Inhibitory effect of commercial inhibitor VCI 379/611 on corrosion behavior of X153CrMoV12 tool steel for cold work

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INHIBITORY EFFECT OF COMMERCIAL INHIBITOR VCI 379/611 ON CORROSION BEHAVIOR OF X153CRMOV12 TOOL STEEL FOR COLD WORK

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Abstract

In this paper, the influence of water and the influence of the commercial inhibitor VCI 379/611 on the corrosion processes of X153CrMoV12 tool steel for cold work were investigated. The research was carried out by electrochemical methods: by measuring the potential of an open circuit, by determining the corrosion parameters using the method of electrochemical impedance spectroscopy (EIS) and method of Tafel extrapolation. After each measurement, the sample surface was analyzed using an optical microscope. The obtained corrosion parameters showed a high efficiency of the applied inhibitor in the protection of tool steels for cold work from corrosion. For the sample that was exposed to distilled water medium with the addition of inhibitor, a significantly lower corrosion rate was registered and no damage to the sample surface was visible. Metallographic images of the electrode surface after polarization measurements in tap water indicate the occurrence of pitting corrosion.

Keywords: *tool steel for cold work, electrochemical techniques, corrosion parameters, inhibitor, microstructure*

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INTRODUCTION

Tool steels are integral parts of industrial machines. They are most often used to make tools with which metal or non-metal products are processed or shaped. Also, tool steels are produced for engine parts, bearings and springs due to very good mechanical properties. They are mainly used in the heat-treated condition and are delivered in the form of bars, strips or plates [1]. They are important for the modern development of the industry and are indispensable in production. Modern materials are obtained by optimizing the composition and microstructure of the material according to the desired properties. Depending on their purpose, the goal is to achieve the most favorable properties of tool steels. The most wanted properties are hardness, wear resistance, high toughness, yield strength and corrosion resistance [2]. Corrosion is the undesirable wear of metals caused by mechanical, biological or chemical action of the environment [3]. Previous research has shown that electrochemical corrosion can occur in water, aqueous solutions of acids, alkalis and salts. The intensity of corrosion depends on the chemical composition and microstructure of the

steel, the type of medium, the pH value of the medium, the presence of ions or various other factors that adversely affect the material [4]. One of the commonly used methods of protecting steel from corrosion can be achieved by changing the corrosion environment, i.e. by removing activators or adding inhibitors. In industrial plants, inhibitors are most often used as liquid emulsion concentrates that are diluted in a certain ratio with water. Inhibitors in the form of powders, greases and oils are also used. The prepared agent with the addition of inhibitor provides adequate protection of metallic materials, especially in warehouses where the presence of moisture is unavoidable [5,6].

The mechanism of inhibitor action is based on the creation of a barrier, i.e. a thin film on the metal surface. Inhibitors are substances that are added in very small concentrations in order to reduce the corrosion rate, and according to the mode of action are divided into anodic, cathodic and mixed (anodic-cathodic) [7]. In this paper, the influence of water and commercial inhibitor VCI 379/611 on the corrosion and microstructural properties of X153CrMoV12 tool steel for cold work marked as K110 was studied. By applying electrochemical tests in the mentioned media and by applying metallographic analysis of the tested sample before and after corrosion, corrosion parameters were obtained which provide insight into the corrosion behavior of the tested sample of tool steel.

MATERIALS AND METHODS

To test the influence of medium and microstructure on corrosion resistance, a sample of tool steel for cold work X153CrMoV12 according to DIN/EN 1.2379, internal code K110 was selected. The chemical composition of the tested sample is shown in Table 1. Chromium is the main alloying element in this type of steel, and in combination with carbon it forms carbides of the $Cr_{23}C_6$ and Cr_7C_3 type. It is known from the literature that corrosion resistance increases with increasing chromium content, especially if the content is higher than 12% [8]. The addition of vanadium results in the grain refinement of the primary austenitic grain. Molybdenum influences the formation of fine-grained structure of steel and most often produces carbides of the Mo_2C type [9].

