PROCEEDINGS OF THE TECHNICAL UNIVERSITY OF SOFIA, ISSN: 2738-8549, VOL. 73, Special Issue, YEAR 2023

The Corrosion Behavior of Low-Alloy Steel 51CrV4

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Abstract — **The aim of this research was to analyze the corrosion behavior of low-alloy steel 51CrV4. To accomplish this, a series of electrochemical tests were conducted to estimate the corrosion rate of the steel samples. These tests were carried out in a 3.5% NaCl solution both before and after subjecting the steel to specific heat treatments, which included quenching, as well as quenching and tempering.**

Furthermore, an additional set of electrochemical tests was performed on 51CrV4 low-alloy steel samples that had previously undergone quenching and tempering process. These tests were designed to evaluate the corrosion rate under various environmental conditions, encompassing tap water, a 1% NaCl solution, a 3.5% NaCl solution, and a 5% NaCl solution. Additionally, a separate electrochemical test was conducted in a 3.5% NaCl solution, introducing two distinct inhibitors: glycerol and sodium thiosulfate pentahydrate.

From the experimental results, it can be concluded that samples immersed in solutions with a higher NaCl concentration exhibited a higher corrosion rate than those in solutions with a lower concentration. It can also be concluded that sodium thiosulfate pentahydrate served as an effective corrosion inhibitor. In contrast, glycerol proved to be an ineffective inhibitor and actually increased the corrosion rate.

Index Terms — **Corrosion, Corrosion rate, Electrochemical testing, Heat treatment, Inhibitors**

I. INTRODUCTION

51CrV4 is a low-alloy steel known for its excellent mechanical properties, especially in applications requiring high strength and toughness. This steel is mainly used for the production of various mechanical components and springs, as it can withstand high loads and maintains its mechanical properties even under stress.

Heat treatment plays a crucial role in improving the mechanical properties of 51CrV4 steel. The most common heat treatment processes for this steel include quenching and tempering [1]. Quenching is rapid cooling of a steel from a high (austenitization) temperature. In the case of 51CrV4, the austenitization temperature is about 850°C. Quenching results in increased hardness and strength, but low ductility. After quenching, a steel is tempered by reheating to a lower temperature (usually in the range of 400-600°C) followed by air cooling. Tempering helps to reduce the brittleness caused by rapid cooling while maintaining a desirable balance between hardness and toughness.

Although the main purpose of heat treatment is to change the mechanical properties, heat treatment can also change the corrosion properties of 51CrV4 steel. Appropriate heat treatment can improve its corrosion resistance [2].

Corrosion is a complex phenomenon driven by the natural tendency of substances to react with each other, especially when a metal is exposed to its environment. This process is influenced by a number of factors, which are divided into internal and external factors. Internal factors include material properties, while external factors include the properties of the environment. Microstructural constituents are the most important material parameters that can affect the corrosion resistance of quenched and tempered steels [2].

Electrochemical corrosion is a redox process that occurs on the surface of a metallic material when it is exposed to an electrolyte, a medium that can conduct electricity. This type of corrosion occurs due to potential differences between the cathodic and anodic sites on the metal surface immersed in the electrolyte.

The formation of a corrosion article is the result of two different processes: oxidation and reduction. Oxidation takes place at the anode, where the metal loses valence electrons. This process leads to an increase in the oxidation number of the metal as it undergoes chemical reactions with the environment. Reduction takes place at the cathode, where substances in the electrolyte absorb the electrons released during the oxidation process. This leads to a decrease in the oxidation number of the substances at the cathode.

In summary, this research focused on conducting electrochemical tests to evaluate the corrosion behavior of low-alloy 51CrV4 steel. It investigated the influence of microstructure, surrounding medium and inhibitors on the corrosion rate of the steel in a 3.5% NaCl solution and shed light on the factors affecting the susceptibility of the material to electrochemical corrosion.

II. EXPERIMENTAL INVESTIGATIONS

A. Material and Heat Treatment

The material subjected to this test is low-alloy 51CrV4 steel. In the normalized state, 51CrV4 steel has a ferrite-pearlite microstructure, as shown in Fig. 1. The proportion of pearlite (darker phase) in this microstructure is significantly higher than that of ferrite (lighter phase). The proportion of pearlite and ferrite was determined from a structural diagram and is as follows: 64% pearlite and 36% ferrite in the microstructure.

