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Influence of microstructure on the resistance of tool steels to local corrosion in 3.5% NaCl medium

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Abstract

In this research, electrochemical and metallographic tests were carried out on tool steel for cold and hot work, as well as steel for cementation, with the goal to obtain corrosion parameters to determine which of the examined samples is more resistant to local pitting corrosion. Electrochemical tests were performed in a medium of 3.5% NaCl, and were based on conducting cyclic anodic polarization in the potential range from -2000 mV to 200 mV vs SCE and vice versa. The results of the research showed that all three samples are subject to pitting corrosion, but the worst was the cementing tool steel sample X19NiCrMo4, which had the lowest pitting potential. The W600 tool steel sample for hot work proved to be the best, with the highest pitting potential.

The results of the electrochemical tests coincide with the metallographic tests, because after corrosion in the chloride medium only the beginnings of pitting corrosion are visible on the surface of the W600 sample in the form of partial accumulations of corrosion products, while the X19NiCrMo4 cementing steel sample was completely covered with corrosion products, which means that of the three tested tool steels, cementing steel is the most susceptible to pitting corrosion and is not recommended for use in conditions where it comes into contact with chloride ions. The martensitic microstructure of cementing tool steel is responsible for the very low pitting potential and, consequently, pronounced pitting corrosion. On the other hand, the W600 tool steel showed better corrosion resistance due to its finer grain and uniform carbide distribution.

Keywords: pitting corrosion, tool steels, cyclic anodic polarization, 3.5% NaCl, microstructure.

1. Introduction

Corrosion is the destruction of the material and its critical characteristics during electrochemical, chemical and other reactions where the surface of the material is in contact with the environment [1,2]. Corrosion of metals and non-metals occurs as an interaction with the environment on the surface of the material. It affects structures and objects of different materials, as well as the ambient air, which is loaded with moisture and oxygen, and can initiate the corrosion process, known as rusting [3,4].

Many factors affect material damage through corrosion. In the case of buried structures and pipelines, the rate of corrosion damage is determined by soil chemistry and moisture [5]. Acid fumes such as sulfuric acid and sodium hydroxide dust also accelerate corrosion. In the case of aluminum, the oxide film created by the initial corrosion attack protects the surface from further damage. In marine environments, where airborne salt crystals are deposited on ships, corrosion of submerged surfaces as well as floating surfaces occurs.

Corrosion affects the microstructure, mechanical properties and physical appearance of the material itself [1-4]. Rusting and other types of deterioration drastically reduce the capacity of pipelines and equipment, resulting in lost production and therefore lost equipment [5].

In the fight against corrosion damage of critical structures and equipment, anti-corrosion coatings are used [6]. Electric currents can produce passive films on metals that do not normally have them. Some metals are more stable in certain environments than others, and scientists have in-

vented alloys like stainless steel to improve properties in certain conditions. Some metals can be treated with lasers to give them a non-crystalline structure, which is resistant to corrosion. During galvanizing, iron or steel is coated with more active zinc, a galvanic cell is created where zinc corrodes and iron does not. Other metals are protected by electroplating with an inert or passivating metal. Non-metallic coatings such as plastics, paints and oils can also prevent corrosion.

Tool steel refers to various carbon and alloy steels that are particularly suitable for tool making [7-9]. Their suitability is a result of their distinct hardness, resistance to wear and deformation and their ability to keep an edge at high temperatures. This makes tool steels suitable for use in shaping other materials. There are six groups of tool steel: water-hardening tool steel, cold-work tool steel, shock-resistant tool steel, high-speed steel, hot-work steel, and special-purpose tool steel (plastic molds) [7-9]. Group selection depends on cost, operating temperature, required surface hardness, strength, impact resistance and toughness requirements. The more difficult the working conditions (higher temperature, abrasiveness, corrosiveness, load), the greater the alloy content and consequently the amount of carbide needed for tool steel.

