

STUDY OF STAINLESS STEEL RESISTANCE IN CONDITIONS OF TRIBOCORROSION WEAR

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ABSTRACT

Analyzed was the influence of tribocorrosion wear due to effects of fatty acids present in the processed medium. The analysis was conducted on samples made of two austenitic and two martensitic stainless steels. Austenitic steels were tested in their nitrided state and martensitic in their induction hardened state. Conducted were laboratory tests of corrosion resistance of samples, analysis of the microstructure and hardness. To see how the applied processes for modifying the surface of stainless steels behave in realistic conditions, it was conducted the examination of samples/parts of a sunflower cake chain conveyer. Based on the comparison of results obtained in the laboratory and in real conditions, it was estimated that steels AISI 420 and AISI 431 with induction hardened surfaces have a satisfactory resistance to abrasive-adhesive wear in the presence of fatty acids.

KEY WORDS

tribocorrosion, wear resistance, thermally-chemically treated, austenitic and martensitic steels

CLASSIFICATION

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INTRODUCTION

Corrosion adversely affects plant parts and equipment. Direct costs can be seen in terms of the earlier replacement of corroded parts and downtime due to implementation of anti-corrosion protection. Indirect costs are a result of reduction in utilization of installed capacity and/or reduced product quality and thus lower profitability [1]. Failure, or termination of functional performance of parts, usually can appear due to fracture – “breakdown” or as a result of wear, although there are other possible causes. While breakdown is a completely unpredictable – usually instantaneous – process, material wear is mostly gradual, but has a limiting effect on the lifespan of parts. Therefore, one of the ultimate goals of studying the process of wear is to enable parts to function under given conditions with known and acceptable values of friction and wear [2]. Examples of complex wear are especially frequent in the process industry, for example, in food and petrochemical industry. They manifest in combined action of several mechanisms of wear: abrasion, adhesion and corrosion. Therefore, due attention should be given to the study of combined wear. Because, ordinary steels are susceptible to corrosion, and in stainless steels as a problem may occur insufficiently high hardness. In the case of martensitic stainless steels good combination of mechanical properties can be achieved by varying the temperature of austenitising and the duration of annealing [3, 4]. Austenitic stainless steels are widely used because of their excellent corrosion resistance. Wear resistance and surface hardness of austenitic stainless steels is significantly increased in the process of nitriding depending on the duration [5, 6]. Nonetheless, there are limits to the industrial application of this type of steel when exposed to different mechanisms of wear. In this paper we will describe tests that have been carried out in order to compare different corrosion resistant steels exposed to acidic aggressive media in conditions of abrasion-adhesion contact of metal surfaces.

LABORATORY TESTING

In the experimental part of this study electrochemical corrosion resistance tests were performed on stainless steels, in order to simulate the action of acid aggressive media. These tests are intended for the comparison of corrosion resistance of modified surfaces of stainless steels and were the criteria for selecting materials for conducting tests on samples/parts in real conditions. Tests were conducted on samples of stainless steels: austenitic AISI 304L and AISI 316L and martensitic AISI 420 and AISI 431 (ASTM A240) [7]. Since samples of materials of various physical and chemical properties were used their chemical composition is shown in Table 1.

The contact surfaces of austenitic steels AISI 304L and AISI 316L were modified by a Tenifer process of nitriding. The samples were preheated to 380°C for 3 hours, and then immersed in the salt bath at 580 °C for 5 hours and after that cooled in air. Martensitic steels AISI 420 and AISI 431 were induction hardened with treatment parameters: current frequency $f = 19$ kHz, austenitization temperature 1050 °C and emulsion quenchant. Wear resistance of these steels is tested on samples/parts in real conditions where they are exposed to abrasion-adhesion wear with the activity of an acidic medium of a pH 5,02 and the presence of abrasive particles of $\text{SiO}_2 \times n\text{H}_2\text{O}$ of hardness ≈ 6 Mohs.

Table 1. Chemical composition of tested steels.

Steel	C, %	Mn, %	Si, %	Cr, %	Ni, %	Mo, %
AISI 304L	0,03	1,58	0,41	18,30	8,04	0,07
AISI 316L	0,02	1,49	0,53	17,06	10,22	2,44
AISI 420	0,20	0,46	0,32	12,98	0,20	0,06
AISI 431	0,22	0,42	0,43	15,93	2,03	0,03

ELECTROCHEMICAL TESTING OF SAMPLES

These tests were conducted in a saturated aqueous solution with CO₂, the pH value of 5,02 in order to simulate actual conditions of the aggressive environment in which wear of equipment takes place in real conditions. The test samples were made to the dimension of Ø 16×8 mm². Electrochemical tests were conducted in accordance with ASTM G5-94 [8] on the unit Potentiostat/Galvanostat Model 273A EG & E with the use of the software program SoftCorr III. The measurements were made in relation to the reference saturated calomel electrode (SCE) of a known potential of + 0,242 V according to standard hydrogen electrode. Parameters of general corrosion were determined: corrosion potential (E_{corr}), corrosion current density (j_{corr}), corrosion rate (v_{corr}), polarization resistance (R_p), pitting potential (E_{pit}) and protective pitting potential (E_{zpit}).