Received: 14.11.2023
Published: 22.12.2023
https://doi.org/10.47978/TUS.2023.73.04.002

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It can be seen from Fig. 1 that the microstructure of 51CrV4 steel is characterized by its fineness, which is due to the presence of vanadium in its chemical composition. It is known that vanadium contributes to the refinement of the microstructure of steel, resulting in smaller and more uniform grain sizes [3].

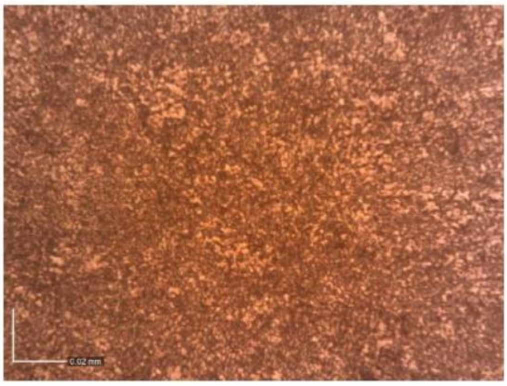


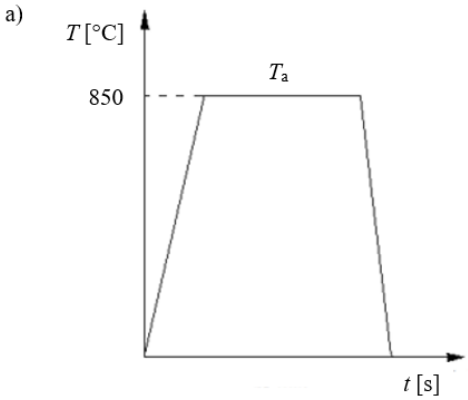
Fig. 1. Ferrite-pearlite microstructure of 51CrV4 steel [4]

Investigated samples were prepared by cutting ϕ16 steel bars of normalized 51CrV4 steel into smaller pieces measuring 4 mm in length. The chemical composition of 51CrV4 steel was determined using a glow discharge spectrometer LECO GDS 500 A (Table 1).

TABLE 1
THE MASS FRACTION OF CHEMICAL ELEMENTS

Chemical element	Mass fraction [%]
Carbon (C)	0.564
Silicon (Si)	0.299
Manganese (Mn)	0.865
Phosphorus (P)	0.0153
Sulfur (S)	0.0162
Nickel (Ni)	0.0381
Chromium (Cr)	1.15
Molybdenum (Mo)	0.0176
Copper (Cu)	0.0260
Aluminum (Al)	0.0306
Vanadium (V)	0.139
Iron (Fe)	96.8

The hardening processes applied in this research are shown in Fig. 2: quenching (Q) and quenching and tempering (QT); T_a is the austenitizing temperature and T_t is the tempering temperature.



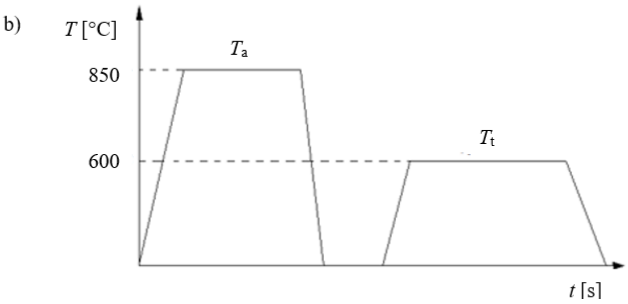


Fig. 2. Hardening processes: a) Q, b) QT

The values of the heat treatment parameters are listed in Table 2. The time of 15 min or 60 min is the time the samples are in the furnace.

TABLE 2
HEAT TREATMENT PARAMETERS

Heat treatment	Parameters
	Temperature / time /cooling medium
Quenching (Q)	850 °C / 15 min / oil
Quenching and tempering (QT)	Q: 850 °C / 15 min / oil T: 600 °C / 60 min / air

B. *Electrochemical investigation*

Prior to the electrochemical tests, the surfaces of the samples were prepared by grinding and polishing on sandpapers. First, the samples were grinded on Presi sandpaper of fineness P320, and then P600. Afterwards, the samples were degreased in ethanol.