Table 1. Chemical composition of tested tool steel K110 (in weight percent)

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

Samples of tool steel for cold work marked as K110 were prepared by pressing into a conductive mass using a device for hot pressing of samples (SimpliMet® 1000). Machine grinding and polishing was performed on an automatic grinding and polishing device (Büehler). Machine grinding was performed with waterproof sandpaper of grade No. 240, 400, 600 and 800, and polishing with a suspension of Al_2O_3 in water. The samples were then washed in distilled water and degreased in ethanol. One prepared sample was used for electrochemical measurements, while the other sample was used for etching in 0.5 % nital (mixture of alcohol and nitric acid) [10]. Tap water and VCI 379/611 inhibitor concentrate mixed with distilled water were used as the working medium during the electrochemical tests. For the purpose of testing the effectiveness of the inhibitor, the solution was prepared as follows: the industrially prepared concentrate was diluted with distilled water in a ratio of

1:1. The sample thus prepared was mixed with distilled water in a ratio of 1%. The inhibitor concentrate was formulated on the basis of thixotropic calcium sulfonate inhibitors. The water-based corrosion inhibitor is intended as an additive for the conservation of metal elements in covered warehouses. The inhibitor agent leaves a very thin transparent, dry film on the metal surface.

Electrochemical tests (E_{corr}, EIS, Tafel)

The E_{corr} corrosion potential determination method, electrochemical impedance spectroscopy (EIS), and the Tafel extrapolation method were used to obtain data on the corrosion behavior of the samples. Measurements were performed in a three-electrode glass cell in which the working electrode, counter electrode and reference electrode were placed. The working electrode was a test sample of tool steel immersed in the working medium. The Pt electrode was used as the counter electrode, and the saturated calomel electrode was used as the reference electrode [11]. All electrochemical measurements were performed using a computer-controlled potentiostat / galvanostat (Parstat 2273) at room temperature (19 ± 2).
Before performing the measurements, a test of the time dependence of the corrosion potential was performed. Stabilization of the potential in the open circuit E_{ocp} was performed in a time period of 1800 seconds.
Electrochemical impedance spectroscopy was performed in the frequency range from 100 kHz to 10 mHz with a sinusoidal voltage amplitude of 5 mV. Impedance parameters were analyzed using ZSIMPWin 3.60 software using appropriate R (Q(R(QR))) circuit models.
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, and the corrosion parameters were determined by PowerCorrTM software using a Tafel extrapolation method and Faraday's laws [10]. One series of electrochemical measurements (E_{corr}, EIS, Tafel) lasted about 60 minutes.

Metallographic tests

Metallographic tests on sample K110 after etching in nital were performed in order to determine the microstructure, while metallographic tests on sample K110 for electrochemical measurements were performed in order to register the condition of the sample surface before and after corrosion. Metallographic images were obtained using an optical microscope with a digital camera (Olympus GX 51) and an automatic image processing system (AnalySIS® Materials Research Lab) [10].

RESULTS AND DISCUSSION

Figure 1 shows the time dependences of the potential in the open circuit for the tested sample marked as K110 in tap water and distilled water with the addition of inhibitor. According to the figure it can be seen that the sample is prone to dissolution in tap water, i.e. the electrode potential is expressed in negative values. The tested tool steel in distilled water with the addition of inhibitor proved to be more stable, because the electrode potential tends to more positive values. The results of electrochemical impedance