Determining the corrosion potential E_{corr}

In electrochemical testing the thing that is usually measured is the time change of potential between the electrodes in a galvanic cell through which a weak electric current passes. To determine the electrode potential the electromotive force is measured between the working electrode and a reference electrode of a known and constant potential, which serves as a standard against which to measure the potential of the working electrode. In order to determine the corrosion potential E_{corr} of tested steels as a function of time, the samples were washed in distilled water and degreased in ethanol. Tests were conducted at room temperature.

Determining corrosion parameters using the Tafel extrapolation

Electrochemical nature of the corrosion process enables the use of different electrochemical measurement techniques to determine the intensity of corrosion. There are techniques with direct current (DC technique) and techniques with alternating current (AC technique). In electrochemical testing process of corrosion there were used polarization methods of measurement, potentiostatic and galvanostatic polarization. The objective of measuring is to record the polarization current-voltage graph and based on the anode and cathode curves to get a picture of corrosion behaviour of a certain material in a certain medium. Multiple methods for determining the rate of corrosion are based on potentiostatic polarization, such as the Tafel extrapolation and determining the polarization resistance. In this paper potentiodynamic polarization of potential from -250 mV to +250 mV vs E_{corr} , at a potential change of 5 mV/s, was derived using the Tafel extrapolation method. Results of electrochemical tests of surface-modified samples of selected steels are shown in Table 2.

Results of electrochemical testing shown in Table 2 indicate that the steels AISI 431 and AISI 316L have twice the value of polarization resistance relative to other samples. Values of corrosion current density displayed in Table 2 show that martensitic steels AISI 420 and AISI 431 in their hardened state have the lowest value of corrosion current density among the tested steels. Nitrided austenitic steels have 4 times higher value of corrosion current density.

Table 2. Results of electrochemical tests of samples of corrosion resistant steels.

Steel	State	E_{corr} vs SCE, mV	R_p , Ωcm^2	β_A , V/dek	β_K , V/dek	j_{corr} , $\mu\text{A}/\text{cm}^2$	v_{corr} , mm/god
AISI 304L	nitrided	-108	3282	0,078	0,103	6,62	0,067
AISI 316L	nitrided	+130	5254	0,988	0,039	6,71	0,069
AISIN420	hardned	-480	3246	0,061	0,083	1,32	0,016
AISI 431	hardned	-212	6766	0,042	0,178	1,65	0,018

The values of corrosion rate for martensitic steels are about the same and 3,3 times less than the ones for samples of nitrided austenitic steels. Generally, less value of corrosion current density and corrosion rate indicates higher corrosion resistance, results in Table 2 indicate that Tenifer procedure in tested case gives less corrosion resistance of austenitic samples in relation to hardened martensitic samples. The cyclic potentiodynamic polarization measurements were carried out in a saturated aqueous solution of CO_2 , with a pH value of 5,02. Figure 1 shows diagrams of cyclic polarization testing samples of austenitic steels.

From the diagram of cyclic polarization (Figure 1) it can be seen that samples of nitrided austenitic steels AISI 304L and 316L are not prone to pitting corrosion or crevice corrosion. After recording the curves of cyclic polarization, there were made macro recordings of surfaces of test specimens exposed to electrochemical corrosion. On surfaces of the samples of austenitic steels that were immersed in the electrolyte during the electrochemical tests there are no visible products of corrosion, which is consistent with the literature data [9-11], in Figure 2.

Figure 3 shows overlapping diagrams of cyclic polarization of tested martensitic steels, and Figure 4 macro images of martensitic steel samples after the test.

Diagram of cyclic polarization of martensitic steel samples (Figure 3) shows that the sample of steel AISI 431 shows little inclination top pitting corrosion and crevice corrosion. On the surfaces of samples of martensitic steel that were immersed in the electrolyte during the electrochemical tests there are not visible corrosion products, Figure 4.