The equipment for the electrochemical corrosion tests includes a computer with the special software PowerSuite, a potentiostat from the company Parrstat, and a five-necked test cell containing: a working electrode with an exposed area of 1 cm^2, a saturated calomel electrode (SCE) placed in a Luggin capillary as a reference electrode, and graphite counter electrodes.

The results of the electrochemical investigation were obtained in the form of a diagram with the curves of the stationary potential of the open circuit and Tafel curves (potentiodynamic polarization curves). Measurements of the open circuit potential, E_{OC}, were made as a function of time over a 1 h period. The potentiodynamic polarization was performed over a potential range of $E_{OC} \pm 250$ mV, starting with the most negative potential.

The corrosion rate was calculated from polarization curves, based on the corrosion current density, i_{corr}, known equivalent weight (EW=27,714 g), and density (ρ=7,85 g/cm^3) of 51CrV4 steel, according to the expression:

$$v_{corr} = \frac{0{,}0033 \times i_{corr} \times EW}{\rho} \text{ [mmpy]} \quad (1)$$

III. RESULTS AND DISCUSSION

A. *The influence of the microstructure on the corrosion behavior of 51CrV4 steel*

The electrochemical testing involved three distinct samples. One of them remained in its as-received normalized state without any heat treatment (N), while the other two underwent different heat treatments: quenching (Q) or quenching and tempering (QT). All three samples were immersed in a 3.5% NaCl solution, prepared by mixing 26.25 g of NaCl with 0.75 l of distilled water [5].

The potentiodynamic polarization curves, presented in a semi-logarithmic format, exhibit both cathodic and anodic branches, reflecting the electrochemical reactions within the system [1]. The anodic branch of the polarization curve describes the dissolution of iron in the NaCl solution and can be expressed using Eq. 2:

$$Fe \rightarrow Fe^{2+} + 2^{e-} \qquad (2)$$

The cathodic branch of the polarization curve describes the oxygen reduction reaction, which is given by Eq. 3:

$$½ O_2 + H_2O + 2^{e-} \rightarrow 2 OH^- \qquad (3)$$

Fig. 3 shows the obtained curves of the dependence of the open-circuit potential on time for three given samples. For all samples, the open circuit potential drops to more negative values. This drop is due to the development of corrosion processes, i.e. the active state of the surface of the samples. For the 51CrV4 steel sample, which is in the normalized state (blue curve), the curve shows relative signs of a stable trend only towards the end of the test, while the steel sample heat treated by quenching (green curve) and the steel sample quenched and tempered at 600 °C (black curve) show a stable trend after about 25 minutes and the slight drop in the curve continues until the end of the test.

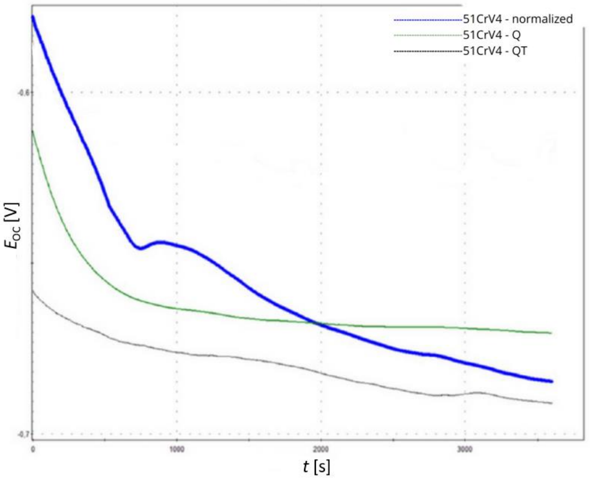


Fig. 3. The open circuit potential vs. time - the influence of the microstructure

The quenched steel sample shows more positive potential values towards the end of the test compared to the normalized sample, but also compared to the sample that was heat treated by quenching and tempering.

Fig. 4 shows the obtained potentiodynamic polarization curves, while Table 3 shows a comparison of the obtained results. The corrosion potential values are as expected, i.e. the corrosion potential is the most negative for normalized steel with a ferrite-pearlite microstructure, and the most positive for quenched sample with a martensite microstructure.

