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**INFLUENCE OF MEDIUM ON CORROSION AND MICROSTRUCTURAL  
PROPERTIES OF HTCS-130 TOOL STEEL FOR HOT WORK**

**Sandra Brajčinović<sup>1</sup>, Anita Begić Hadžipašić<sup>1\*</sup>, Jožef Medved<sup>2</sup>, Stjepan Kožuh<sup>1</sup>**

<sup>1</sup> University of Zagreb Faculty of Metallurgy, Sisak, Croatia

<sup>2</sup> University of Ljubljana Faculty of Natural Sciences and Engineering, Ljubljana, Slovenia

**Poster presentation**

**Original scientific paper**

**Abstract**

In this paper the corrosion resistance of tool steel for hot work in the industrial emulsion medium (Lenox Band-Ade semi-synthetic oil + water, in ratio 1:10), water and 3.5% NaCl medium was tested. By Tafel's extrapolation from polarization curves it was established that the tested tool steel showed extremely high corrosion rate in water and 3.5% NaCl medium in contrast to medium of Lenox Band-Ade emulsion. The double higher corrosion rate of tool steel is recorded in the chloride medium as opposed to that obtained in water, indicating that the tested steel is more corrosion resistant in water. The obtained results were confirmed by the method of electrochemical impedance spectroscopy. The sample of tool steel in the Lenox Band-Ade emulsion medium showed far greater value of charge transfer resistance  $R_{ct}$  than that obtained in the water medium and 3.5% NaCl, which means that the Lenox Band-Ade emulsion formed a thicker oxide layer that has the role of barrier in further penetration of aggressive ions from the solution.

The conducted SEM analysis after electrochemical measurements in 3.5% NaCl medium indicate the occurrence of pitting corrosion caused by breaking the passive surface of the material as a result of the action of aggressive ions from the solution. The EDS analysis of formed pits has been shown the increased oxygen content, but also the higher presence of sodium and chlorine, which accumulate in the pits, and come from the medium. Molybdenum and tungsten showed the highest presence in white deposits on the sample surface, which represent parts that did not completely cover with oxide layer, which is why the smallest oxygen content was recorded at these sites.

The obtained corrosion rate values in the water medium and the chloride medium indicate that the studied tool steel is poorly stable in water and chloride media, and because of that it can only be used in exceptional cases under conditions in which it will come into contact with water or chloride medium.

**Keywords:** *tool steel for hot work, pitting corrosion, corrosion rate, impedance, microstructure*

\*Corresponding author (e-mail address): [begic@simet.hr](mailto:begic@simet.hr)



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### INTRODUCTION

Tool steels for hot work are designed for tools, which are heated during operation to a temperature higher than 200 °C. In such conditions, this group of tool steels is exposed to sudden temperature changes, high mechanical and impact loads, so extremely good properties are required from tool steels for hot work. The most important property of tool steels for hot work is tempering resistance [1].

Tempering resistance involves the phenomena that may occur during exposure to elevated temperatures, such as hardness reduction, microstructural changes and thermal fatigue. Also high impact strength, good shape and dimension stability, high wear resistance, good tempering resistance, high resistance to thermal fatigue and high-temperature corrosion resistance [2,3] are also required from tool steels for hot work. These properties are achieved by alloying tool steels with alloying elements that create the carbide phases (W, Mo, Cr, V) and with low carbon content.

In addition, by alloying it is trying to achieve the better corrosion resistance of the material. The corrosion resistance is achieved by alloying with chromium, which besides that increases the fire resistance and resistance to hydrogen. Molybdenum in combination with chromium prevents pitting corrosion. Nickel does not produce carbides because it has a low carbon affinity, but it is used in the production of corrosion resistant steels, especially for steels designed to work at elevated temperatures [1,4]. Some properties may be deteriorated by alloying, which is why it is necessary to know relationship and the effect of alloying elements. In addition to the alloying elements, there are elements which are usually combined with carbon in carbides, but they can also be substituted in the iron crystal grid and create undesirable intermetallic compounds, i.e. phases with a structure different from the structure of the starting metals [5].

The tool steel structure depends on the condition of the alloying and on the condition of the thermal processing. The metal base with high carbon content is pearlite, but a share of ferrite may also be present. Also, isolated carbide phases (primary, secondary or tertiary) and eutectic compounds [6,7] are present. For this group of tool steels, it is characteristic that during operation they must be resistant to high temperatures. Namely, machine parts are subjected to continuous heating and cooling of the surface, which is in contact with heated metals. Therefore, tensile stress can occur in tool steels for hot work, resulting in cracks [8]. If the tool steels for hot work are sufficiently tough, cracks spread more slowly and do not penetrate into the depth of the material. Otherwise, because of insufficient toughness, cracks are spreading very rapidly, but their number is also growing intense, so a visible mesh of cracks can be detected on the surface of the tool. In special cases, the depth of the cracks can also cause the breakage of the material [9,10]. The cracking is affected by the chemical composition, microstructure (negative effect has separated ferrite or carbide phases of larger dimensions and sharp shapes), lower hardness values which also contribute to thermal fatigue, tool form and surface roughness, the existence of notches etc. [11].

Tool steels for hot work are mainly intended for making molds (forgings, moldings, die-castings) or for cutting (blades, saws, drills, milling machines etc.). In addition to the above-mentioned requirements expected from this group of steel, it is very important to know the



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influence of medium in which they are exposed. If used in various metal treatments, they are most often exposed to oil and water based emulsions. Also, it is of great importance to explore the additional capabilities of these materials, such as corrosion resistance testing in various media, to which these tool steels could be exposed in practice.

It is generally known that corrosion shortens the service life of the tools, which results in work stoppages and reduced production capacity. Electrochemical corrosion can occur in water, aqueous solutions of acids, alkalis, salts, in the soil, atmospheres, etc. Although the atmosphere is not an electrolyte, the condensate resulting from the metal surface as a result of air humidity leads to the formation of an electrolyte and thus the electrochemical corrosion process starts [12].

Due to the insight into the corrosion behavior of the HTCS-130 tool steel for hot work under the conditions of exposure to the marine atmosphere or in the conditions of contact with sea water, in this paper the influence of 3.5% NaCl on the corrosion and microstructure properties of the tested tool steel was studied and compared with obtained results in water and Lenox Band-Ade emulsion.

### MATERIALS AND METHODS

For testing the influence of medium and microstructure on the corrosion resistance of tool steel, a sample of HTCS-130 tool steel for hot work was used, whose chemical composition is shown in Table 1.

Table 1. Chemical composition of tested HTCS-130 tool steel for hot work (mas. %)

C	S	Si	Cr	Ni	V	W	Co	Al	Fe
0.31	0.001	0.07	0.1	0.04	0.01	1.9	0.01	0.012	rest
Cu	Mn	Mo	P	Sn	Ti	Nb	B	N	
0.04	0.08	3.2	0.007	0.005	0.01	0.01	0.001	0.001	

Tool steel HTCS-130 contains low carbon content and tungsten (W) and molybdenum (Mo) are added as alloying elements for purpose of producing the carbides, which favorably affect the properties of tool steels. Tungsten and molybdenum are classified into elements that are the strong carbide makers. Tungsten creates carbides that are resistant to wear and allows the increase of yield strength and tensile strength. Molybdenum also affects the increase of yield strength, tensile strength and creep limit, increases the hardenability and strength of steel, creates carbides and increases the wear resistance of steel [13,14].