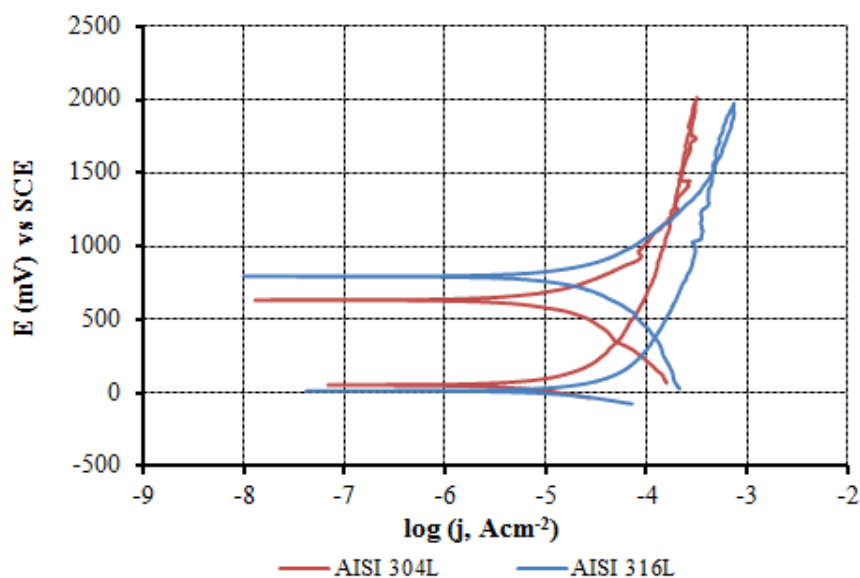


Figure 1. Diagram of cyclic polarization of austenitic steel samples.

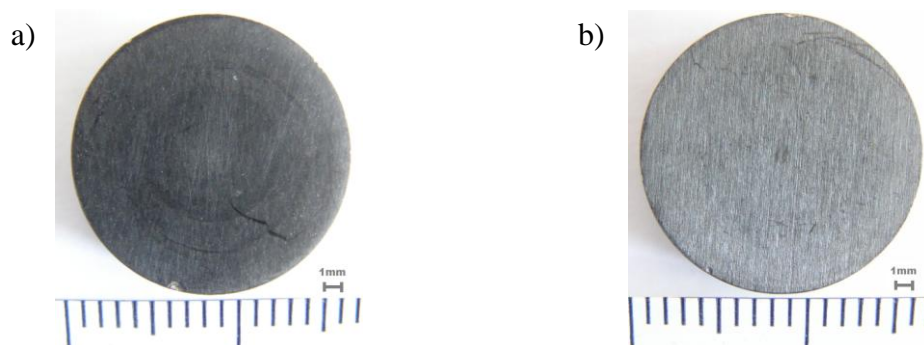


Figure 2. The appearance of the surface samples of nitrided austenitic steels after recording a cyclic polarization curve a) AISI 304L, b) AISI 316L.

Tested steels AISI 420 and AISI 431 in their hardened state showed the best corrosion properties both among the hardened martensitic and nitrided austenitic stainless steels. The achieved corrosion resistance represents good prerequisites for the implementation in a real tribosystem, where in addition to mechanical wear the aggressive action of fatty acids is also present. Therefore, martensitic steels were selected for the implementation of wear resistance tests in real conditions.

MICROSTRUCTURAL ANALYSIS OF MODIFIED SURFACE SAMPLES

Metallographic tests along with hardness measurements provide a complete picture of the material after induction hardening and nitriding. Samples of austenitic stainless steels were corroded with Glycergia and martensitic samples were corroded with solution of HNO_3 and HCl in H_2O . Microstructure of samples of austenitic stainless steels after nitriding is shown in Figure 5.

Metallographic analysis of samples shows that samples of materials AISI 304L and AISI 316L (Figure 5a and 5b) have an austenitic crystalline structure with strong doubles and finely distributed various precipitates. Along the edges of samples there is a clearly visible nitrided layer onto which continues the austenitic structure of the base material.

The characteristic microstructures of induction hardened martensitic steel samples are shown in Figure 6.

Metallographic analysis of specimens of martensitic steels after surface modification by a method of induction hardening, shows undissolved carbides in the martensitic matrix (Figure 6a) and some retained ferrite in the martensitic matrix (Figure 6b).

HARDNESS TESTING OF MODIFIED SURFACES OF SAMPLES

Tests of micro-hardness of austenitic steel samples were conducted with a unit DURIMET Leitz, using the method Vickers HV 0,025 for nitrided samples and HV1 for surface hardened samples. Results of hardness testing of nitrided austenitic samples are shown on diagrams in Figure 7, and induction hardened martensitic samples in Figure 8.