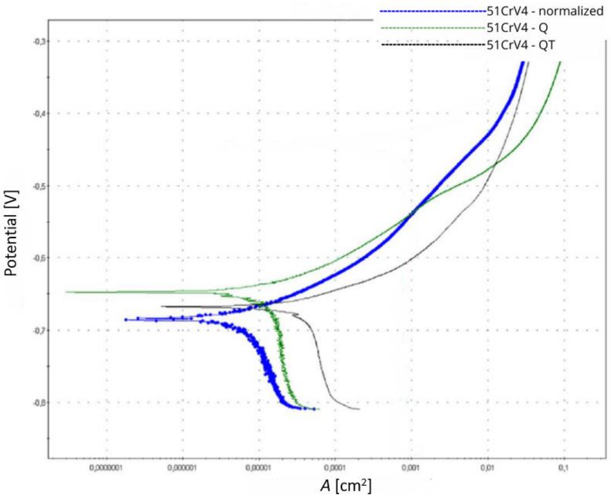


Fig. 4. Potentiodynamic polarization curves - the influence of the microstructure

TABLE 3
THE RESULTS OF ELECTROCHEMICAL TESTING (FIG. 4)

Obtained values	Sample 1 N	Sample 2 Q	Sample 3 QT
Corrosion potential E_{corr} [mV]	-690.59	-647.16	-675.79
Corrosion current density j_{corr} [μA/cm^2]	13.01	16.25	49.87
Corrosion rate v_{corr} [mmpy]	0.15	0.19	0.58

Expected values were obtained for some of the corrosion rates. The value of the corrosion rate of quenched steel is three times lower than the corrosion rate of quenched and tempered steel, because quenched steel has a martensite microstructure, while quenched and tempered steel contains carbides formed during tempering, which can lead to the appearance of microgalvanic articles. The corrosion rate of normalized steel is the lowest, which is unexpected.

B. The influence of the medium on the corrosion behavior of quenched and tempered 51CrV4 steel

Electrochemical tests included three quenched and tempered samples immersed in tap water, 1% NaCl solution, 3.5% NaCl solution, and 5% NaCl solution [6].

Fig. 5 shows the curves of the open circuit potential as a function of test time in each of the above media. The lowest values of the open circuit potential are shown by the sample immersed in tap water (blue curve). For this sample, the steepest drop is seen in the first 15 minutes of the measurement. After that, the trend stabilizes and the potential value is almost constant until the end of the measurement. The sample immersed in a 3.5% NaCl solution (black curve) shows the smallest drop in the open circuit potential, as its curve is the most positive. For the sample immersed in a 5% NaCl solution (brown curve), an uneven drop is observed, i.e., there is an uncontrolled rise and fall of the potential, which was not the case for the other three samples. Since the open circuit potential drops negatively for all samples, it can be concluded that corrosion takes place in all measurements, regardless of the type of medium and the percentage of NaCl concentration.

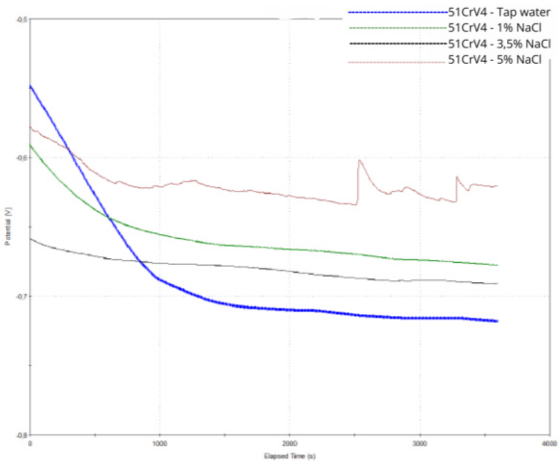


Fig. 5. The open circuit potential vs. time - the influence of the medium

For comparison purposes, the potentiodynamic polarization curves of all four measurements are shown in Fig. 6.

