were used. The sample represented a working electrode was immersed in a working medium in a three-electrode glass cell containing a saturated calomel electrode-SCE as a reference electrode and a Pt-grid as a counter-electrode [9].
Measurements were performed using a computer-controlled potentiostat/galvanostat (Parstat 2273). Electrochemical tests were performed in solutions of 5% NaOH and 5% H$_2$SO$_4$, and the sample area was 0.98 cm^2.

Determination of corrosion potential E$_{corr}$

Before starting the polarization measurement, it is necessary to stabilize the metal-electrolyte system. This means that after immersion in the electrolyte, the electrical circuit between the working and counter electrode is kept open, and the potential difference between the working and reference electrode is monitored as a function of time. Stabilization of the open circuit potential *OCP* was performed at room temperature T = (19 ± 2) °C using a computer-controlled potentiostat/galvanostat (Parstat 2273) and for 1800 seconds. By monitoring the time changes of the stationary open circuit potential *OCP*, data on the corrosion behavior of the sample in the tested medium were obtained [9].

Determination of corrosion parameters using electrochemical impedance spectroscopy (EIS)

In order to investigate the electrode/electrolyte phase boundary, impedance measurements are performed in the frequency range from 100 kHz to 10 mHz with a sinusoidal voltage amplitude of 5 mV. The impedance parameters were analyzed using ZSimpWin 3.60 software using the appropriate electrical circuit R(Q(R(QR))). This method is based on the application of alternating current, and is based on the response of the circuit to alternating voltage or current as a function of frequency [10].

Determination of corrosion parameters using the Tafel extrapolation method

Corrosion parameters (corrosion potential E_{corr}, corrosion rate v_{corr}, anode slope b_a and cathode slope b_c) were determined by PowerCorrTM software using the Tafel extrapolation method and Faraday's laws. The Tafel extrapolation method was performed using

potentiodynamic polarization in the potential range from -250 mV to +250 mV vs E_{corr}, with a potential change rate of 1 mV/s [9].

METALLOGRAPHIC TESTS

An optical microscope with a digital camera (Olympus GX 51) and an automatic image processing system (AnalySIS® Materials Research Lab) was used for metallographic testing. Metallographic tests were performed on a sample previously etched in 0.5 % nital. Nital is a mixture of alcohol and nitric acid suitable for etching carbon steels for the purpose of recognizing their microstructure [8].
The second prepared sample was used for electrochemical tests, and after each measurement was observed using an optical microscope before and after exposure to the media.

RESULTS AND DISCUSSION

In order to prove the acidity or alkalinity of the medium, the pH values of the solution were measured before and after the electrochemical measurements with a pH meter. The obtained pH results are shown in Figure 1.
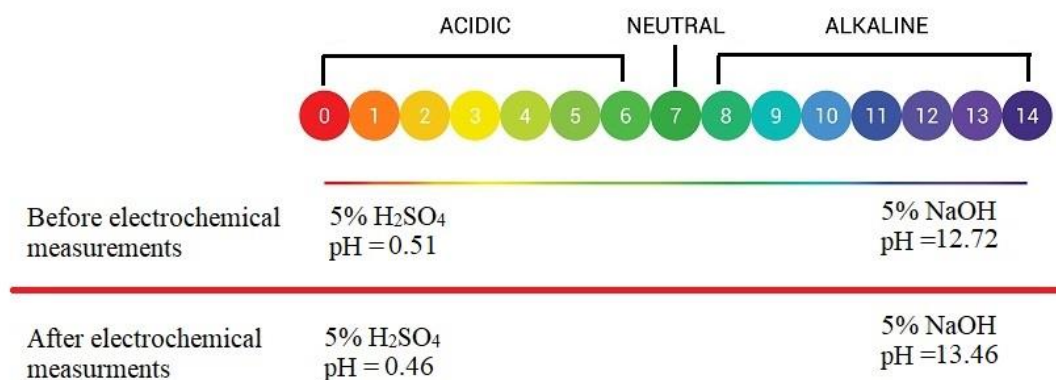