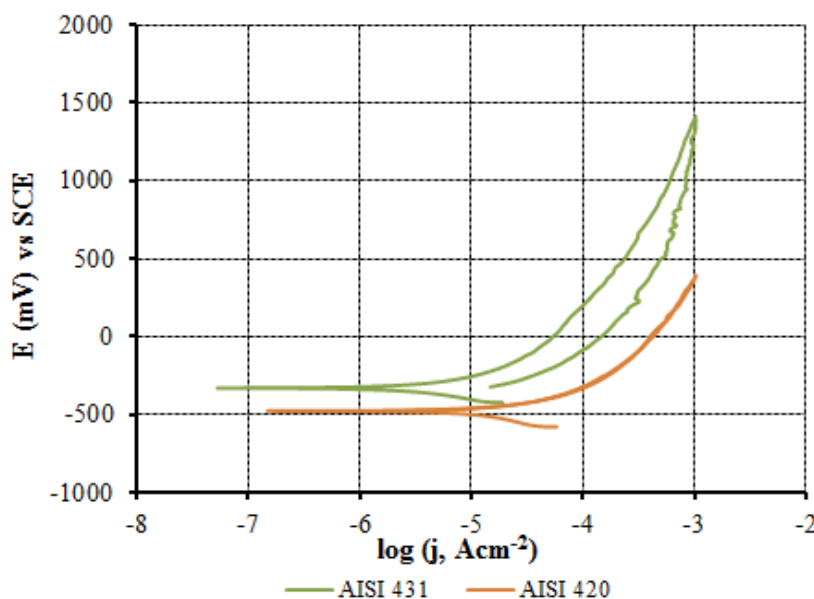


Figure 3. Diagram of cyclic polarization of martensitic steel samples.

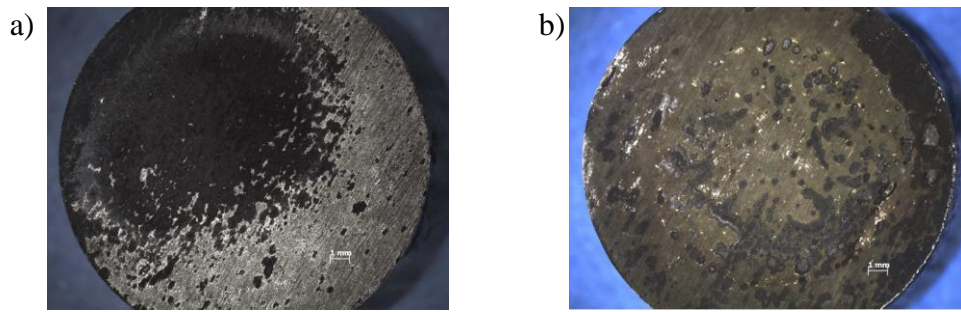


Figure 4. The appearance of the surface of hardened martensitic steel samples after recording a cyclic polarization curve a) AISI 420, b) AISI 431.

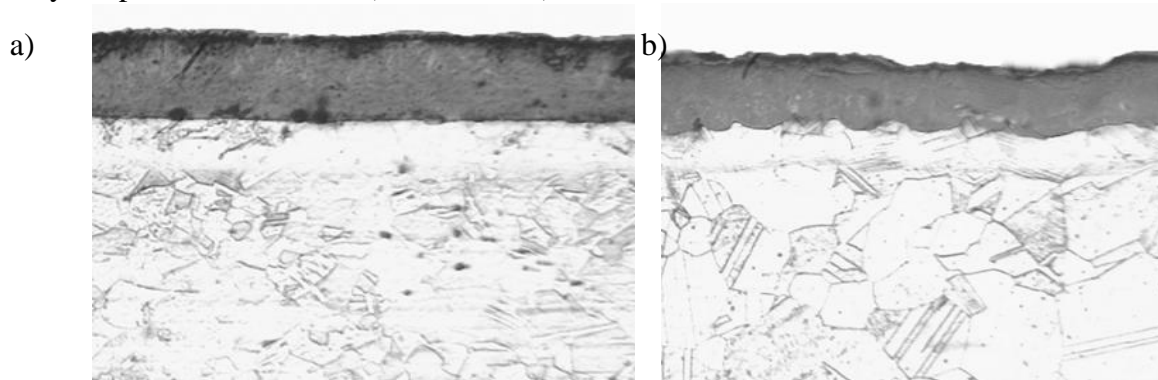


Figure 5. Characteristic microstructure of nitrided steel, magnification of 240:1 a) AISI 304L, b) AISI 316L.

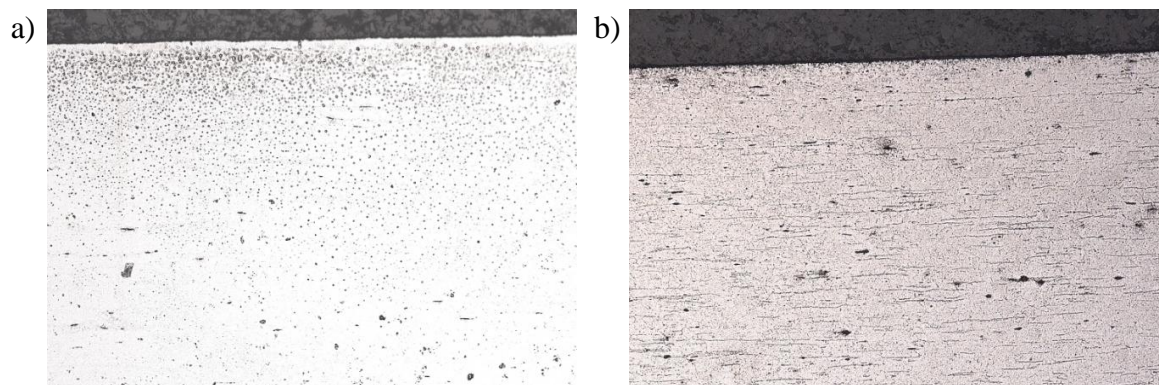


Figure 6. Characteristic microstructure of hardened steel, magnification of 200:1 a) AISI 420, b) AISI 431.