#### *Electrochemical testings ( $E_{corr}$ , 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's extrapolation method were used. For these measurements, a three-electrode glass cell was



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used with a working electrode (with surface of  $0.5 \text{ cm}^2$ ), a counter electrode and a reference electrode along with the potentiometer and a computer to measure and record the data. The working electrode represents a test sample of tool steel which is immersed in the working medium. The counter electrode is a platinum electrode, which represents a conductor that closes the electric circuit. The reference electrode is an electrode of known potential and does not participate in the electric circuit, but it is used to measure the potential of the working electrode [15,16]. In laboratory conditions as a reference electrode mainly a saturated calomel electrode is used, with a standard electrode potential of  $+0,242 \text{ V}$  with respect to a hydrogen electrode. Potential stabilization at open circuit  $E_{ocp}$  was performed at room temperature ( $19 \pm 2$ ) ° C using computer-controlled potentiostat/galvanostat (Parstat 2273). As a working medium in electrochemical experiments, water, 3.5% NaCl medium and industrial emulsion (Lenox Band-Ade semi-synthetic oil + water, in ratio 1:10) were used for simulating working conditions in practice. The measured pH for water was 6.7, and for 3.5% NaCl pH was 6.75. For electrochemical testings, the tool steel sample is cut and pressed in conductive mass by device for hot pressing (SimpliMet® 1000). Before each series of electrochemical measurements the sample was prepared by machine grinding (gradations No. 240, 400, 600 and 800) and polishing ( $\text{Al}_2\text{O}_3$  suspension in water) on the automatic grinding and polishing machine (Bühler) and then washed in distilled water and degreased in ethanol [15,16].

### *Determination of corrosion potential $E_{corr}$*

For the tool steel sample, the time corrosion dependence of the corrosion potential was first tested. Prior to the polarization measurement, the metal electrolyte system should be stabilized. The corrosion potential or the open circuit potential is determined in such a way that the current circuit between the working electrode and the counter electrode is kept open and the potential difference between the working electrode and the counter electrode is measured over a period of 1800 seconds. After a certain time, an approximate stationary state at certain potential value is established. Along with the observation of time changes of the stationary potential of the open circuit  $E_{ocp}$ , data on the corrosion behavior of the sample in the tested medium are obtained [16].

### *Determination of corrosion parameters by the method of electrochemical impedance spectroscopy (EIS)*

Electrochemical impedance spectroscopy is a method based on the application of alternating current by supplying the electrode with alternating potential of low amplitude (5 mV) and wide range of frequencies (100 kHz - 10 mHz). As the response, the amplitude and the phase shift of the alternating current of the same frequency are followed. The impedance parameters were analyzed by ZSIMPWin 3.21 software using the appropriate electric circuit models [15]. The obtained data are presented graphically in different shapes, and the most commonly used display of the EIS results is Nyquist's diagram.



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The Nyquist's view of the impedance spectrum represents the dependence of the imaginary impedance component  $Z_{imag}$  ( $Z''$ ), relative to the real component  $Z_{real}$  ( $Z'$ ), for each frequency, and consists of a capacitive and inductive loop. By analysis of results the following values of parameters are obtained: the electrolyte resistance  $R_{el}$ , a constant phase element of double-layer  $Q_{dl}$ , measure of the surface heterogeneity  $n$  and charge transfer resistance  $R_{ct}$  [16].

### *Detremination of corrosion parameters by the method of Tafel's extrapolation*

Tafel's extrapolation method is performed by means of potentiodynamic polarization in the potential range of -250 mV to +250 mV vs  $E_{corr}$ , with the rate of potential change of 1 mV/s, and the corrosion parameters are determined using the software application PowerCorrTM according to Tafel's extrapolation method and the Faraday's law. The electrode is polarized to a certain potential, and then the anode and cathode curves are recorded. By extrapolating the anode and cathode Tafel's linear section of the curves, the values of corrosion current density  $I_{corr}$  and corrosion potential  $E_{corr}$  are determined. This method provides corrosion parameters (corrosion potential  $E_{corr}$ , corrosion rate  $v_{corr}$ , anode slope  $b_a$  and cathode slope  $b_c$ ) that give insight into the corrosion behavior of the material in the tested medium [17].

### *Metallographic analysis*

For the purposes of metallographic analysis, the HTCS-130 tool steel sample was prepared by pressing into the conductive mass with a hot pressing device (SimpliMet® 1000). The sample was then grinded by waterproof abrasive paper gradation No. 240, 400, 600 and 800 and polished ( $Al_2O_3$  suspension in water) on the automatic grinding and polishing machine (Bühler), after which it was washed in distilled water and degreased in ethanol. The thus prepared sample was etched by 3% Nital solution (97 ml of ethyl alcohol and 3 ml of nitric acid) to highlight the microstructure.

The sample was observed on an optical microscope with a digital camera (Olympus GX 51) and the Automatic Image Processing System (AnalySIS® Materials Research Lab), followed by a scanning electron microscope (Tescan Vega LSH (TS 5130 LS)) after etching in Nital solution and after corrosion in the investigated media [15,16]. Also, energy dispersion spectroscopy (EDS) was carried out to determine the chemical composition.

## RESULTS AND DISCUSSION

After measuring the open circuit potential  $E_{ocp}$ , electrochemical impedance spectroscopy at the value of open circuit potential was performed. The time dependences of open circuit potential for the tested tool steel in different media are shown in Figure 1, and Figure 2 shows a comparative view of Nyquist's EIS diagrams obtained for tested tool steel in various media.



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The modeling of the obtained EIS diagrams is derived by the model of the equivalent electric circuit  $R(Q(R(QR)))$ . The simulated curves were well matched with experimental curves, and the registered deviation was of the order of  $10^{-4}$ . By modeling EIS diagrams the following impedance parameters were obtained: electrolyte resistance  $R_{el}$ , the resistance of the oxide layer  $R_{ox}$ , a constant phase element of double-layer  $Q_{dl}$ , measure of the surface heterogeneity  $n$  and charge transfer resistance  $R_{ct}$  (Table 2).