In this work, the resistance of three different types of tool steels (one for hot work, one for cold work and one for cementing) to local corrosion in a medium of 3.5% NaCl was tested. Electrochemical techniques were used to obtain corrosion parameters such as pitting potential, repassivation potential, and hysteresis potential, as indicators of the resistance of the tested tool steels to local corro-

sion. In addition, metallographic tests were performed on sample surfaces before and after corrosion in a specified medium, with the aim of finding out which of the specified tool steels is the most resistant to local corrosion in the chloride medium.

2. Experimental part

2.1. Samples

In the experimental part of this work, three samples of tool steels were tested: tool steel for cold and hot work and tool steel for cementing.

Cold work tool steels include a group of steels for shaping and processing at temperatures up to 200°C [7,8]. They can be unalloyed or low-alloyed. Cold working non-alloyed steels have a carbon content of 0.5-1.3%, less hardenability and better toughness than other tool steels, and are used to make tools with a smaller section and simpler shapes. Low-alloy steels for cold processing have significantly better properties, which are achieved by adding alloying elements: chromium, tungsten, vanadium and molybdenum. The purpose of alloying is to obtain refractory carbides that ensure good toughness, high hardness and dimensional stability at elevated operating temperatures [7,8,10]. This group of tool steels is used to produce tools that are prone to corrosion, and chromium fulfills the purpose of corrosion resistance. In addition to chromium, there are other alloying elements such as V, Mo and W. Cold work tool steels must be impact and wear resistant [7-10]. Table 1 shows the chemical composition of the tested cold work tool steel marked as K110.

Table 1. Chemical composition of K110 cold work tool steel (wt.%) [11,12]

C	1.55	Ni	-
Si	0.30	V	0.75
Mn	0.30	W	-
Cr	11.30	Co	-
Mo	0.75	Fe	balance

Among the supporting elements, the tested steel contains silicon and alloying elements: chromium, molybdenum and manganese. Chromium is added to steel because it increases its hardenability and lowers the martensite formation temperature. Molybdenum in combination with other alloying elements increases the hardenability and prevents brittleness when yielding. Manganese has a deoxidizing effect. In combination with chromium, molybdenum increases corrosion resistance [9]. The composition shown in the Table 1 meets the prescribed qualities related to production [11,12].

Hot work tool steels are used to make tools that are heated to a temperature higher than 200°C during operation [7,8]. The most essential attribute of this steel is its resistance to yielding. Resistance to yielding refers to occurrences that can occur when exposed to high temperatures (e.g. reduc-

tion of hardness, microstructural changes). In addition to resistance to yielding, tool steels must meet additional requirements such as resistance to [9]: appearance of plastic deformations, wear, high temperature corrosion, satisfactory impact load (toughness).

Favorable properties are achieved by alloying (e.g. carbide formers: W, Mo, Cr and V) and low carbon content. Nickel is added to increase toughness and hardenability, and silicon to improve dynamic durability. Table 2 shows the chemical composition of the tested hot work tool steel marked as W600 [12].

Table 2. Chemical composition of W600 hot work tool steel (wt.%) [12]

C	0.32
S	0.001
Si	0.12
Cr	0.11
Ni	2.1
V	0.01
W	1.9
Co	0.01
Al	0.009
Cu	0.01
Mn	0.23
Mo	3.2
P	0.005
Sn	0.005
Ti	0.01
Nb	0.01
B	0.001
N	0.008
Fe	balance

The tested steel includes silicon from the supporting elements, as well as phosphorus and sulfur from the undesirable elements, in small quantities that can never be fully removed. Alloying elements include chromium, nickel, aluminum, manganese and molybdenum. Hot work tool steels enable hot forming of work pieces made of iron and non-ferrous metals, as well as alloy derivatives at high temperatures. They are used in processes such as die casting, extrusion and forging, as well as in the production of pipes and glass [7,8,12]. Tools made of hot work tool steel are not only subject to constant high temperatures when in use, but also to fluctuating thermal loads that occur where the tool surfaces come into contact with the materials being worked. Combined with wear caused by abrasion or impact, thermal loads present very specific requirements for hot working tool steels. The key requirements are high tempering resistance, temperature strength, thermal shock resistance, high temperature resistance and wear resistance [7,8,12].