spectroscopy is shown by the Nyquist diagram (Figure 2). Modeling of the EIS diagram was performed using the appropriate model of the equivalent electrical circuit R (Q(R(QR))), after which the impedance parameters were obtained: electrolyte resistance R_{el}, oxide layer resistance R_{ox}, constant phase element of double layer Q_{dl}, surface heterogeneity measure n and charge transfer resistance R_{ct} (Table 2). By modeling, it was found that the experimental values match well with the modeled ones with a registered deviation of the order of 10^{-3}.
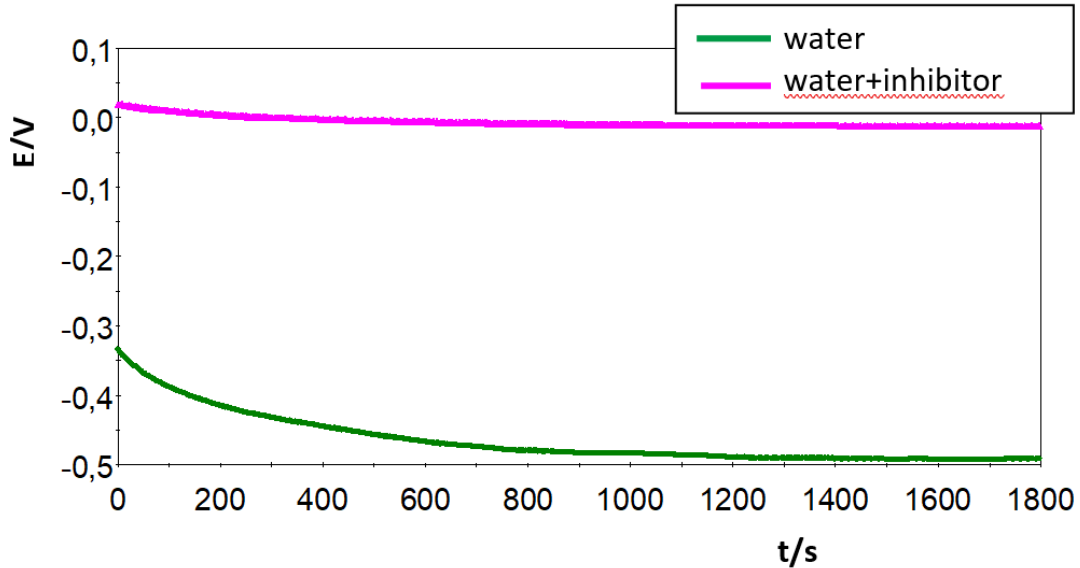

Figure 1. Time dependence of the open circuit potential for tool steel K110 in tap water and the concentrate of the inhibitor solution mixed with distilled water
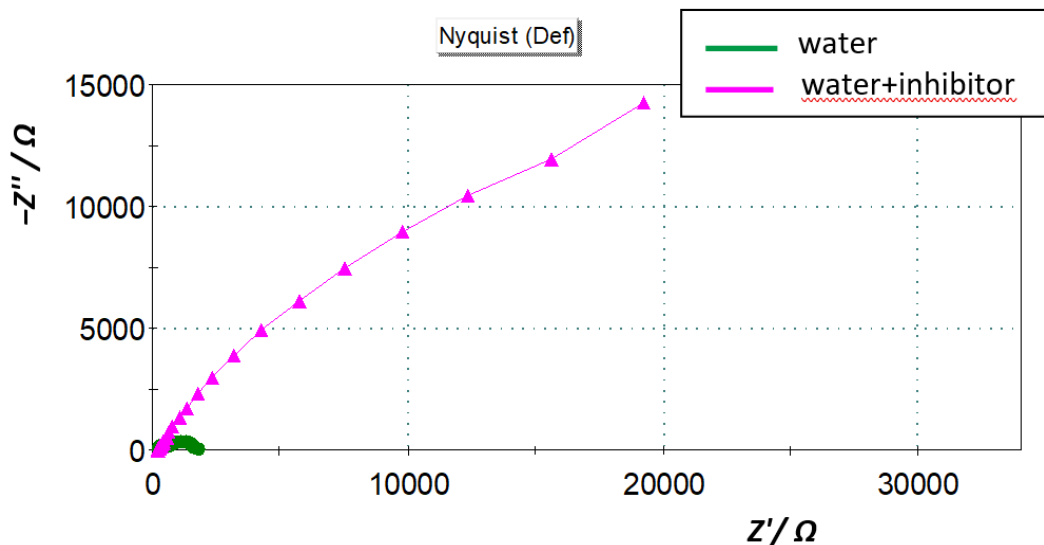