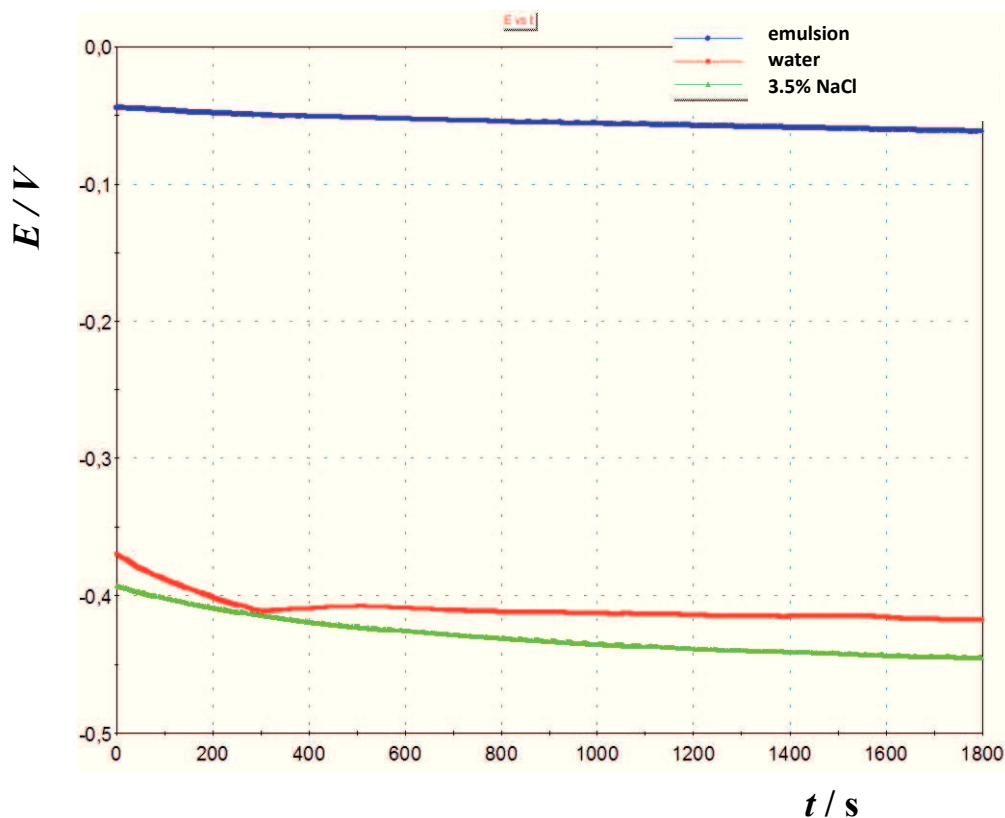


Figure 1. Time dependance of open circuit potential for HCTS-130 tool steel in medium of Lenox Band-Ade emulsion, water and 3.5% NaCl



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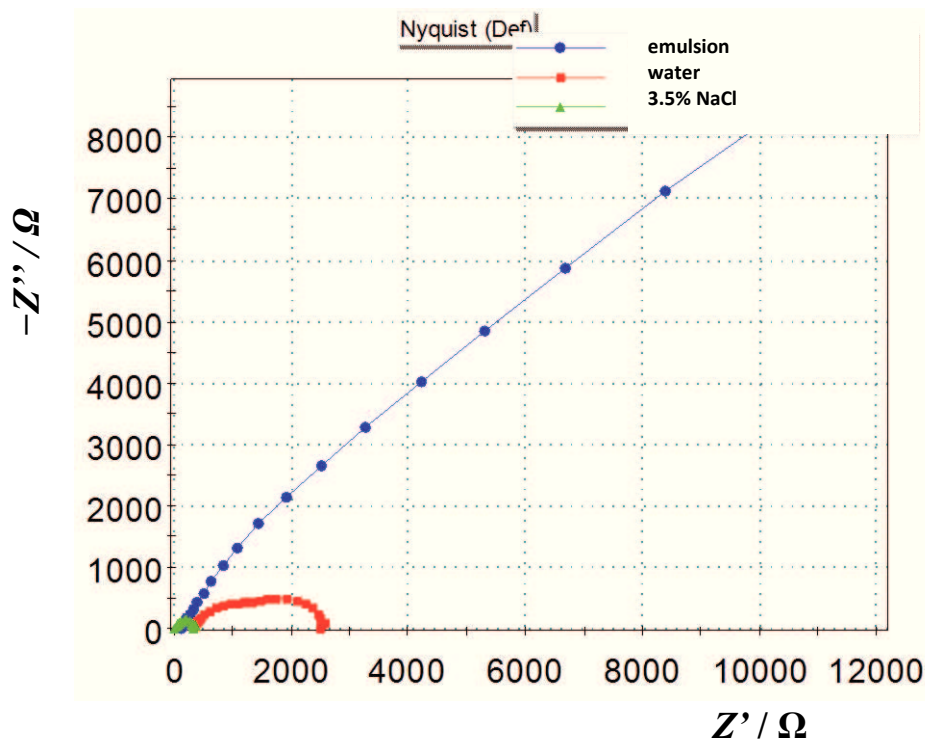


Figure 2. The comparative view of Nyquist's EIS diagrams obtained for HCTS-130 tool steel in medium of Lenox Band-Ade emulsion, water and 3.5% NaCl

Table 2. Impedance parameters of tested HTCS-130 tool steel for hot work

Medium	$E_{corr}$ vs. SCE	$R_{el}$	$Q_{dl} \times 10^6$	$n$	$R_{ox}$	$Q_{dl} \times 10^6$	$n$	$R_{ct}$
	mV	$\Omega \text{cm}^2$	$\Omega^1 \text{s}^n \text{cm}^{-2}$		$\Omega \text{cm}^2$	$\Omega^1 \text{s}^n \text{cm}^{-2}$		$\Omega \text{cm}^2$
Lenox Band-Ade emulsion	-61.6	129.4	197.1	0.70	4953.0	185.9	0.40	327000.0
Water	-417.0	343.2	35.4	0.73	1172.0	400.1	0.79	1067.0
3.5% NaCl	-445.0	8.8	1028.0	0.75	20.1	1244.0	0.79	351.1

From Figure 1 it is apparent that the sample tested in the selected media (Lenox Band-Ade emulsion, water, 3.5% NaCl) rapidly achieves its stationary potential, i.e. open circuit potential. In water and medium of 3.5% NaCl, the potentials are shifted to negative values indicating the presence of corrosion or instability of the electrode, so that the sample dissolves. In the Lenox Band-Ade emulsion medium, the potential is shifted to positive values, meaning the electrode is stable. For the stability of the electrodes in the emulsion, the inhibitor contained in the emulsion is partly responsible, because its task is to slow down the corrosion process.



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From Figure 2 it can be seen that Nyquist's impedance display in the water medium and 3.5% NaCl are actually depression semicircles with a center above the real axis, which is characteristic for solid electrodes. In this respect, the charge transfer resistance  $R_{ct}$  and the double-layer capacity  $C_{dl}$  are connected parallel in the passive electrode system. The impedance measurements result in a deviation of the mentioned double-layer capacity and instead it a surface-constant phase element of the double-layer  $Q_{dl}$  introduces, which represents a combination of surface roughness properties and inhomogeneities of metal electrodes [15,16].