Cementing steels belong to the group of structural steels. With their help, the edge layer is carbonized after processing, separating the particles. After carburizing comes tempering, in order to increase the toughness of the non-carburized core and to obtain high wear resistance of the edge layers [12,13]. This type of tool steel contains 0.1-0.2% carbon before carburizing and can be low-alloyed

or unalloyed. After carburizing, the edge layer contains 0.8 - 0.9% carbon, so its hardness is 61 - 64 HRC [7,8,13]. Table 3 shows the chemical composition of X19NiCrMo4 cementing tool steel.

Table 3. Chemical composition of X19NiCrMo4 cementing tool steel (wt.%) [12,13]

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

The tested steel contains silicon as a supporting element, and phosphorus and sulfur in permitted amounts as undesirable elements. The tested steel also contains alloying elements such as manganese, chromium, nickel and molybdenum. Nickel has good properties, so we add it to increase the toughness of steel and to increase corrosion resistance [7,8]. Chromium is added to steel because it increases its hardenability and lowers the martensite formation temperature. Molybdenum is added in combination with other alloying elements and increases the hardenability and prevents brittleness during yielding. Manganese has a deoxidizing effect. Molybdenum in combination with chromium increases corrosion resistance [7,9]. The chemical composition listed in the table satisfies the production's required quality standards. [12,13].

2.2. Media for conducting electrochemical tests

A 3.5% NaCl solution is employed as the medium for electrochemical testing of tool steel resistance to local corrosion. The 3.5% NaCl solution was chosen to simulate the application of tool steels in real conditions, i.e. conditions similar to seawater solution. A 3.5% NaCl solution was prepared by adding 8.75 g of NaCl to 250 ml of distilled water. The solution was stirred and allowed to stand. Using a laboratory pH-meter and a conductometer, the pH value was measured before and after electrochemical tests (Table 4).

Table 4. pH values of the medium before and after electrochemical tests

Sample	pH (before the test)	pH (after the test)
K110	6.80	6.96
W600	6.80	6.89
X19NiCrMo4	6.80	7.10

From the data in table 4, it can be seen that all three tested samples had the same pH value before the measurement, i.e. all three samples were neutral before the test. They continue to be in a neutral medium after the test, but the

pH levels have slightly risen. The biggest difference in the pH value before and after the measurement was observed in the third sample. Its pH changed from 6.80 to 7.10.

2.3. Test methods

During this research, metallographic and electrochemical tests were used [11-13].

2.3.1. Metallographic tests

For easier handling of the samples, as well as for metallographic testing of the samples, two samples were cut from each tested tool steel. For this purpose, the samples were prepared by hot investment in conductive mass using a device for investment in carbon mass by hot pressing process (SimpliMet® 1000). After that, the samples were ground and polished on an automatic grinding and polishing device (Bühler) for 5 minutes at a force of 10 N [11-13].

Grinding was carried out using waterproof sandpaper with gradation Nos. 240, 400, 600 and 800 and polished on Microcloth felt using Al_2O_3 suspension in water. After polishing, the samples were washed in distilled water and degreased in ethanol. After the aforementioned sample preparation, one representative of each tool steel was used for electrochemical tests and observation of the surface of the samples after corrosion, and the other sample from each tool steel taken was intended for metallographic tests [11-13]. Metallographic tests were first carried out "on white" in order to observe the purity of the material itself, i.e. the presence of inclusions or cracks. After that, the samples were etched in 3% nital in order to highlight their microstructure. An optical microscope with an Olympus DP27 digital camera and an automated image processing system was used to record everything (Steram Motion) [12].

2.3.2. Electrochemical tests

Electrochemical tests were based on performing cyclic anodic polarization of the tested samples in the range from -2000 mV to 200 mV vs SCE and vice versa, with a potential rate of $dE/dt = 5$ mV s^{-1} . This test was performed in the three-electrode glass cell shown in Figure 1, at room temperature in a medium of 3.5% NaCl [12].