Figure 1. Measured pH values of 5% H_2SO_4 and 5% NaOH solutions

Figure 2 shows the time dependences of the open circuit potential for the tested sample of cementing steel in solutions of 5% NaOH and 5% H_2SO_4. It can be determined that after about one minute, a fairly stable *OCP* value is reached. According to the obtained curves, it can be seen that the sample weighs more negative potential values in the 5% H_2SO_4 solution than is the case for the NaOH solution. Sulfuric acid was corrosive to the metal, i.e. it caused the faster dissolution of metal.
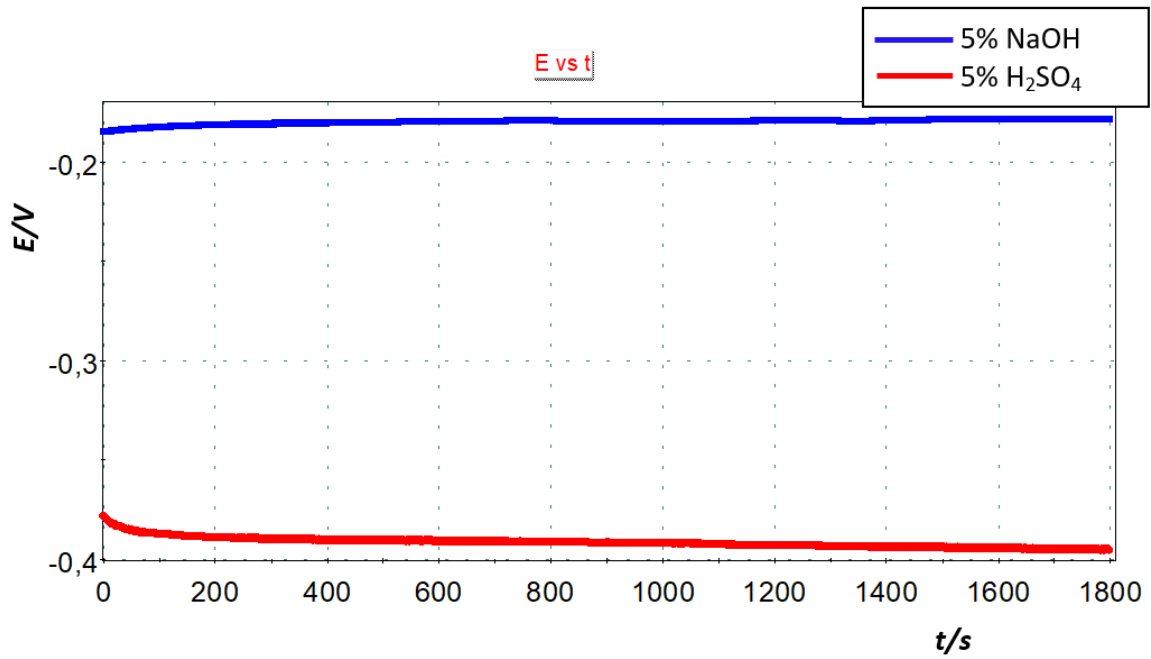
Figure 2. Time dependance of open circuit potential for X19NiCrMo4 steel in medium of 5% NaOH and 5% H_2SO_4

The result of electrochemical impedance spectroscopy is shown by Nyquist diagram before (Figure 3) and after electrical circuit modeling (Figure 4 and 5). Table 2 shows the obtained impedance parameters: electrolyte resistance R_{el}, oxide layer resistance R_{ox}, constant phase element of the two-layer Q_{dl}, measure of surface heterogeneity n and charge transfer resistance R_{ct}.