From the data in Table 2, it is apparent that the tool steel in the Lenox Band-Ade emulsion showed a much higher oxide layer resistance  $R_{ox}$  and the charge transfer resistance  $R_{ct}$  than that in the water medium and 3.5% NaCl. The reason is that in the Lenox Band-Ade emulsion a thicker oxide layer formed on tested sample, which has a protective role, and acts as a barrier to further penetration of the aggressive ions from the solution.

Lower values of charge transfer resistance in the water and 3.5% NaCl indicate that the surface of the formed oxide layer is thinner, and cannot prevent the penetration of aggressive ions from the solution, so the consequence of this is increase in the corrosion rate. Furthermore, from Table 2, it can be seen that the highest value of the surface constant phase element of the double layer  $Q_{dl}$  is recorded on the tool steel in the medium of 3.5% NaCl, indicating that the resulting passive layer growing on the surface of the tested tool steel is not enough compact in the chloride medium, due to which the capacity of the intermediate layer metal/oxide layer or inside the passive layer increases [15,16].

The resulting passive layer on the studied tool steel is three times thinner in the chloride medium in comparison with the water medium. The above facts can be explained by the fact that dissolved oxygen and hydrogen cations play an important role in aqueous electrolytes. If the water contains enough  $O_2$ ,  $Fe^{2+}$  can be oxidized to  $Fe^{3+}$ , before  $Fe^{2+}$  ions diffuse from the metal surface to the solution. Therefore, a layer of  $Fe(OH)_3$  is formed on the surface. However, if sufficient amount of chloride ions entering the formed layer is present, the corrosion rate continues to increase [18].

Results obtained by electrochemical impedance spectroscopy correspond to the parameters resulting from the Tafel's extrapolation method. Potentiodynamic polarization in the range of potentials from -250 mV to +250 mV vs.  $E_{corr}$  was performed for the determination of corrosion parameters such as corrosion potential  $E_{corr}$ , corrosion rate  $v_{corr}$ , anode slope  $b_a$  and cathode slope  $b_c$ . The polarization curves of the tested tool steel sample in all three tested media are shown in Figure 3, and the obtained corrosion parameters are listed in Table 3.

From Figure 3 it can be seen that as the polarization curve is shifted to the left, the corrosion rate density and thus the corrosion rate will be smaller. Table 3 shows a very small value of corrosion rate registered for tool steel in the Lenox Band-Ade emulsion medium, while in the water and 3.5% NaCl medium a much higher corrosion rate was recorded.





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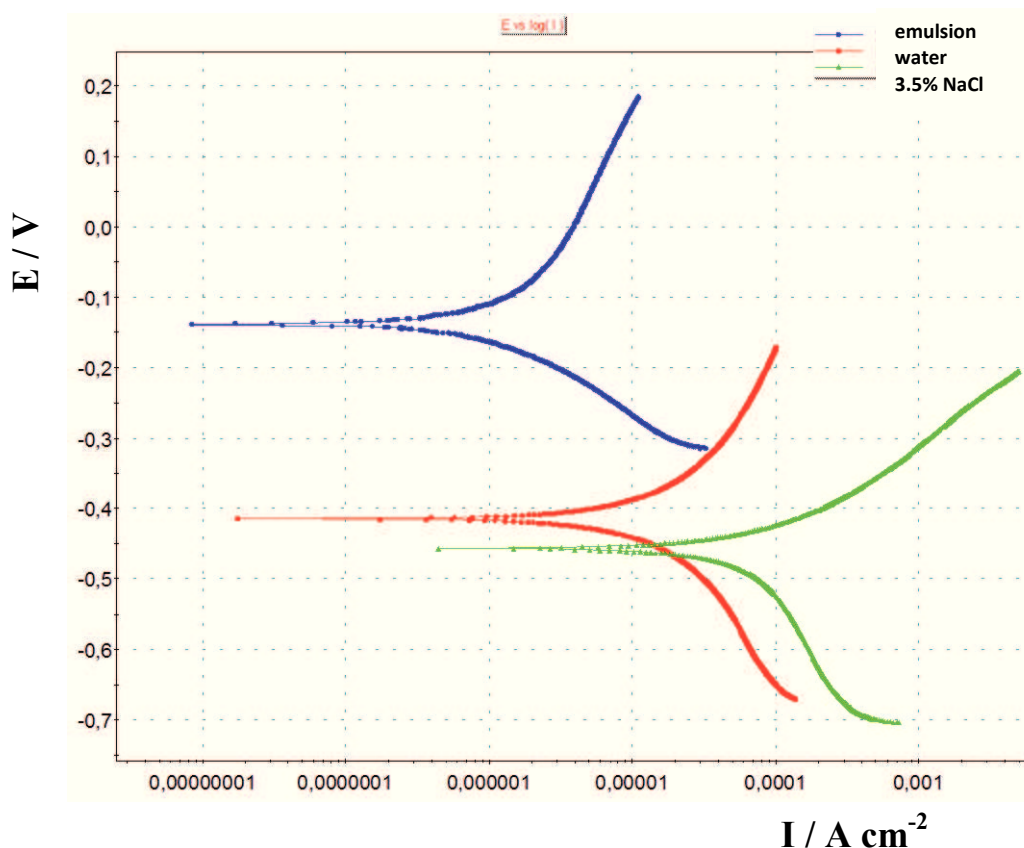


Figure 3. Polarization curves of tested tool steel obtained in medium of Lenox Band-Ade emulsion, water and 3.5% NaCl

Table 3. Corrosion parameters of tested tool steel in medium of Lenox Band-Ade emulsion, water and 3.5% NaCl

Medium	$E_{corr}$ vs. SCE	$b_a$	$b_c$	$v_{corr}$
	mV	mV dec <sup>-1</sup>	mV dec <sup>-1</sup>	mm god <sup>-1</sup>
Lenox Band-Ade emulsion	-138.8	441.2	171.7	0.05
Water	-414.4	664.0	718.0	1.28
3.5% NaCl	-456.2	154.1	629.4	2.79

However, it is important to emphasize that corrosion rate of tested tool steel is more than double higher in the chloride medium, compared to those registered in the water, which points to the fact that investigated tool steel is more corrosion resistant in water, although the pH value for both solutions is approximately the same. It is to be expected, since chloride ions are very aggressive and selectively etches the surface of the material. The Lenox Band-Ade emulsion has the role of cooling liquid in the processing of materials and its primary function is to extend the working life of the tool and reduce the wear of the machine parts, so the obtained corrosion rate was expected. As for the anode and cathode slope, a higher



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value of the anode slope has been obtained in the emulsion medium, indicating that the metal dissolution reaction is more pronounced in this medium. However, since the corrosion potential of the tested tool steel in the emulsion media is shifted to more positive values, this means that the metal dissolution reaction is of very low intensity, which also resulted in less corrosion rates. In water media and chloride media, cathode reactions are more pronounced, as evidenced by the greater number of cathode slopes compared to the anode slope. On the other hand, the corrosion potential of tool steel in water medium and chloride media has been shifted to more negative values, which means that corrosion reaction and dissolution of the tested sample occur.