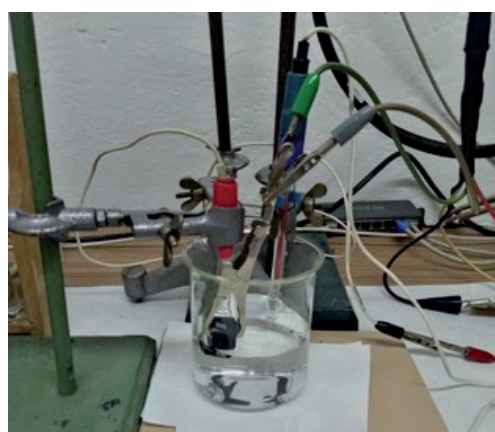


Fig. 1. Three-electrode glass cell for electrochemical tests [12]

The working electrode is the sample, the counter electrode is the Pt electrode, and the reference electrode is the saturated calomel electrode (SCE) [11-13]. The potential of the working electrode is measured using the reference electrode, and the Pt electrode is the conductor that closes the circuit [11-13]. The working surface of the tested samples is 0.98 cm², which was determined by measuring the sides a (1.4 cm) and b (0.7 cm) of the samples and multiplying them. The specific working surface of the samples is marked with a black strip [12].

The samples were degreased in ethanol and dried after metallographic preparation. First, the working medium is added to the glass (the glass represents the cell), then the reference electrode and the counter electrode are immersed, and finally the sample is immersed, in our case the working electrode up to the black strip. Measurement parameters are set on the computer. The electrodes are connected to a computer-controlled potentiostat/galvanostat [11-13].

During the measurement, the sample submerged in the medium must first be stabilized, which takes around 30 minutes or 1800 seconds. When the sample is in a stationary state, then the open circuit potential E_{ocp} is read. This completes the first part of the measurement [11-13].

In the continuation of the measurement, cyclic anodic polarization of the samples was performed in the range -2000 mV to 200 mV in relation to the SCE and vice versa with the potential rate $dE/dt = 5 \text{ mV s}^{-1}$. Potentiodynamic measurements were plotted on a two-coordinate plot on a computer using PowerCore™ software. After that, the corrosion parameters E_{corr} , E_{pitt} , E_{rep} and E_{hyst} were read from the polarization curves, which are indicators of the resistance of the tested tool steels to local corrosion [12,14]. Electrochemical tests were performed in 3.5% NaCl medium, at least twice for each sample. If two measures differed, a third measurement was taken to ensure that the results were reproducible.

3. Results and discussion

3.1. Results and discussion of electrochemical tests

Anodic and cathodic processes occurred throughout the test. The anodic process occurs at the tested sample, during which the metal dissolves and electrons are generated. The cathodic process is the depolarization of hydrogen or oxygen, and this depends on the medium in which the measurement is performed. The purpose of conducting electrochemical tests is to obtain the following parameters of resistance to local corrosion [12,14]:

- E_{corr} - corrosion potential,
- E_{pitt} - pitting potential,
- E_{rep} - repassivation potential and
- E_{hyst} - hysteresis potential.

The corrosion potential, E_{corr} , of the open circuit is read after the sample immersed in the medium (electrolyte) is stabilized. The stabilization time lasted 30 minutes. The pitting potential together with the repassivation potential

is used to evaluate the resistance of metals to pitting corrosion [1-3,12,15]. The pitting potential, E_{pitt} , can be read by drawing tangents on both parts of the starting curve and reading the value on the x-axis at their intersection, i.e. the pitting potential is determined according to the criterion of a marked increase in current on the initial polarization curves [1-3,12]. The pitting potential is actually the critical potential at which the passive electrode surface is activated and the breakdown of the passive layer occurs. The lower the E_{pitt} , i.e. more negative, the material is more susceptible to local corrosion, i.e. pitting corrosion. The repassivation potential, E_{rep} , can be read at the first intersection of the initial and return curves, i.e. at the point where the anode hysteresis loop closes.

The hysteresis potential, E_{hyst} , is then calculated according to the equation [1-3,12]:

$$E_{hyst} = E_{pitt} - E_{rep} \quad (1)$$

Figure 2 shows the diagram of the time dependence of the open circuit potential of the tested samples of tool steels in a medium of 3.5% NaCl.