The obtained Nyquist EIS spectra show the dependence of the imaginary impedance on the real impedance, and their analyzes were performed using the model of the electrical circuit R(Q(R(QR))).
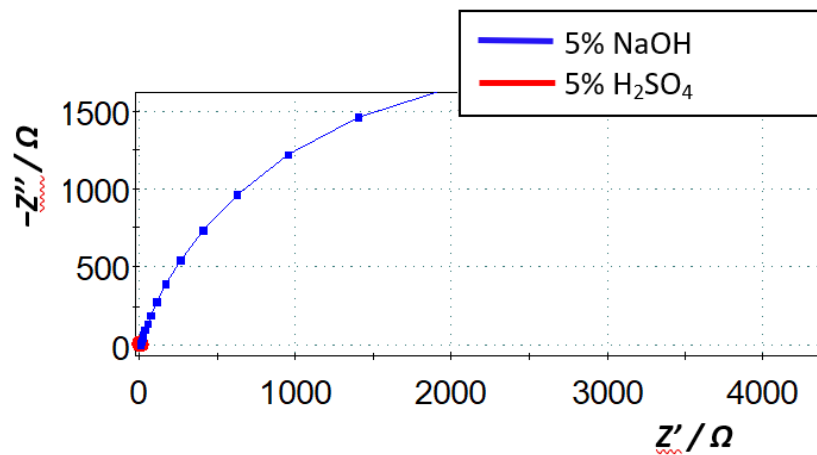

Figure 3. The comparative view of Nyquist's EIS diagrams obtained for X19NiCrMo4 steel in solution of 5% NaOH and 5% H_2SO_4
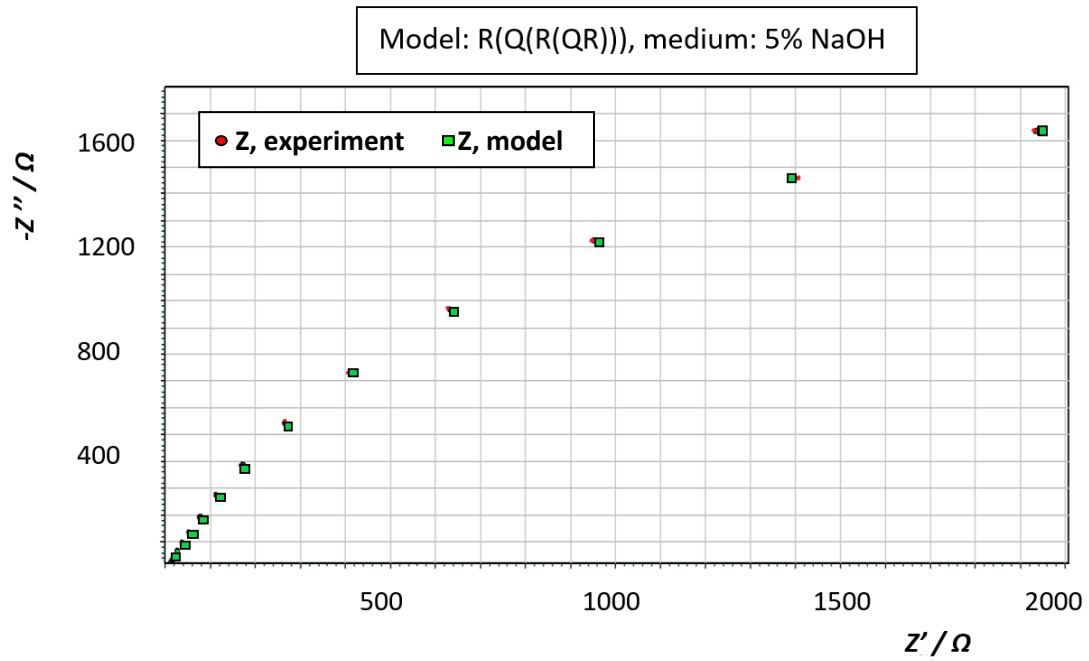
Model: R(Q(R(QR))), medium: 5% NaOH