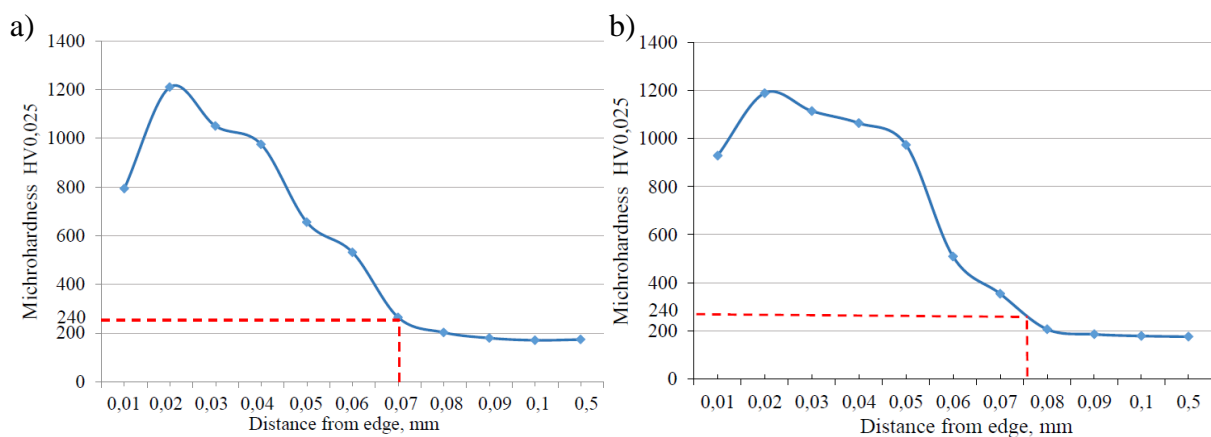


Figure 7. Hardness curve of nitrided austenitic samples, a) AISI 316L, b) AISI 304L.

The values of the microhardness on cross-sections of samples of AISI 304L and AISI 316L measured from the edge to the core (Figure 7a and 7b) show that the microhardnesses of samples are equal (1200 HV0,025 on the surface) and appropriate for the applied procedure for modifying the surface by nitriding. The effective nitriding depth was $NHD = 0,07$ mm for nitrided steel AISI 316L, and $NHD = 0,075$ mm for nitrided steel AISI 304L. Method of Vickers hardness HV1 was used to measure the hardness on cross-sections of induction hardened samples from the edge to the core. The measurement results are shown in the diagrams in Figure 8.

The sample of the steel AISI 420 showed greater surface hardness (610 HV1) relative to the sample of steel AISI 431 which had a surface hardness of (530 HV1), Figure 8. From the hardness curve HV1 according to layer depth measured at the reference line, it is observed the effective depth of surface hardening $SHD = 2,25$ mm for the sample steel AISI 420 and $SHD = 1,25$ mm for the steel AISI 431; diagrams in Figure 8.

TESTING SAMPLES IN REAL CONDITIONS

After the laboratory tests of modified surfaces of stainless steels, martensitic steels AISI 420 and AISI 431 in their induction hardened state were selected for the implementation of wear resistance tests in real conditions. To see the way the surface hardened martensitic steels behave in real conditions of tribocorrosion wear, it was conducted the testing of samples/parts of a sunflower cake chain conveyer, Figure 9.