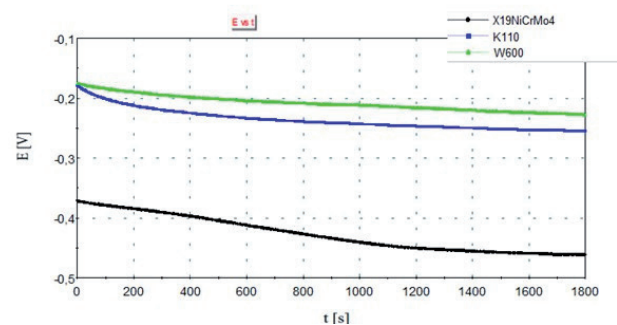


Fig. 2. Diagram comparing the time dependency of the open circuit potential of the tested tool samples in a 3.5% NaCl medium

The tool steels W600 and K110 attain their open circuit potential in 1150 seconds in the 3.5% NaCl medium, as shown in the diagram. The potential tends to a more positive value of the open circuit potential. In contrast to them, the corrosion potential of X19NiCrMo4 steel tends to a more negative value, which points to the dissolution of the sample. Figures 3 to 5 show cyclic voltammograms of tested samples in 3.5% NaCl medium. The peak indicating pitting can be seen in the tested chloride medium, which means that pitting corrosion can be observed in the chloride medium in all three of the tested tool steel samples, according to the presented voltammograms.

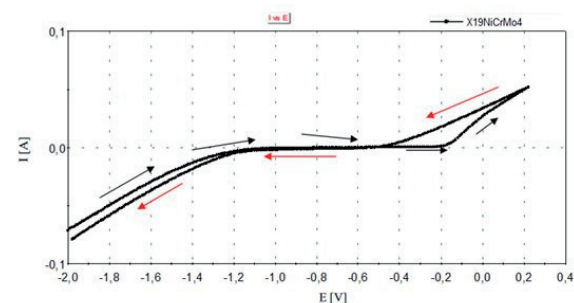


Fig. 3. Cyclic voltammogram of X19NiCrMo4 sample in 3.5% NaCl medium

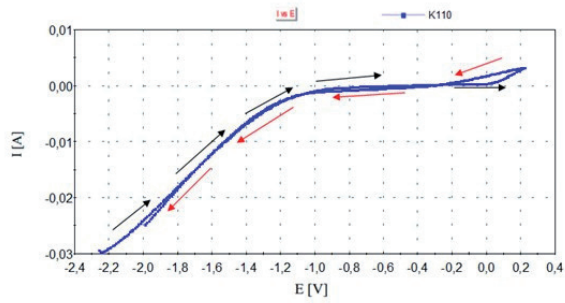


Fig. 4. Cyclic voltammogram of K110 sample in 3.5% NaCl medium

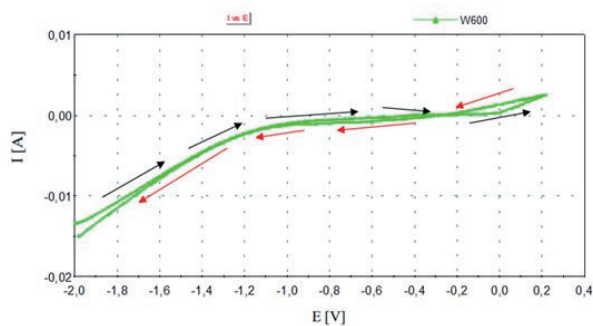


Fig. 5. Cyclic voltammogram of W600 sample in 3.5% NaCl medium

Table 5 shows the corrosion parameters obtained for steels X19NiCrMo4, K110 and W600 in 3.5% NaCl medium. If the corrosion potential value is negative, this indicates a more pronounced dissolution process, i.e. stronger corrosion in chloride media tested [1-3, 12, 15].