Based on the obtained values of corrosion rate between 1 and 10 mm/year it can be concluded that the tested tool steel is poorly stable in water and chloride medium, which can be used only in exceptional cases in conditions in which it will come into contact with water or chloride medium [12].

The cause of this corrosion behavior was also studied in the microstructure of the tested tool steel, obtained by etching in Nital (Figure 4).

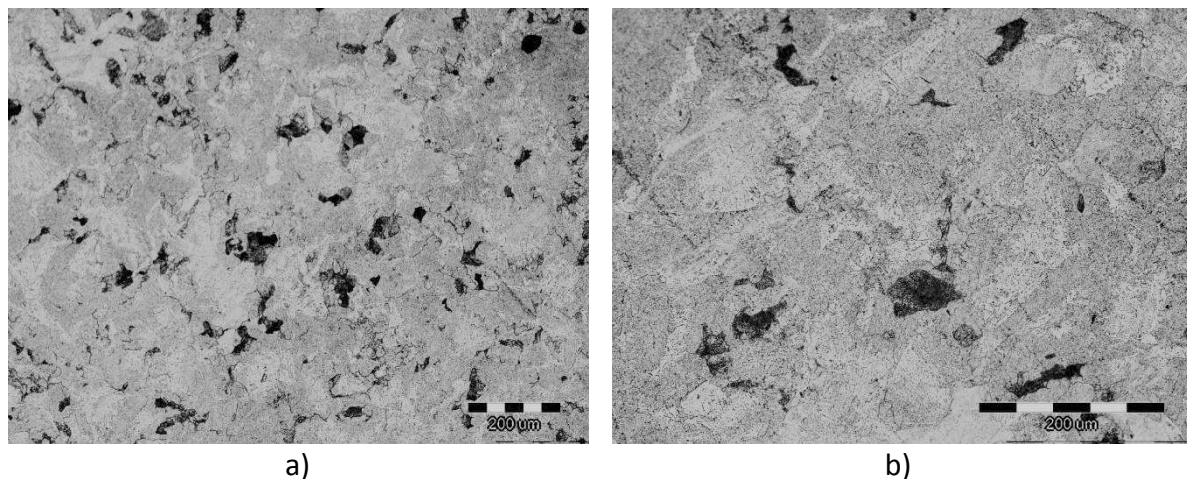


Figure 4. Microstructure of HTCS-130 tool steel for hot work after etching in Nital:  
a) magnification 100x and b) magnification 200x

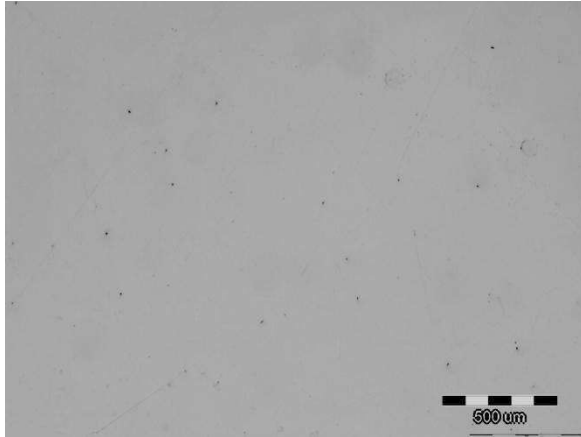
Figure 4 shows that the studied tool steel has a ferrite-pearlite structure. The darker parts of the picture represent pearlite and lighter ferrite. Given the carbon content in the chemical composition, the studied tool steel belongs to the group of hypoeutectoid steel because it contains less than 0.8% C [1]. According to the chemical composition of the tested steel, it can be seen that this is a high quality steel, because the proportion of sulfur and phosphorus is low. Therefore, the surface of the examined tool steel observed "on white" was very pure, with no registered inclusions. For the purpose of observing the microstructural changes of the examined tool steel, the sample was observed using an optical microscope before and after exposure to various media (Figure 5).



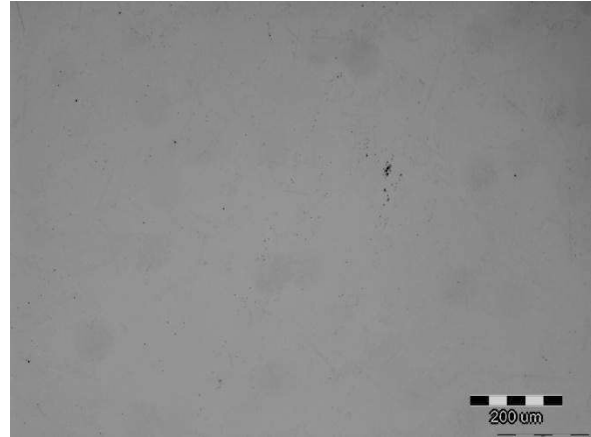
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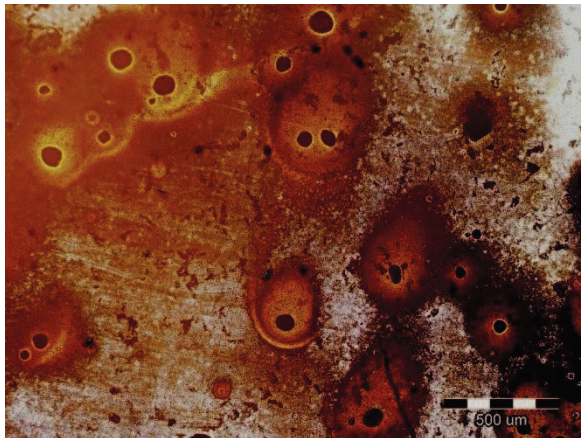
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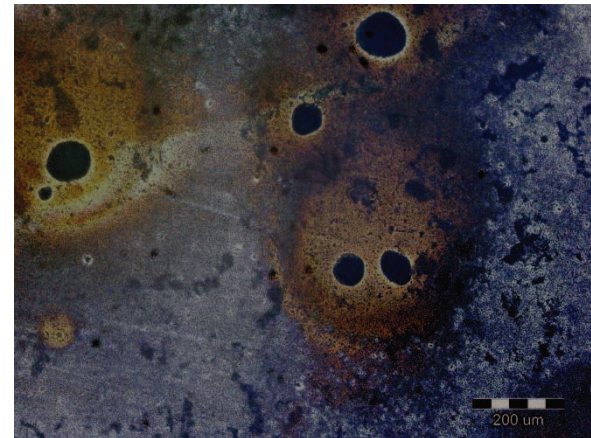
a) emulsion: magnification 50x