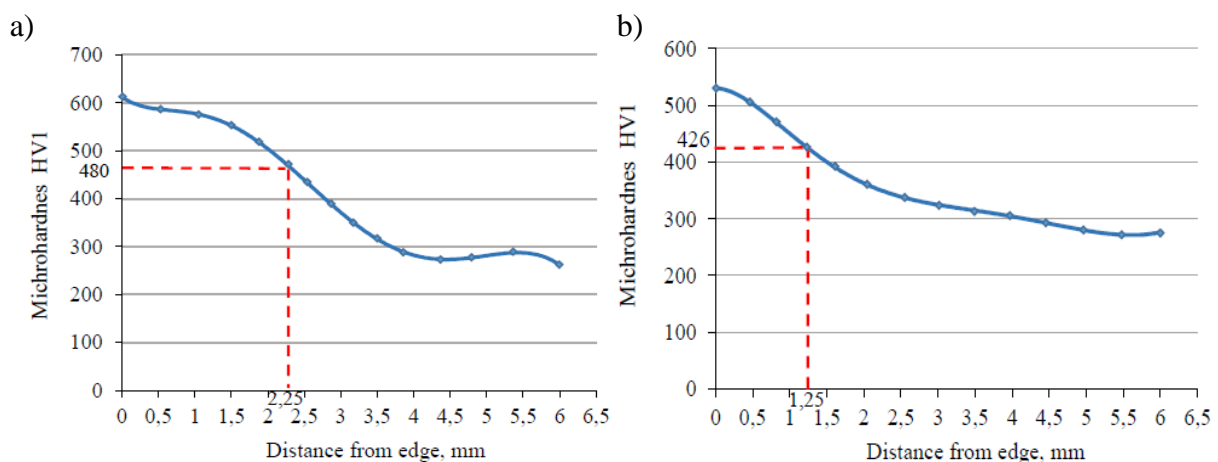


Figure 8. Hardness curve of hardened martensitic samples, a) AISI 420, b) AISI 431.



Figure 9. The appearance of the chain of the elevator

During transport of the sunflower cake, the chain of the elevator operates in conditions of fatty acids present in the sunflower cake, which “aggressively” act on the chain parts. In addition to the aggressive action of fatty acids, another cause of wear for the parts of the chain is also the effect of microabrasive particles of SiO_2 contained in the sunflower cake [9]. Samples of stud bolts were made from selected martensitic steels and built into the chain of the conveyor, and were effectively working for eight months. According to a previous agreement, elevator chain was dismantled and disassembled in order to analyze the wear resistance of test samples of stud bolts. Figure 10 shows a macro image of wear of the sample bolts 1A and 1 in induction hardened state.

In a dimensional control using calipers it was found that there was no construction significant reduction in diameter of bolts. Measured reduction of diameter on induction hardened stud bolts was 0,15 mm for sample 1A (AISI 420) and 0,22 mm for sample 1 (AISI 431). After dimensional control, stud bolts were prepared for recording traces of wear. Recording was performed on a light microscope Leica DM 2500. For the sample of a stud bolt (AISI 420) Figure 11a is showing the traces of wear typical for pure abrasion that is characterized by grooves of different width and depth in the direction of the relative motion of the abrasive/body. Figure 11b is showing the area in which the adhesive wear mechanism is present and where we can see smaller cavities. It is the traction side of the stud bolt 1A, positions P1 and P2.

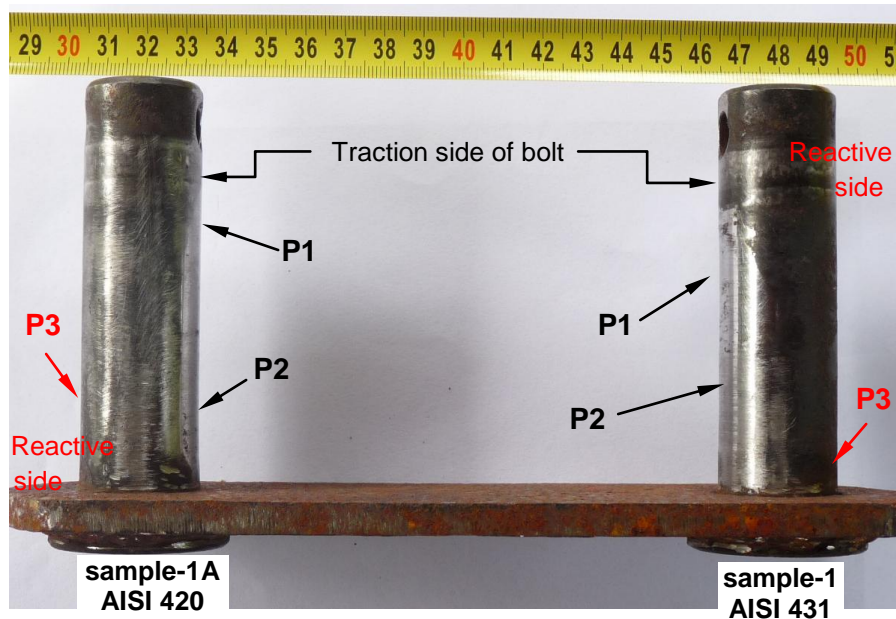


Figure 10. Macro image of wear of stud bolts after tests in use.