Table 5 shows that the value of the corrosion potential is the lowest for X19NiCrMo4 steel, and the highest for W600 steel. As for the value of the pitting potential, it is the lowest (most negative) for X19NiCrMo4 steel, and the highest (most positive) for W600 steel, which points to the fact that W600 steel is the most resistant to local corrosion in the tested chloride medium. On the other hand, it is significant to note that there aren't many differences between the pitting potentials of the K110 and W600 samples, which means that the K110 steel is roughly equivalent to the W600 steel in its ability to fend off local corrosion in the chloride medium. If we look at the repassivation potential values, we see that the K110 and W600 steels do not differ much, but that is why the X19NiCrMo4 steel has a significantly lower repassivation potential.

Table 5. Corrosion parameters of X19NiCrMo4, K110 and W600 steel in 3.5% NaCl medium

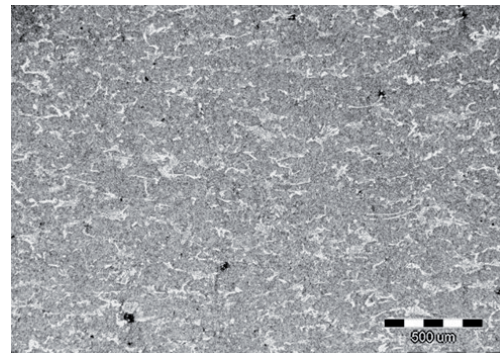
Steel	E_{corr} vs SCE [mV]	E_{pitt} vs SCE [mV]	E_{rep} vs SCE [mV]	E_{hyst} vs SCE [mV]
X19NiCrMo4	- 461	-180	- 500	320
K110	- 254	50	- 280	330
W600	- 227	60	- 260	320

In terms of hysteresis potential, steel with a narrower hysteresis loop is generally more resistant to local corrosion [1-3,12]. However, a more relevant parameter for determining corrosion resistance is the pitting potential.

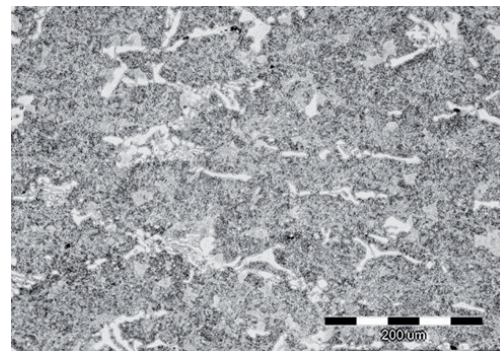
3.2. Results and discussion of metallographic tests

Figure 6 shows metallographic images of K110 cold work tool steel after etching in nital.

Figure 6 shows that the primary structure of K110 cold work steel is ledeburite, which after hardening and low yielding achieves the structure of martensite + secondary carbides [11,12,16]. The steel matrix is dark in the image and the carbides stand out in white.



a)



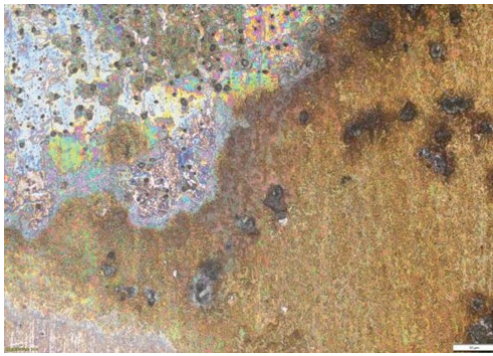
b)

Fig. 6. Microstructure of K110 sample after etching in nital: a) magnification 50x; b) magnification 200x

Figure 7 shows metallographic images of the tested K110 cold work tool steel following electrochemical tests in 3.5% NaCl medium.



a)



b)

Fig. 7. Metallographic image of K110 sample after electrochemical tests in 3.5% NaCl medium:

a) magnification 50x; b) magnification 200x

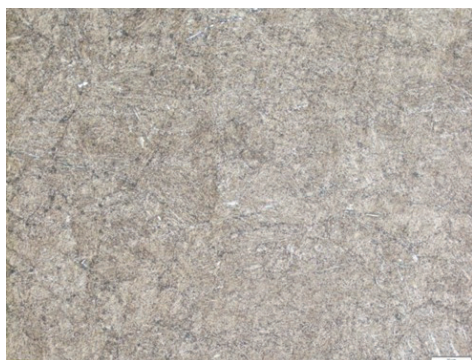
This type of steel belongs to the group of semi-stainless tool steels. It contains a significant amount of carbon and chromium. Due to its very good properties, such as extraordinary hardness and strength and wear resistance, it is used to make hand tools and blades [9,11,12].