Figure 2. Comparative presentation of Nyquist EIS diagrams obtained for tool steel K110 in tap water and concentrate of inhibitor solution mixed with distilled water

Table 2. Impedance parameters of tested K110 tool steel

Medium	E_{corr} vs. SCE	R_{el}	$Q_{dl}\times10^6$	n	R_{ox}	$Q_{dl}\times10^6$	n	R_{ct}
	mV	Ωcm^2	$\Omega^1 s^n cm^{-2}$		Ωcm^2	$\Omega^1 s^n cm^{-2}$		$\Omega\ cm^2$
Tap water	-492	277.0	10.67	0.8	315.9	429.6	0.6	1230
Distilled water + inhibitor	-12.7	229.4	135.5	0.7	27210	276.8	0.6	75160

It can be seen from Figure 2 that the Nyquist impedance representation of the sample in tap water is in the form of a depressive semicircle, and such a result is characteristic for solid electrodes. However, the tested sample in distilled water medium with the addition of inhibitor showed a tendency to form a semicircle of wider scale. This points to the fact that the addition of inhibitor can slow down corrosion processes, because a thicker protective layer is formed on the steel surface. This is confirmed by the data in Table 2, which shows that the tested tool steel in distilled water medium with the addition of inhibitor showed far higher oxide layer resistance R_{ox} and charge transfer resistance R_{ct} than that in tap water. The higher amount of charge transfer resistance indicates that a thicker surface layer has formed on the sample to protect the sample from further corrosion attack. In contrast, the tested tool steel showed a higher value of Q_{dl} in tap water. This can be explained by the fact that the passive layer growing on the surface of the K110 tool steel is not compact enough and there is an increase in capacity on the metal/oxide layer interface or inside the passive layer.

Figure 3 shows the polarization curves of the tested sample of tool steel K110 in tap water and distilled water with the addition of inhibitor. The results are presented graphically in semi - logarithmic form (E - log$I$) where the corrosion current density logarithm is on the x - axis and the potential is on the y - axis.
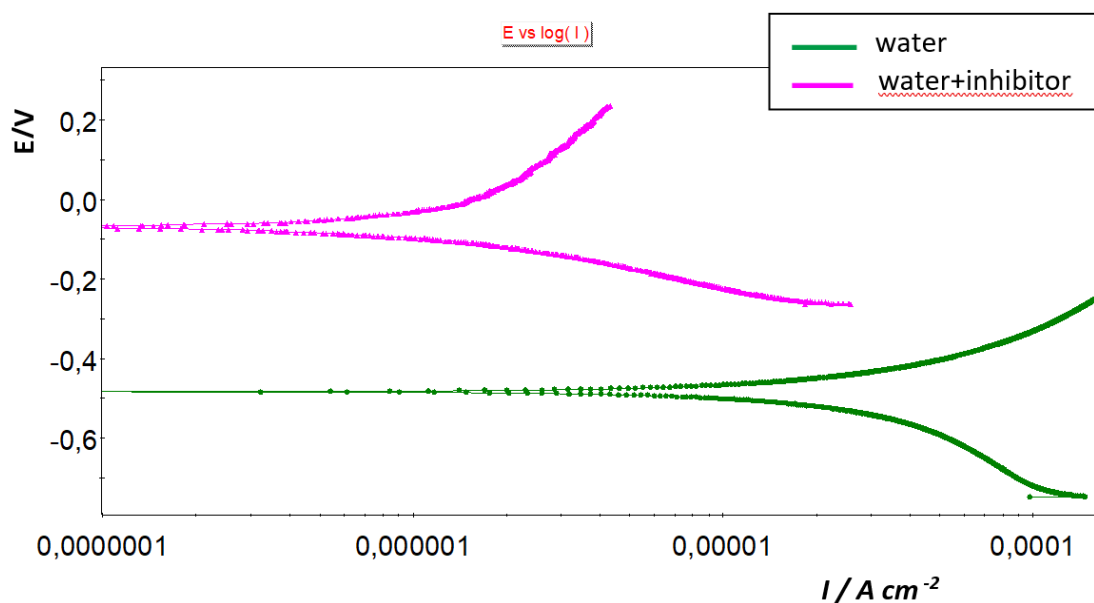