Figure 4. The comparative view of Nyquist's EIS diagrams obtained for X19NiCrMo4 steel in solution of 5% NaOH
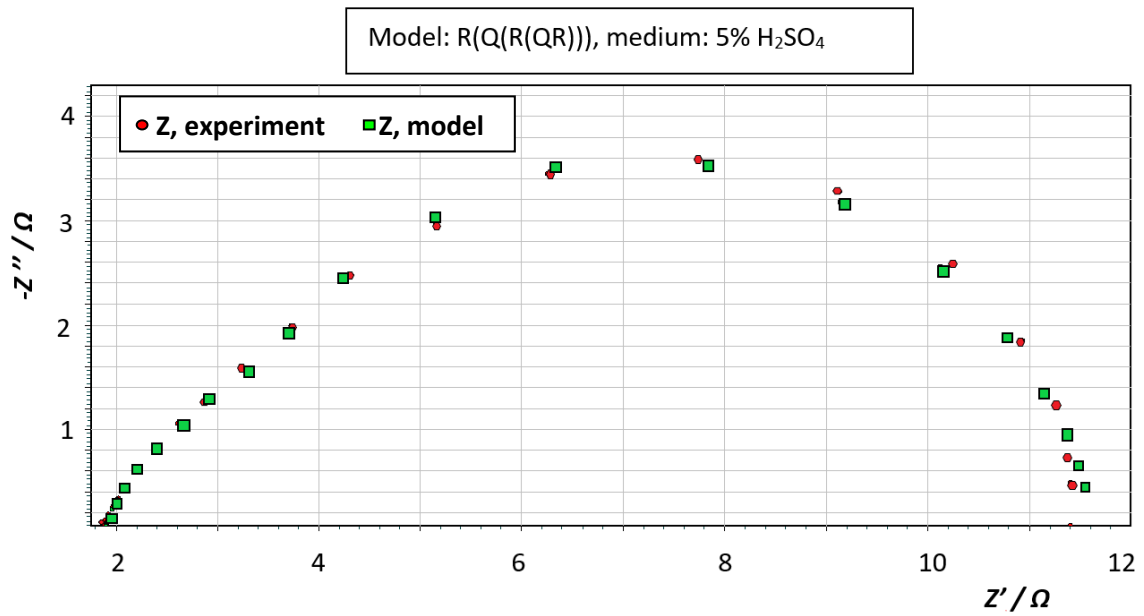
Model: R(Q(R(QR))), medium: 5% H_2SO_4

Figure 5. The comparative view of Nyquist's EIS diagrams obtained for X19NiCrMo4 steel in solution of 5% H_2SO_4

Table 2. Impedance parameters of tested X19NiCrMo4 steel

Medium	E_{corr} vs. SCE	R_{el}	$Q_{dl} \times 10^3$	n	R_{ox}	$Q_{dl} \times 10^3$	n	R_{ct}
	mV	Ωcm^2	$\Omega^1 s^n cm^{-2}$		Ωcm^2	$\Omega^1 s^n cm^{-2}$		$\Omega\ cm^2$
5% NaOH	-178	1.986	0.197	0.20	5.174	2.201	0.81	7793
5% H_2SO_4	-395	1.873	2.351	0.80	3.562	2.531	0.94	6.259

The Nyquist impedance representation of the sample in 5% H_2SO_4 solution is in the form of a semicircle which is characteristic of solid electrodes, and in 5% NaOH solution it is in the linear form. The obtained diagrams are characteristic for certain configurations of electrical equivalent circuits, and are ideally composed of semicircles and straight lines. The appearance of the equivalent circuit by which the observed system can be described depends on a number of factors: electrode type, electrolyte type and composition, potential, temperature, pH.