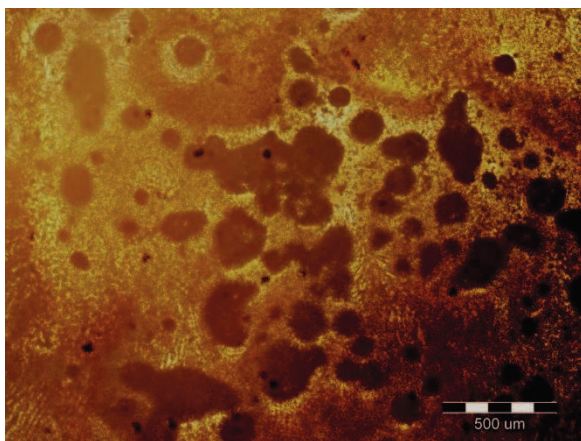
b) emulsion: magnification 100x



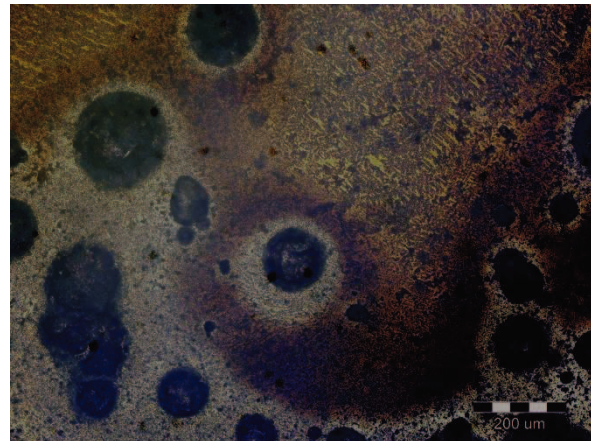
c) water: magnification 50x



d) water: magnification 100x



e) 3.5% NaCl: magnification 50x



f) 3.5% NaCl: magnification 100x

Figure 5. Microstructure of HTCS-130 tool steel for hot work in medium of Lenox Band-Ade emulsion, water and 3.5% NaCl



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Figure 5 shows that the microstructure of the HTCS-130 tool steel after electrochemical testing in the Lenox Band-Ade emulsion medium remained unchanged. However, in water and 3.5% NaCl, corrosion products were deposited on the surface of the sample, which means that the mentioned media strongly attacked the metal base.

Namely, the corrosion products do not have a protective role in the corrosion process, which can be confirmed by results obtained after electrochemical measurements. It can be concluded that local corrosion takes place, i.e. pitting corrosion, because the occurred holes (pits) are characteristic for pitting corrosion. Generally, the pitting corrosion caused by the existence of large cathode and small anode surfaces, which is why the severity of attack on the anode is large. The potential difference can be caused by mechanical damage, thin coating oxide, acidic media, and corrosion due to salt, holes or cracks [18,19]. In a highly aggressive medium such as 3.5% NaCl, this kind of corrosion occurs at the destruction of the passive layer on the metal surface in the middle of the chloride action. Chloride accumulates in the destroyed pits, which encourages deeper material destruction.

Because of the aggressiveness of chloride ions, from Figure 5 it is apparent that the holes are thicker and larger on the surface of the tested sample, than in the case of water media. Therefore, by combining different alloying elements in tool steels, the aim is to achieve better corrosion resistance. Nickel increases corrosion resistance, and molybdenum with chromium increases the resistance to the occurrence of pitting corrosion. However, the low chromium and nickel content in the investigated tool steel points to the fact that insufficient corrosion resistance is ensured in the tested media.

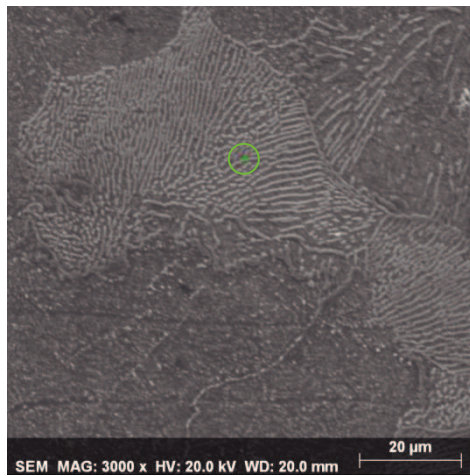
Results of testing the surface condition of the HTCS-130 tool steel conducted by scanning electron microscopy after etching in Nital are shown in Figure 6, and after the electrochemical measurements in a medium of 3.5% NaCl are shown in Figure 7.



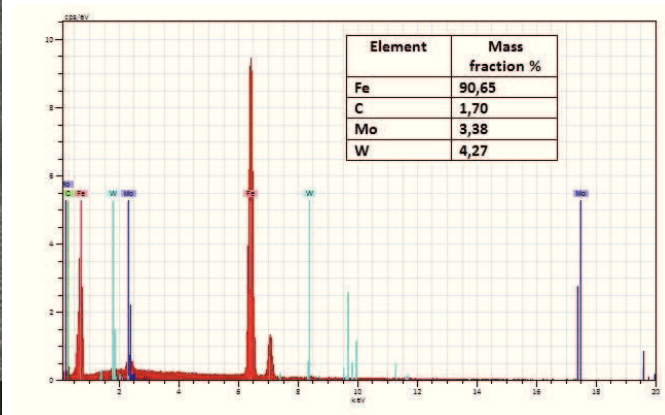
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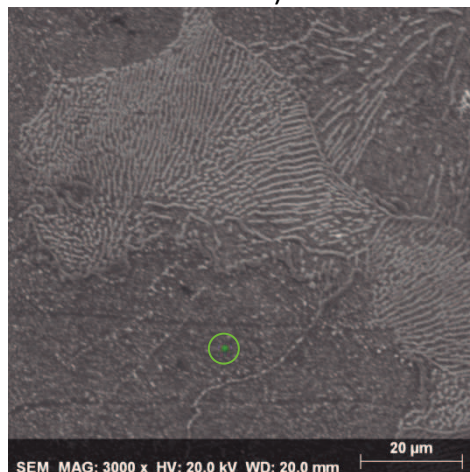
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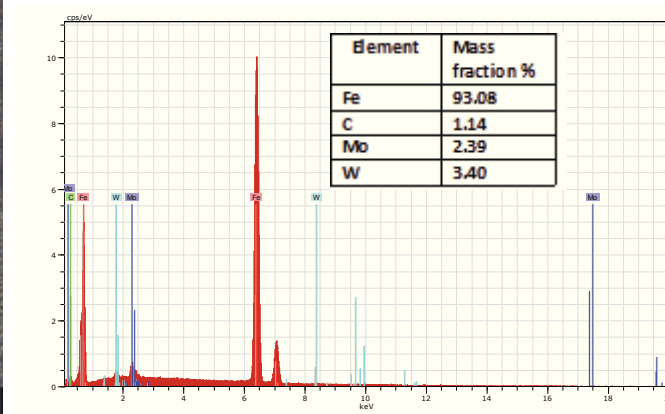
a)



b)