Figure 3. Polarization curves of the tested tool steel K110 obtained in tap water and concentrate of inhibitor solution mixed with distilled water

Potentiodynamic polarization was performed for the purpose of determining corrosion parameters (corrosion potential E_{corr}, corrosion rate v_{corr}, anodic slope b_a and cathodic slope b_c), and the obtained results are given in Table 3. According to the Tafel extrapolation method, a significantly lower corrosion rate was registered in distilled water with the addition of inhibitor. In order to determine the effectiveness of the inhibitor, the coefficient of effectiveness of the inhibitor Z [12] was calculated, in the amount of 0.98, which means that the effectiveness of the inhibitor at this added concentration is 98 %. This means that the added amount of inhibitor in the distilled water was sufficient to prevent the formation of corrosion products on the test sample. With the addition of inhibitor, the corrosion

potential shifts towards more positive values, which reduces the corrosion current density, but also the corrosion rate.

Table 3. Corrosion parameters of tested K110 tool steel

Medium	E_{corr} vs. SCE	b_a	b_c	v_{corr}
	mV	mV dec^{-1}	mV dec^{-1}	mm god^{-1}
Tap water	-483.30	855.0	3824.7	2.115
Distilled water + inhibitor	-68.54	1277.8	215.7	0.028

For the purpose of analyzing the microstructure of tool steel marked as K110, the microstructure was observed using an optical microscope after etching in nital (Figure 4). It is known from the literature that after etching with nital, the distribution of carbides in tool steel is achieved in such a way that the carbides are highlighted in white and the matrix is dark [13]. Tool steel for cold work marked as K110 belongs to the group of ledeburite steels which, after hardening and low yielding, achieve the structure of martensite + secondary carbides.

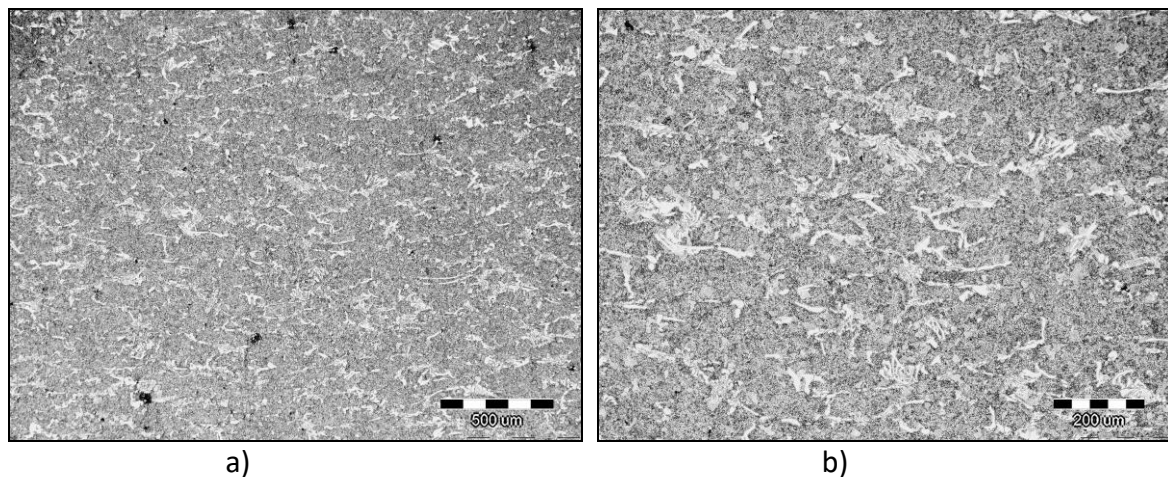a)   b)