From the data in Table 2 it can be seen that the tested steel in 5% NaOH solution showed higher oxide resistance R_{ox} and charge transfer resistance R_{ct}. Namely, during the exposure of the sample in 5% NaOH solution, an oxide layer of greater thickness was formed on the sample surface, which slowed down the corrosion processes. In contrast, the obtained parameters for the sample in 5% H_2SO_4 solution indicate low values of charge transfer resistance. The acid with an extremely low pH value acts very aggressively, whereby the created oxide layer is quickly destroyed and allows further penetration of aggressive ions from the solution. Due to the dissolution of the sample, a more negative electrode potential was recorded in the acid.

The polarization curves of the tested sample of cementing steel in 5% NaOH solution and 5% solution H_2SO_4 are shown in Figure 6. Table 3 shows the values of corrosion parameters (corrosion potential E_{corr}, corrosion rate v_{corr}, anode slope b_a and cathode slope b_c).
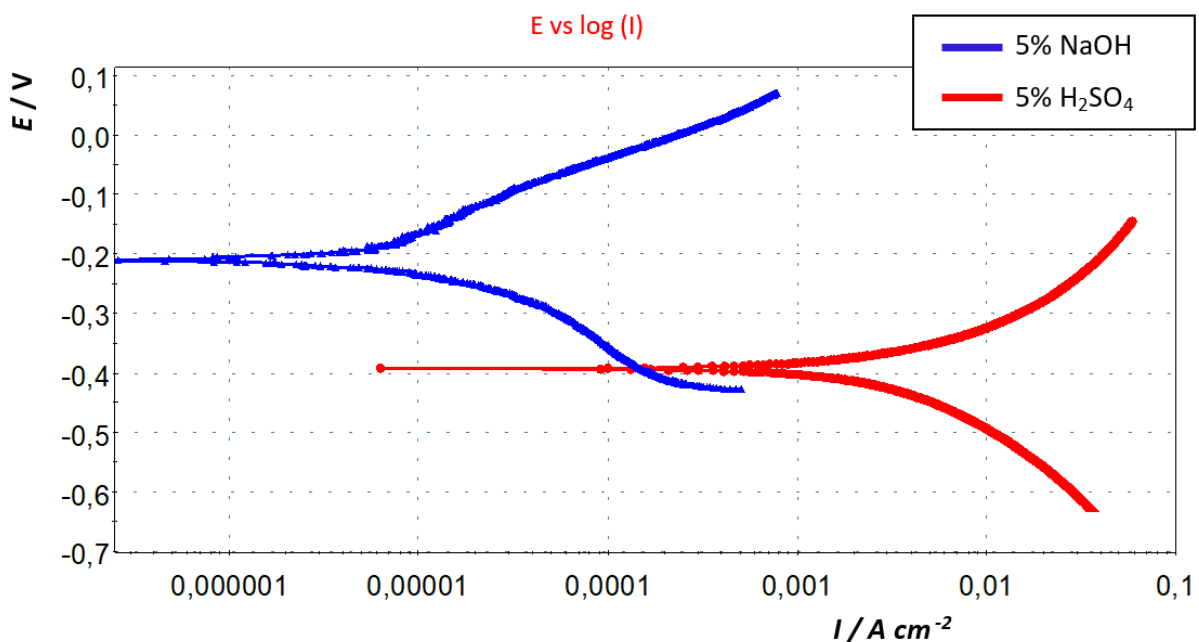

Figure 6. Polarization curves of tested X19NiCrMo4 steel in solution of 5% NaOH and 5% H_2SO_4

Table 3. Corrosion parameters of tested X19NiCrMo4 steel in solution of 5% NaOH and 5% H_2SO_4

Medium	E_{corr} vs. SCE	b_a	b_c	v_{corr}
	mV	mV dec^{-1}	mV dec^{-1}	mm god^{-1}
5% NaOH	-210.18	142.19	124.78	0.075
5% H_2SO_4	-392.56	227.79	317.14	73.02

The results obtained from the impedance and polarization measurments are in good agreement. A large difference was observed in the obtained values after testing the steel in the 5% NaOH and 5% H_2SO_4 solutions. The corrosion rate of steel in 5% H_2SO_4 is far higher than the corrosion rate in 5% NaOH. Also, the electrode potential is more negative, and the amounts of cathode and anode slope are higher than the results in the solution of 5% NaOH. These results lead to the conclusion that the cathode and anode iron dissolution reactions are more pronounced in the case of sample exposed in 5% H_2SO_4 solution.