After conducting electrochemical tests in a solution containing 3.5% NaCl, we can see that the tested steel's surface is partially covered in corrosion products, primarily on the edges of the sample. It was also discovered that chloride ions attack the steel matrix more aggressively than precipitated carbides.

Figure 8 shows metallographic images of W600 hot work tool steel after etching in nital.



a)



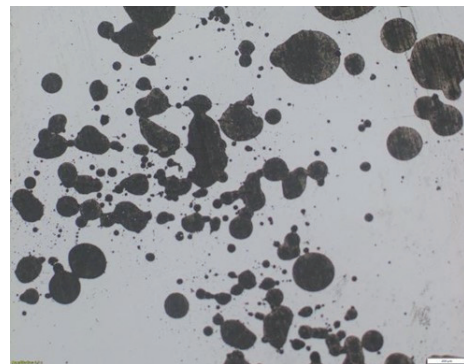
b)

Fig. 8. Microstructure of W600 sample after etching in nital: a) magnification 50x; b) magnification 200x

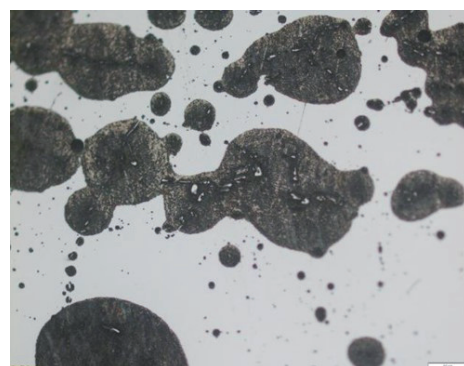
Figure 8 shows that the microstructure of W600 hot work tool steel is martensitic, but the structure is fine-grained with a uniform distribution of carbides [12,16].

Figure 9 shows metallographic images of W600 hot work tool steel after electrochemical tests in 3.5% NaCl.

Figure 9 shows that the surface of the sample exposed in a medium of 3.5% NaCl is not completely but only partially covered by the corrosion product. The W600 sample turned out to be the best, because there are dotted black spots visible on the surface, which indicates the beginning of pitting corrosion [12]. It most often occurs where the passive coating layer is physically damaged or chemically attacked. In particular, when the sample was reground, the corrosion products from the surface were easily removed, indicating that the corrosion damage was not deep [12]. The tested tool steel includes a significant quantity of nickel and hence has strong corrosion resistance, making it the best of the three tested steels. Additionally, its fine-grained microstructure and uniform carbide distribution significantly increased its resistance to pitting corrosion [12].



a)

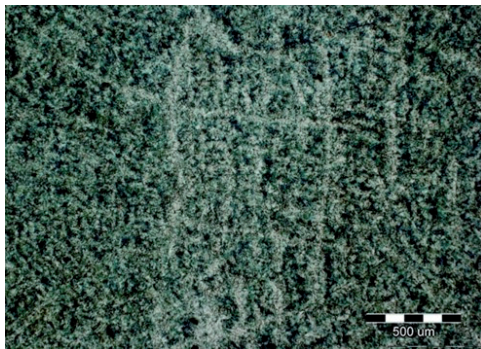


b)