Figure 4. Microstructure of K110 tool steel for cold work after etching in Nital:
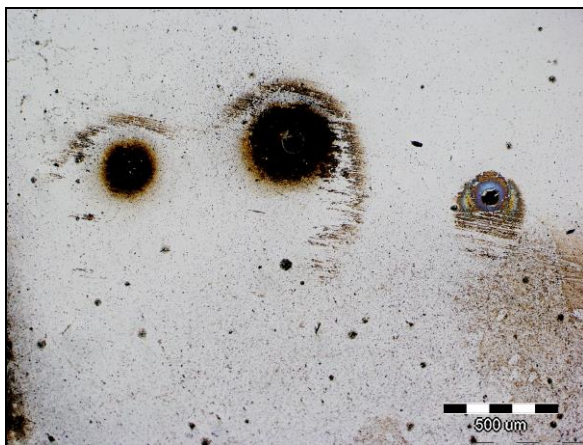a) magnification 50x and b) magnification 100x

Figure 5 shows the microstructures recorded using an optical microscope after electrochemical measurements in tap water and distilled water with the addition of inhibitor. The recorded microstructures of the sample before exposure in the media indicate the presence of inclusions. The inclusions are evenly distributed throughout the cross section. After electrochemical tests in tap water, pits were observed on the sample, i.e. the occurrence of pitting corrosion was detected at the sites of inclusions. The behavior of steel in aqueous solutions depends on the natural oxide layer. It is very important to what extent a thin protective layer of oxide will be formed which will prevent further electrochemical reactions and protect the material from aggressive corrosive media [14]. Local inhomogeneities in the structure of the material can affect the occurrence of pitting corrosion. The formation of hydrated iron oxides depends on the anodic reaction. Namely, the less noble parts of the surface are the anodes where the metal melts due to the action of an aggressive medium. Excess released electrons travel to the nobler parts of the surface that represent the cathodes that bind to oxidants from the environment [10,15].
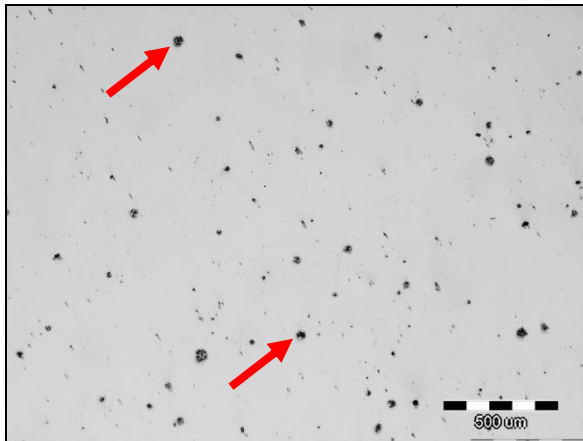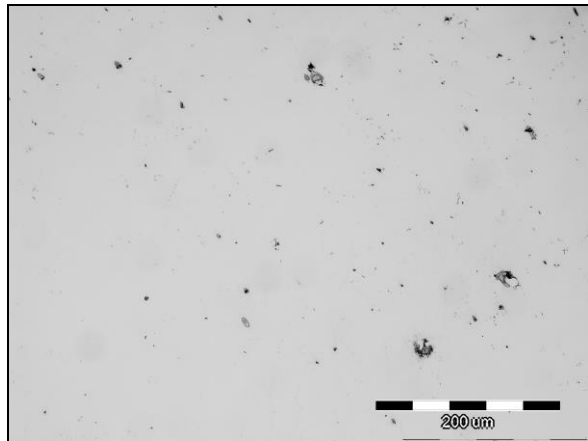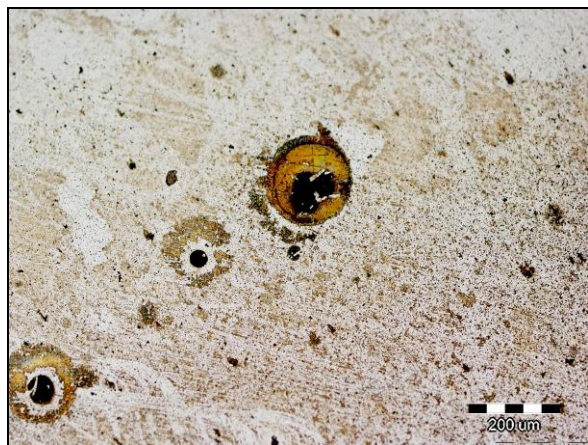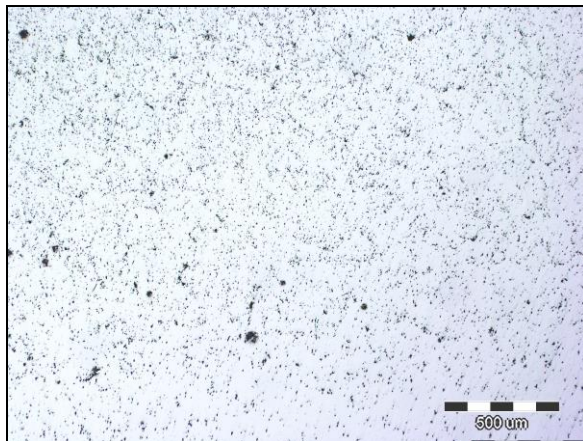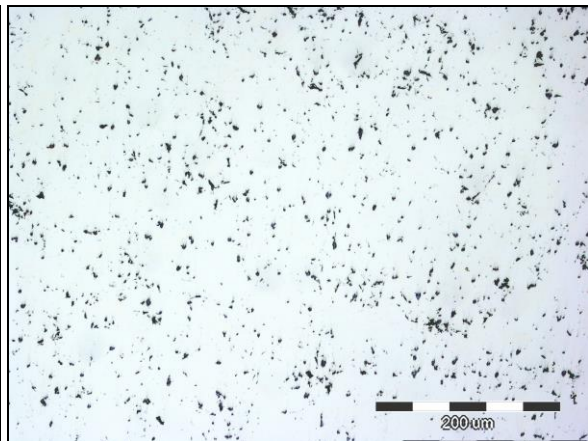
Figure 5. Microstructure of K110 tool steel for cold work: no media, in water, water and 1% inhibitor