For the purpose of analyzing the microstructure of the tested tool steel, the sample was observed using an optical microscope after etching in nital (Figure 7). The microstructure of the tested steel after electrochemical tests in solutions of 5% NaOH and 5% H_2SO_4 is shown in Figure 8.
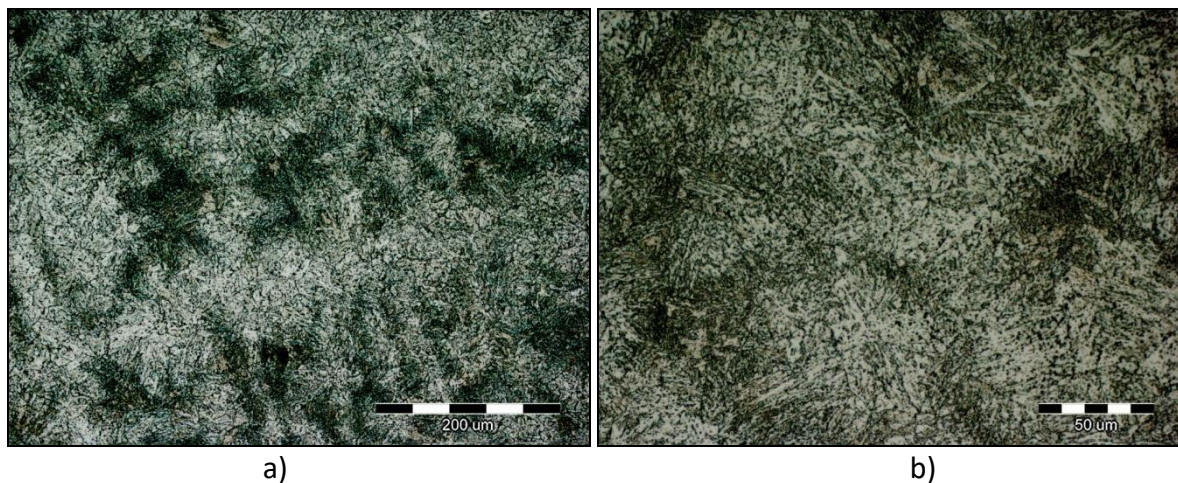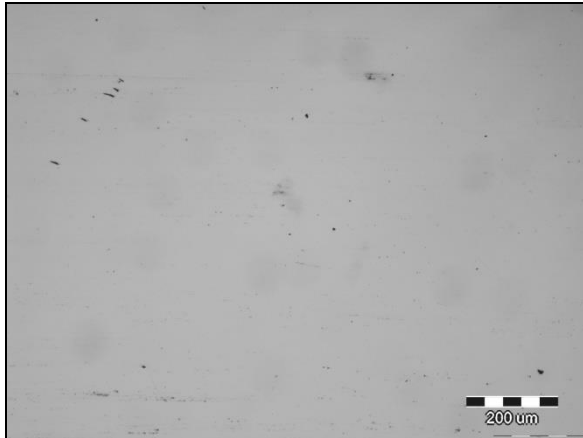