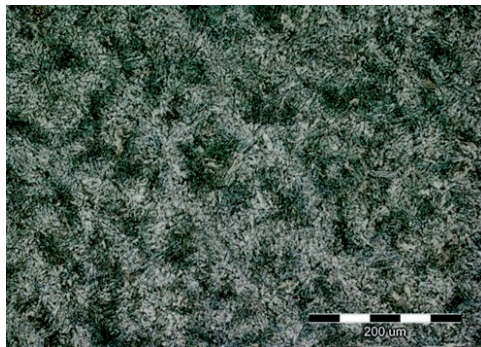
Fig. 9. Metallographic image of W600 sample after electrochemical tests in 3.5% NaCl medium:

a) magnification 50x; b) magnification 200x

Figure 10 shows metallographic images of X19NiCrMo4 cementing steel after etching in nital.



a)



b)

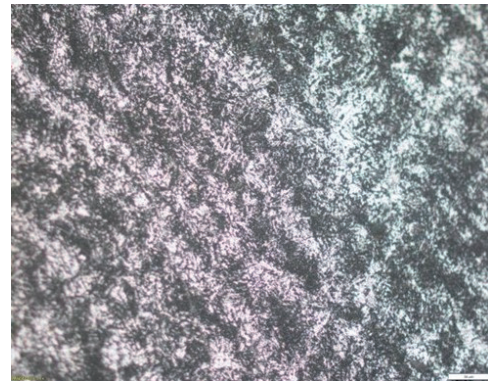
Fig. 10. Microstructure of X19NiCrMo4 sample after etching in nital: a) magnification 50x; b) magnification 200x

Figure 10 shows the martensitic structure of X19NiCrMo4 cementing tool steel [12,13,16]. Martensite is formed by transformation of austenite during rapid cooling below the temperature at which martensite begins to form. It can also be produced as low-carbon steel laths, though plates are the most common form [12,13,16]. The martensite microstructure is particularly unfavorable in terms of corrosion resistance due to its characteristics, as shown in the present research. X19NiCrMo4 in the chloride medium showed a very low, i.e. the most negative, pitting potential among the tested tool steels [12,13].

After conducting electrochemical tests on the X19NiCrMo4 steel in a chloride medium, we can see that the corrosion progressed very quickly and that the tested steel was completely covered with corrosion products (Figure 11). This surface condition corresponds to the obtained corrosion parameters, so the tested cementing tool steel cannot be recommended for use in contact with chloride ions [12,13].



a)



b)

Fig. 11. Metallographic image of X19NiCrMo4 cementing tool steel after electrochemical tests in 3.5% NaCl medium: a) magnification 50x; b) magnification 100x;

4. Conclusion

At the end of the test carried out, the following can be concluded:

- The resistance to local corrosion of K110 and W600 tool steels for cold and hot work and X19NiCrMo4 cementing steel was tested using metallographic and electrochemical methods.
- Cyclic anodic polarization of the mentioned steels in a 3.5% NaCl medium in the potential range of -2000 mV to 200 mV vs SCE and vice versa was carried out, all with the aim of collecting corrosion parameters as an indicator of the resistance of the tested samples to local corrosion.
- Resistance to local corrosion is determined using the pitting potential parameter E_{pitt} . Since the pitting potential was recorded in all three tested samples, it is evident that all three tool steel samples are subject to pitting corrosion in a chloride medium. The lowest E_{pitt} was obtained for the X19NiCrMo4 steel sample, while the highest E_{pitt} was recorded for the W600 steel, indicating that the W600 hot work tool steel is the most resistant to local corrosion among the tested steels. However, due to the very small difference in potential levels of pitting, K110 cold work tool steel can be considered equally resistant.
- Metallographic tests confirmed the results of electrochemical measurements, showing that the surface after corrosion was completely covered by corrosion products on the X19NiCrMo4 cementing tool steel sample, and that the martensitic microstructure of the tested steel was responsible for such the rapid propagation of pitting corrosion.
- Unlike the X19NiCrMo4 sample, the W600 sample was partially covered by corrosion products after corrosion in a chloride medium, and the fine-grained martensitic microstructure and the uniform distribution of carbides were the reason for the lower susceptibility to pitting corrosion.

- Finally, it can be concluded that although they are susceptible to pitting corrosion, the durability of the tested steels in the chloride medium can be increased to some extent by an adequate choice of anti-corrosion protection.

5. Acknowledgments

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