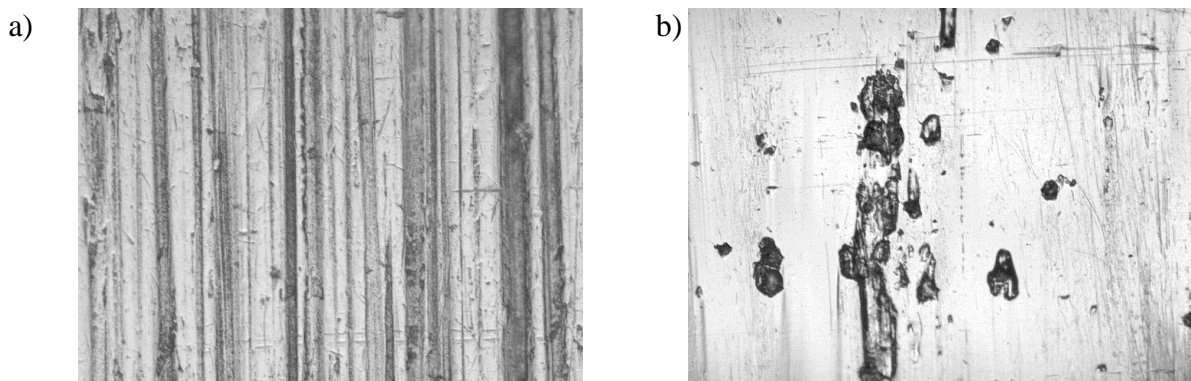


Figure 11. Traces of wear of hardened bolts 1A for the steel AISI 420 a) abrasion, position P1, magnification 100:1, b) adhesion, position P2, magnification 50:1.

Figure 12a shows the area with the predominant adhesion mechanism of wear where we can observe cavities of different size and depth, i.e. places where the particles were torn from the surface. It is the traction side of the stud bolt 1 (AISI 431), positions P1 and P2. The part of the stud bolt sample that is not in contact with the sleeve, reveals corrosion products, position P3, Figure 12b.

The same mechanisms of wear were determined on surfaces of induction hardened stud bolts made of steels AISI 420 and AISI 431, with no evidence of significant differences in intensity of both abrasion and adhesion wear. The reasons for the appearance of abrasion wear should be sought within the sunflower cake content, more precisely in $\text{SiO}_2 \times n\text{H}_2\text{O}$ from the sunflower shell as the main carrier of tribological properties. On both parts of the test bolts that are not in contact with the sleeve (position P3) we can notice corrosion products, resulting from the oxidation and/or chemical reactions with aggressive media.

Figure 13 is showing a macro image of worn samples of the stud bolts 1T (AISI 420) and 2T (AISI 431) in a quenched and tempered (as-received) condition.

From Figure 13 it is evident that the stud bolts in a quenched condition have high wear on the traction side, and the dimensional control measured a reduction in diameter of 5 mm.

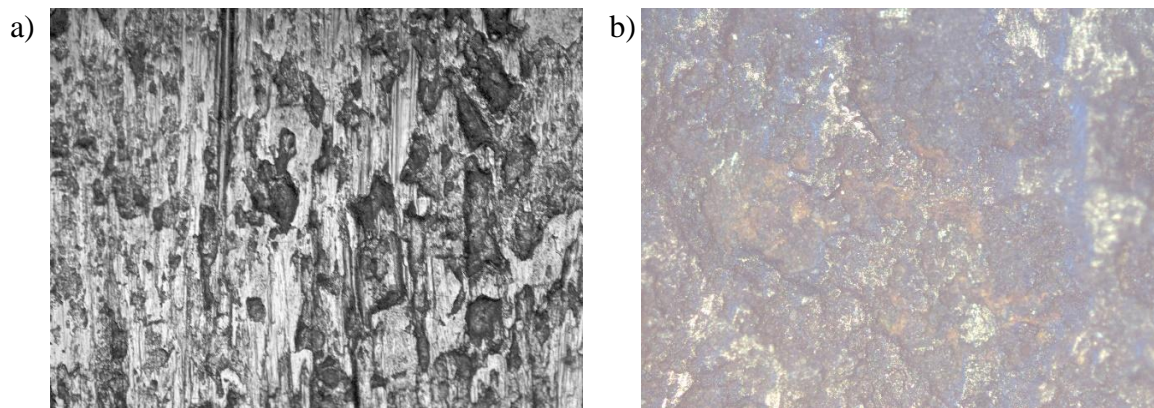


Figure 12. Traces of wear of the hardened stud bolt for steel AISI 431, magnification 50:1, a) adhesion + abrasion, position P1, b) corrosion, position P3.