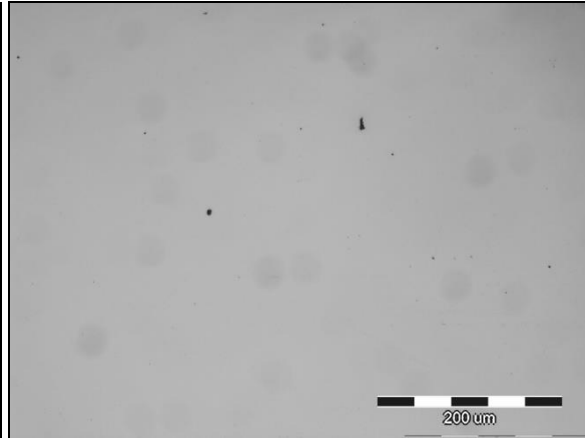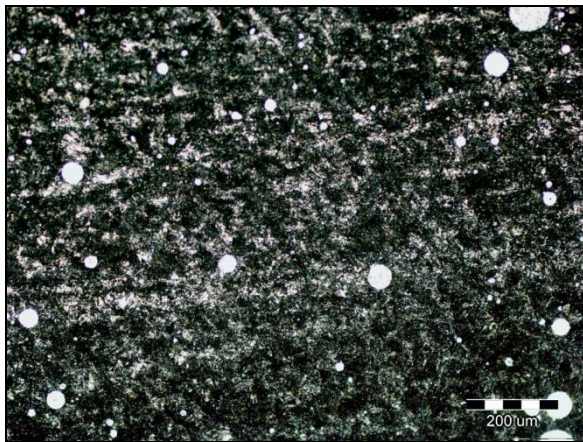a)   b)

Figure 7. Microstructure of X19NiCrMo4 steel after etching in nital:
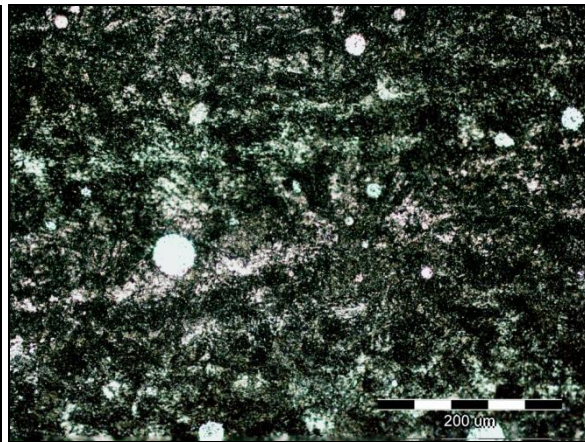a) magnification 200x and b) magnification 500x

a) 5% NaOH: magnification 100x

b) 5% NaOH: magnification 200x

c) 5% H_2SO_4: magnification 100x

d) 5% H_2SO_4: magnification 200x

Figure 8. Microstructure of X19NiCrMo4 steel in solution of 5% NaOH and 5% H_2SO_4

According to the analysis of the microstructure after etching in the nital, it can be seen that the cementing steel marked X19NiCrMo4 consists of a martensitic phase.

After electrochemical measurements in alkaline medium (5% NaOH) no changes were observed on the sample surface. The condition of the surface remained the same as before the electrochemical tests.

In the case of testing in an acid medium, the surface of the sample is completely covered by corrosion products. The corrosion in this case is of high intensity and occurred very quickly. The sample surface is completely corroded and parts of the martensite stand out with the separation of carbides. After the steel is immersed in the acid, the acid first dissolves the oxide layer that formed naturally on the steel, followed by a rapid attack on the metal base itself. The obtained results correspond to the registered higher corrosion rate and lower charge transfer resistance.

CONCLUSIONS

- By monitoring the changes in the open circuit potential E_{ocp}, data on the corrosion behavior of the tested sample in a medium of 5% NaOH and 5% H_2SO_4 were obtained. Extremely negative *OCP* values obtained for the sample in acid indicate instability and dissolution of the sample. Although negative *OCP* values were also observed in the case of sample immersed in the alkaline solution, it is assumed that in that case a thicker oxide layer was formed on the electrode surface in time. This prevented further penetration of ions from the solution and the development of corrosion on the electrode.