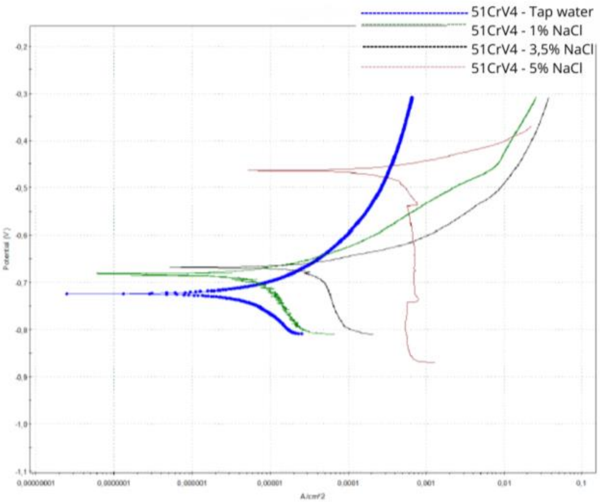


Fig. 6. Potentiodynamic polarization curves - the influence of the medium

The highest corrosion potential is present in the sample immersed in a 5% NaCl solution and the lowest in the sample immersed in tap water. The corrosion current and corrosion rate values are lowest when measured in tap water and continue to increase with increasing NaCl concentration.

TABLE 4
THE RESULTS OF ELECTROCHEMICAL TESTING (FIG. 6)

Obtained values	Sample 1 tap water	Sample 2 1% NaCl	Sample 3 3.5% NaCl	Sample 4 5% NaCl
E_{corr} [mV]	-729.46	-698.50	-657.79	-464.40
j_{corr} [μA/cm^2]	5.24	10.79	49.87	650.80
v_{corr} [mmpy]	0.06	0.13	0.58	7.56

C. The influence of inhibitors on the corrosion behavior of 51CrV4 steel in a 3.5% NaCl solution

In this experiment, samples of quenched and tempered steel were immersed in a 3.5% NaCl solution to which inhibitors were later added. Corrosion inhibitors are substances of inorganic or organic origin that are added to an aggressive medium and, at low concentrations, can greatly reduce the corrosion rate of alloys and metals to certain optimum levels. The inhibitors used in this test are neither toxic nor dangerous to handle, unlike most inhibitors which should be used with caution.

The tests were performed with two inhibitors: glycerol and sodium thiosulfate pentahydrate at concentrations of 4% by weight of inhibitor per 750 ml of distilled water [7]. Glycerol is an organic compound in the form of a clear, yellowish liquid with no odor and a sweet taste. Sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) is a chemical compound of sodium, sulfur and oxygen. This compound is in the form of crystals, is colorless and odorless, and is soluble in water.

Fig. 7 shows the open circuit potential curves as a function of time for all two tests with the application of the mentioned inhibitors compared to the measurements where no inhibitors were applied. The potential curve when Glycerol is used (green curve) initially shows an increased value, but drops very quickly and then remains approximately constant. It can also be seen that the open circuit potential curve of the sample tested in a solution containing sodium thiosulfate pentahydrate inhibitor (black curve) continues to rise after a certain time, in contrast to the sample tested in a 3.5% NaCl solution without inhibitor (blue curve), indicating surface passivation.

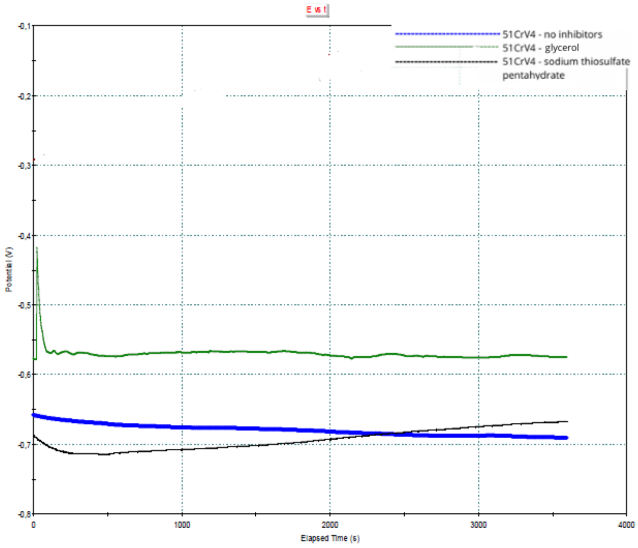


Fig. 7. The open circuit potential vs. time - the influence of inhibitors

Fig. 8 shows the potentiodynamic polarization curves of the above tests, while Table 5 lists the results of the electrochemical corrosion tests.