No surface damage was observed after testing in distilled water with the addition of a commercial VCI inhibitor. The inhibitor used is water-soluble and forms a water-transparent coating that can be observed in the form of uniformly distributed particles on the sample surface.

CONCLUSIONS

Using electrochemical tests, the results were obtained which indicate that the sample of tool steel for cold work marked as K110 in contact with water is subject to corrosion. However, after testing in a solution of distilled water with the addition of a commercial inhibitor VCI 379/611, a significantly lower corrosion rate v_{corr} and a significantly higher charge transfer resistance R_{ct} were registered. The obtained electrochemical and impedance parameters, as well as the inhibitor efficiency coefficient of 98% indicate that the commercial inhibitor VCI 379/611 is highly effective and is fully applicable in corrosion protection of X153CrMoV12 tool steel intended for cold work. The addition of inhibitors enabled the formation of a barrier on the surface, i.e. the anodic reaction of metal ionization was slowed down. The results obtained by electrochemical tests coincide with the results of metallographic analysis. Metallographic images on a sample that was exposed only to tap water indicate pitting corrosion. After the use of the commercial inhibitor, no corrosion products were observed on the steel surface, because the applied water-soluble inhibitor was adsorbed on the sample surface in the form of uniformly distributed particles. The coating thus formed reduces the number of potential sites on the sample surface for active penetration of the aggressive medium and increases the corrosion resistance of the tested tool steel for cold work.

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