- The potentiodynamic polarization method showed that the corrosion rate of the tested sample after exposure to 5% H_2SO_4 was higher than in the case when the sample was exposed to 5% NaOH solution. Also, higher values for b_a and b_c were recorded after the sample was immersed in the acid. This means that in the case of steel in an acid medium, the reactions at the anode and cathode are more pronounced than in the case of steel immersed in alkaline media.

- The results obtained by the method of electrochemical impedance spectroscopy confirmed the higher corrosion resistance of the sample after testing in alkaline solution. The tested steel in 5% NaOH solution showed higher resistance of oxide layer R_{ox} and charge transfer resistance R_{ct}, which again indicates the formation of a thicker oxide layer on the sample surface. Unlike alkaline medium, the acid acted very aggressively on the tested steel. The passive layer on the sample surface was not compact enough which allow aggressive ions to penetrate from the solution.

- The consequences of the action of aggressive H^+-ions were established by metallographic analysis of the tested steel surface after corrosion in H_2SO_4 solution. Namely, aggressive H^+-ions contributed to the destruction of the passive layer on the surface of the material and thus deteriorated the martensitic microstructure of steel.

- From the above tests it can be concluded that the tested steel proved to be a bad material for use in operating conditions where it can come into contact with acid. The chemical composition of X19NiCrMo4 steel did not show satisfactory quality in acidic medium, despite a favorable combination of alloying elements. Further alloying can improve corrosion resistence of steel; for instance corrosion resistence of steel increase with increase in chromium content as the addition of chromium results in the formation of a passive oxide film.

- The performed tests can serve as a basis for finding inhibitors that might be suitable for preventing the development of corrosion on steels.

REFERENCES

[1] W. E. Bryson, Heat treatment, selection and application of tool steels, 2nd Edition, Hanser Publications, Cincinnati, 2013.

[2] J. Szumera, The tool steel guide, First edition, Industrial Press, Inc., New York, 2003.

[3] D. C. Silverman, R. B. Puyear, Effects of environmental variables on aqueous corrosion, ASM Handbook, Volume 13, USA, 1987, pp. 71-88.

[4] R. W. Revie, H. H. Uhlig, Corrosion and corrosion control: An introduction to corrosion science and engineering, Fourth edition, A John Wiley & Sons, INC., Publication, New Jersey, 2008.

[5] Z. Panossian, N. Lira de Almeida, R. M. Ferreira de Sousa, Gutemberg de Souza Pimenta, L. B. Schmidt Marques, Corrosion of carbon steel pipes and tanks by concentrated sulfuric acid: A review, Corrosion Science, 58(2012), 1-11.

[6] M. Ahmadi, S. H. Seyedin, Investigation of NaOH properties, production and sale mark in the world, Journal of Multidisciplinary Engineering Science and Technology (JMEST) ISSN: 2458-9403, 6(2019)10, 10809-10813.

[7] D. W. Shoesmith, Effects of metallurgical variables on aqueous corrosion, ASM Handbook, Volume 13, USA, 1987, pp. 89-98.

[8] Buehler® SumMet™, A Guide to Materials Preparation & Analysis, Fourth Edition, 2007, USA, Accessible on Internet:
http://www.trimid.rs/upload/documents/buhler/Buehler%20Summet.pdf,
(15.11.2020)

[9] S. Brajčinović, A. Begić Hadžipašić, J. Medved, S. Kožuh, Influence of medium on corrosion and microstructural properties of HTCS-130 tool steel for hot work, Proceedings of 18th International Foundrymen Conference, (N. Dolić, Z. Zovko Brodarac, A. Begić Hadžipašić, Edts.), University of Zagreb Faculty of Metallurgy, 15-17.05.2019, Sisak, Croatia, pp. 188-205.

[10] A. Lasia, Electrochemical impedance spectroscopy and its applications, Modern aspects of electrochemistry, (B. E. Conway, J. Bockris, and R. E. White, Edts.), Kluwer Academic/Plenum Publishers, 32(1999), New York, pp. 143-248.