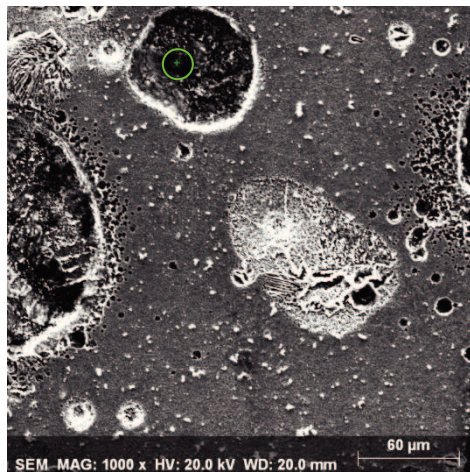
c)



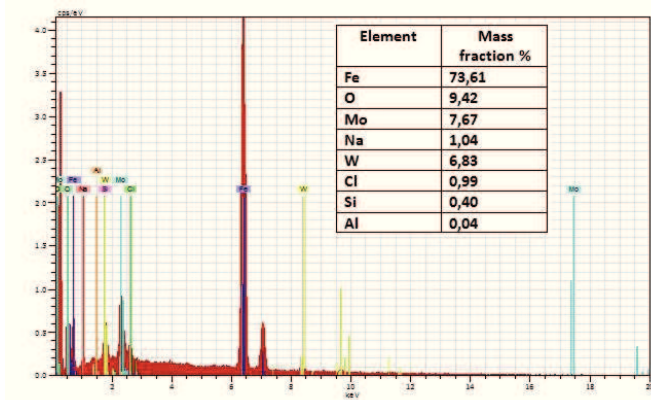
d)

Figure 6. a) c) SEM micrographs of HTCS-130 tool steel surface after etching in Nital (magnification 3000x) and b) d) EDS analyzes

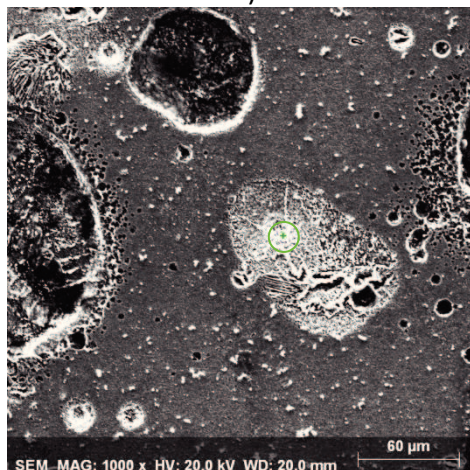
SEM micrographs of the sample after etching in Nital showed the presence of a ferrite-pearlite phase (Figure 6). Pearlite structure is composed of alternately stacked white or matrix base ferrite and cementite thin tiles. The results of the EDS analysis (Figure 6b) indicate the increased content of molybdenum and tungsten, i.e. the presence of their carbides. Namely, molybdenum and tungsten as alloying elements are considered to be strong carbide forming elements, which form  $\text{Mo}_6\text{C}$  and  $\text{W}_6\text{C}$  types of carbides.



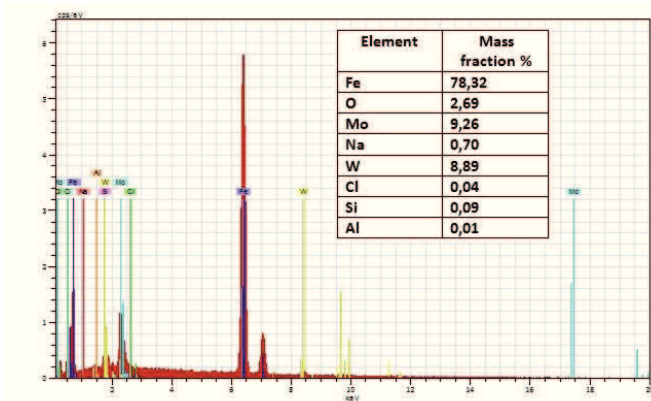
a)



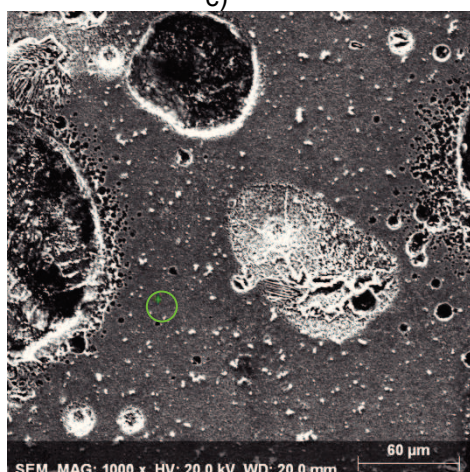
b)



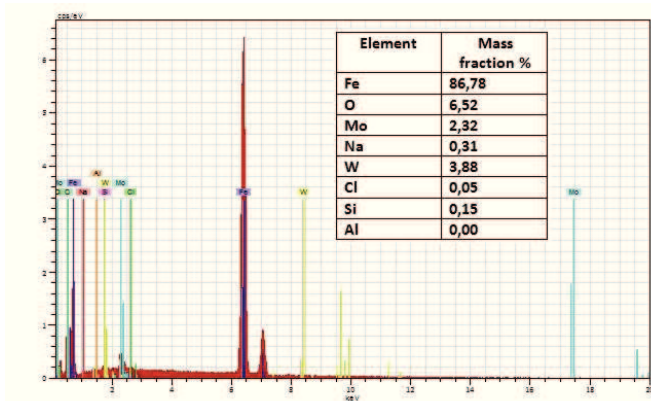
c)



d)



e)



f)

Figure 7. a),c),e) SEM micrographs of HTCS-130 tool steel surface after electrochemical measurements in the medium of 3.5 % NaCl (magnification 1000x) and b),d),f) EDS analyzes



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The SEM images in Figure 7 show pitting corrosion or local corrosion caused by the breaking of the passive metal surface and can be identified by the large black holes/pits formed on the sample. The breaking of the passive layer was most likely due to the presence of chloride ions, and the additional factors that might have contributed to it were: the difference in the amount of oxygen, the pH value, the flow rate and the physical and chemical inhomogeneity of the passive layer.

The chemical composition determined by EDS analysis after electrochemical testing in the medium of 3.5% NaCl shows the elevated oxygen content at the metal base (Figure 7e), indicating that the sample is covered with an oxide layer. However, the oxide layer is not compact but is filled with black holes/pits, in which is also the oxygen content increased, but there is a higher presence of sodium, chlorine, molybdenum and tungsten inside the pits, than outside the pits. Chlorine and sodium come from the tested medium and it is logical that they accumulate more in the pits than on the sample surface.

Molybdenum and tungsten showed the highest presence on white deposits on the sample surface, which represent parts that did not completely cover by the oxide layer, which is the reason why the smallest oxygen content was recorded at these sites. Because of the low chromium content in the chemical composition of the tested steel, creating a passive layer on the surface was not entirely possible, i.e. no insoluble surface layer was created that would prevent further oxygen diffusion on the surface and thus prevent oxidation of the iron in the material matrix.