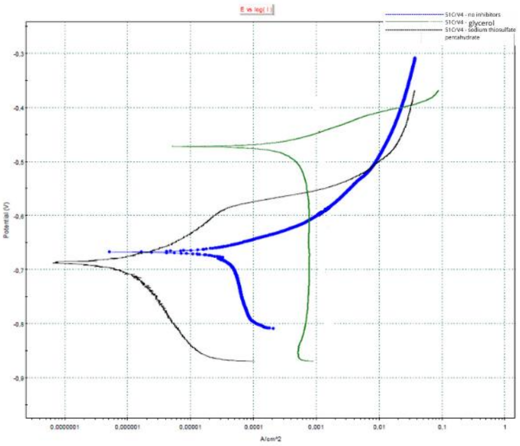


Fig. 8. Potentiodynamic polarization curves - the influence of inhibitors

TABLE 5
THE RESULTS OF ELECTROCHEMICAL TESTING (FIG. 8)

Inhibitor	E_{corr} [mV]	j_{corr} [μA/cm^2]	v_{corr} [mmpy]
no inhibtor	-675.787	49.9	0.579
glycerol	-472.519	703	8.16
sodium thiosulfate pentahydrat	-687.746	1.3	0.0151

Steel 51CrV4 immersed in a 3.5% NaCl solution is susceptible to corrosion and therefore has a lower durability, while the use of glycerol as an inhibitor is useless. Glycerol increases the corrosion rate by 14 times.

Sodium thiosulfate pentahydrate showed effective protection in a 3.5% NaCl solution, where it reduced the corrosion rate 38-fold. It can be concluded that steel 51CrV4 is stable in this solution.

IV. CONCLUSIONS

The corrosion behavior of low-alloy 51CrV4 steel was analyzed by electrochemical corrosion tests. The test was conducted in three parts: the influence of microstructure on corrosion behavior, the influence of medium on corrosion behavior, and the influence of inhibitors on corrosion behavior of low-alloy steel in 3.5% NaCl solution.

In studying the influence of microstructure on the corrosion behavior of 51CrV4 steel, it was found that quenched steel has the most positive corrosion potential, while normalized steel has the most negative potential. The corrosion rate of quenched steel is three times lower than the corrosion rate of steel quenched and tempered due to the homogeneous martensite microstructure, while carbides are formed during tempering, which may be the cause of the appearance of microgalvanic articles.

When investigating the influence of the medium on the corrosion behavior of the low-alloy steel 51CrV4, it was found that the concentration of NaCl solution is an important factor in the corrosion behavior of the steel. Samples immersed in solutions with higher concentration exhibited higher corrosion rate compared to samples with lower concentration.

The study of the influence of inhibitors on the corrosion behavior of the low-alloy steel 51CrV4 showed that sodium thiosulfate pentahydrate can be used as a corrosion inhibitor, while glycerol is not an inhibitor and even increases the corrosion rate.

REFERENCES

[1] A. Kubita, M. Buciora , W. Zieleckia, F. Stachowicz, “The impact of heat treatment and shot peening on the fatigue strength of 51CrV4 steel”, in *21st European Conference on Fracture ECF21*, Catania, Italy, 2016.

[2] S. Smokvina Hanza, L. Štic, L. Liverić, V. Špada, “Corrosion behaviour of tempered 42CrMo4 steel”, in *Materials and Technology 55* (2021) 3, 427-433. DOI: 10.17222/MIT.2021.014

[3] M. Uljar, *Microstructure characterization of low-alloy steel* (bachelor degree thesis), Rijeka, Croatia, 2021. (in Croatian)

[4] F. Mansfeld, U. Bertocci (Eds.), “*Electrochemical corrosion testing*“, Vol. 727, ASTM International, 1981.

[5] M. Uljar, *Effect of microstructure on the corrosion behavior of low-alloy steel* (master degree thesis), Rijeka, Croatia, 2023. (in Croatian)

[6] R. Ramljak, *Analysis of the Influence of Media on the Corrosion Behavior of Low-alloy Steel* (master degree thesis), Rijeka, Croatia, 2023. (in Croatian)

[7] H. Dundović, *Effect of Inhibitors on the Corrosion Behavior of Low-alloy Steel in a 3.5% NaCl solution* (master degree thesis), Rijeka, Croatia, 2023. (in Croatian)