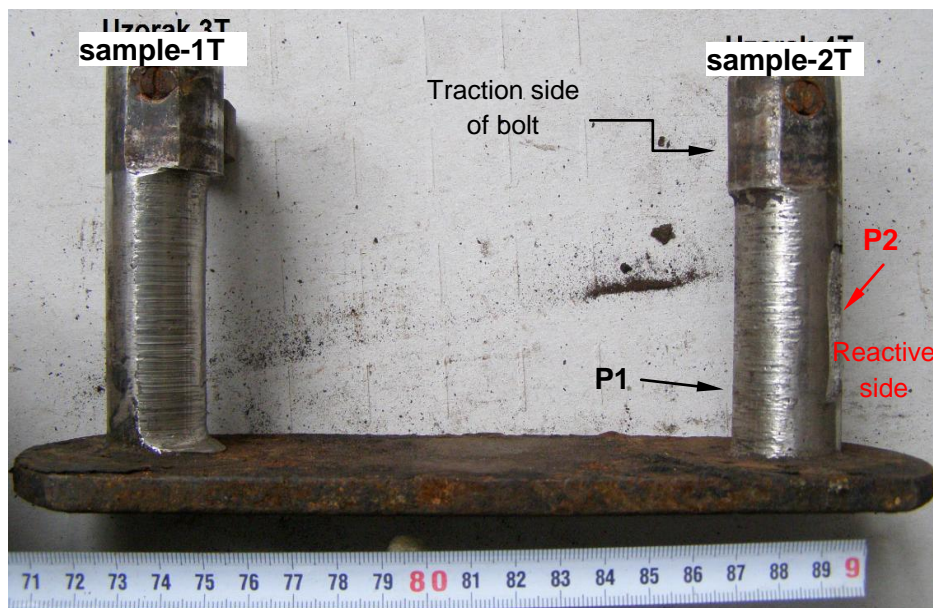


Figure 13. Macro image of wear of stud bolts in a quenched condition, 1T – steel AISI 420 and 2T – steel AISI 431.

Figure 14a shows the traces of abrasion wear at the position P1, and in Figure 14b the resulting corrosion products are on the reactive side of the stud 2T, position P2.

Unlike heat-treated stud bolts, stud bolts in a quenched and tempered condition (as-received) have extreme wear on the reactive side.

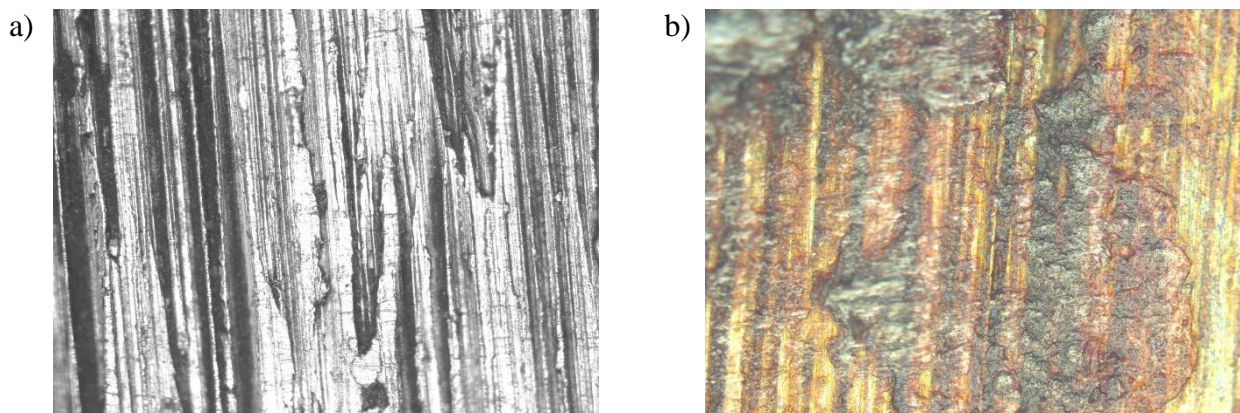


Figure 14. Traces of wear on the traction and reactive side of the stud bolt 4T for AISI 431, a) adhesion + abrasion, position P2, magnification 100: 1, b) corrosion, position P1, magnification 200: 1.

CONCLUSIONS

Application of corrosion protection in industry today lags behind the theoretical knowledge, which is mainly due to reasons of rapid advances in technology of corrosion protection. Numerous studies have shown that one dollar invested in corrosion protection gives from three to six dollars in terms of longer shelf life and higher reliability of equipment [1].

Given the working conditions of process equipment in the oil industry whose parts are exposed to tribocorrosion activity, their lifespan is shortened and there is system failure. Material losses and maintenance costs are increased. There is a risk of fracture of plant elements, resulting in delays in production. When replacing parts care must be taken about the benefits of materials for producing the parts that are to be installed in equipment in relation to the medium in which the equipment is used. It is necessary to know the mechanical and tribological durability in the selection phase of materials during designs. Strength of materials is based on the use of appropriate coatings during long-term exploitation and can extend the life of equipment parts.

On the basis of tests and analysis of the results obtained, it was conclude that between samples, somewhat greater wear resistance was achieved by steel AISI 420. The achieved greater wear resistance can certainly be attributed to the higher surface hardness and effective hardening depth of 2,25 mm for the surface-hardened steel AISI 420 compared to 1,25 mm for the hardened steel AISI 431. Steel AISI 431 has a slightly higher corrosion resistance due to the higher content of Cr and Ni, but from an economic point of view, taking the price of the base material into account, AISI 420 is up to 50 % cheaper than AISI 431. For this reason it is proposed to use the steel AISI 420 for parts that are used in tribocorrosion conditions that are present in transport of sunflower cake.

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