### CONCLUSIONS

1. By the electrochemical measurements corrosion resistance of HTCS-130 tool steel for hot work of in medium of Lenox Band-Ade emulsion, water and 3.5% NaCl was investigated.
2. The potentiodynamic polarization of the tool steel in the Lenox Band-Ade emulsion medium has resulted in a low corrosion rate relative to the water medium and 3.5% NaCl, where the corrosion rate was significantly higher. The Lenox Band-Ade emulsion has the role of coolant in the processing of materials and its primary function is to extend the service life of the tool and reduce the wear of machine parts, therefore the obtained corrosion rate was expected.
3. In the chloride medium there is more than double higher the value of corrosion rate registered in tool steel than that obtained in the water, indicating that the tested steel is more corrosion resistant in water, although the pH value for both solutions is approximately the same. The cause of this behavior is aggressive chloride ions that destroy the newly formed oxide layer and reduce its protective role in the fight against corrosion.
4. From the impedance parameters obtained by modeling the EIS spectrum, a much higher value of charge transfer resistance  $R_{ct}$  was noted in the Lenox Band-Ade emulsion medium than that in the water medium and 3.5% NaCl, which means that a thicker oxide layer formed that acts as a barrier and prevents further penetration of



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potential aggressive ions from the solution. Conversely, the lower charge transfer resistance recorded in the chloride medium indicates the formation of a thin oxide layer on the tool steel, which cannot be further expanded and strengthened due to the aggressive action of chloride ions.

5. SEM micrographs of the sample after etching in Nital showed the presence of ferrite-pearlite phase. Pearlite structure is composed of alternately stacked white or matrix base ferrite and cementite thin tiles. EDS analysis showed an elevated content of molybdenum and tungsten, i.e. the presence of their carbides.
6. The metallographic analysis of the tool steel exposed to the Lenox Band-Ad emulsion medium showed no microstructural changes. However, corrosion products on the surface of the tested tool steel were observed in the medium of water and chloride media. The resulting corrosion products suggest that iron oxidation has occurred in the material matrix, which is why an elevated oxygen content is registered.
7. SEM analysis of tool steel exposed to the chloride medium has shown a bigger distribution of pitting corrosion rather than in a water medium attributed to the presence of chloride ions, which lead to the destruction of the passive layer on the metal surface and the formation of pits. EDS analysis of pits characteristic for the appearance of pitting corrosion has been shown the increased content of oxygen, but also the higher presence of sodium and chlorine, which accumulate in the pits, and result from the tested medium. Molybdenum and tungsten showed the highest presence on white deposits on the sample surface, which represent parts that did not completely cover by the oxide layer, which is the reason why the smallest oxygen content was recorded at these sites.
8. The obtained values of corrosion rate in the water and 3.5% NaCl medium indicate to the fact that the investigated tool steel for hot work is poorly stable in water and chloride medium, and it can be used only in exceptional cases in conditions in which it will come into contact with water or chloride medium.

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### REFERENCES

- [1] G. Roberts, G. Krauss, R. Kennedy, Tool Steels, 5th ed., ASM International, Materials Park, 1998.
- [2] M. Novosel, F. Cajner, D. Krumes, Alatni materijali, Strojarski fakultet u Slavonskom Brodu, Slavonski Brod, 1996.
- [3] W. E. Bryson, Heat treatment, selection and application of tool steels, 2nd Edition, Hanser Publications, Cincinnati, 2013.
- [4] S. J. Huang, Tribological properties of the low-carbon steels with different micro-structure processed by heat treatment and severe plastic deformation, *Wear*, 271(2011), pp. 705-711.
- [5] S. Kožuh, Specijalni čelici, Skripta, Sveučilište u Zagrebu, Metalurški fakultet, Sisak, 2010.
- [6] A. F. Rousseau, Metallurgical characterization and performance of high speed steel tool materials used in metal cutting applications, School of Applied Sciences College of Science, Engineering and Health, RMIT University, Melbourne, 2016.
- [7] J. Szumera, The tool steel guide, Industrial Press Inc., New York, 2013.
- [8] R. W. Staehle, Engineering with advanced and new materials, *Materials Science and Engineering: A*, 198(1995)1-2, pp. 245-256.
- [9] D. J. Young, High temperature oxidation and corrosion of metals, School of Materials Science and Engineering, University of New South Wales, Sydney, 2016.
- [10] N. Birks, G. H. Meier, F. S. Pettit, Introduction to the high-temperature oxidation of metals, 2nd Edition, University of Pittsburgh, Cambridge, 2006.
- [11] C. R. Sohar, Lifetime controlling defects in tool steels, Doctoral Thesis, Vienna University of Technology, Austria, 2011.
- [12] V. Alar, Kemijska postojanost metala, Sveučilište u Zagrebu, Fakultet strojarstva i brodogradnje, Zagreb, 2015.
- [13] T. Kostadin, Čelici i željezni ljevovi, Materijali II, Interna skripta, Veleučilište u Karlovcu, Karlovac, 2017.
- [14] H. Kim, J. Kang, D. Son, T. Lee, K. Cho, Evolution of carbides in cold-work tool steels, *Materials Characterization*, 107(2015), pp. 376-385.
- [15] S. Mitić, A. Begić Hadžipašić, G. Gojsević Marić, Z. Zovko Brodarac, Utjecaj medija i mikrostrukture na korozijsko ponašanje nodularnog lijeva, Proceedings of 16<sup>th</sup> International Foundrymen Conference, (ur.: Z. Zovko Brodarac, N. Dolić, A. Begić Hadžipašić), University of Zagreb Faculty of Metallurgy, 15-17.5.2017, Opatija, Croatia, pp. 173-188.
- [16] A. Begić Hadžipašić, S. Brajčinović, G. Gojsević Marić, Z. Zovko Brodarac, Utjecaj medija i mikrostrukture na korozijsko ponašanje sivog lijeva, Proceedings of 17<sup>th</sup> International Foundrymen Conference, (ur.: N. Dolić, Z. Zovko Brodarac, A. Begić Hadžipašić), University of Zagreb Faculty of Metallurgy, 16-18.5.2018, Opatija, Croatia, pp. 98-112.
- [17] E. Stupnišek-Lisac, Korozija i zaštita konstrukcijskih materijala, Sveučilište u Zagrebu Fakultet kemijskog inženjerstva i tehnologije, Zagreb, 2007.



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- [18] N. Bakula, Zaštita konstrukcijskog ugljičnog čelika inhibitorima korozije, diplomski rad, Fakultet kemijskog inženjerstva i tehnologije, Zagreb, 2005.
- [19] H. Ezuber, A. Alshater, S. O. Nisar, A. Gonsalvez, S. Aslam, Effect of surface finish on the pitting corrosion behavior of sensitized AISI 304 austenitic stainless steel alloys in 3.5% NaCl solutions, *Surface Engineering and Applied Electrochemistry*, 54(2018), pp. 73-80.
- [20] M. Atapour, H. Sarlak, M. Esmilzadeh, Pitting corrosion susceptibility of friction stir welded lean duplex stainless steel joints, *Int. J. Adv. Many Technol*, 83(2016)5, pp. 721-728.