# TRIBOCORROSION WEAR OF AUSTENITIC AND MARTENSITIC STEELS

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This paper explores the impact of tribocorrosion wear caused by an aggressive acidic media. Tests were conducted on samples made of stainless steel AISI 316L, 304L and 440C. Austenitic steels were tested in their nitrided state and martensitic in quenched and tempered and then induction hardened state. Electrochemical corrosion resistance testing and analysis of the microstructure and hardness in the cross section was carried out on samples of selected steels. To test the possibility of applying surface modification of selected materials in conditions of use, tests were conducted on samples/parts in a worm press for final pressing.

Key words: alloyed steels, tribocorrosion, wear resistance, microstructure and hardness, surface modification

### INTRODUCTION

Tribocorrosion is described as a process that leads to the degradation of metallic materials as a result of mechanical contact (sliding, friction, shock...) combined with a corrosive effect [1, 2]. Carbon steels are susceptible to corrosion, and in stainless steels as a problem may occur with insufficiently high hardness, which results in increased wear.

Martensitic stainless steels are used in the manufacture of parts of excellent mechanical properties and moderate corrosion resistance, so they can be used for operation at high and low temperatures [3 - 5].

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 [6]. In this study, tests were made in order to compare austenitic and martensitic stainless steels exposed to tribocorrosion wear.

### **EXPERIMENTAL PART**

During the experimental part tests were carried out on samples of stainless steels: austenitic AISI 304L and AISI 316L, martensitic AISI 440C (ASTM A240) [7], and as control for comparison an "ordinary" steel 42CrMo4 was selected, in quenched and tempered state (EN-10083) [8]. Chemical composition of selected material for the manufacture of test samples is given in Table 1.

The contact surfaces of austenitic steels AISI 304L and AISI 316L were modified by a Tenifer process of

Table 1 Chemical composition of steels / wt. %

Steel	С	Mn	Si	Cr	Ni	Мо
304L	0,03	1,58	0,41	18,30	8,04	0,07
316L	0,02	1,49	0,53	17,06	10,2	2,44
440C	1,05	1,02	0,43	16,71	0,62	0,53

nitriding, and the martensitic steel AISI 440C was induction hardened. Austenitic samples were preheated to a temperature of 380 °C for a period of three hours. After that, they were immersed in a salt bath heated to 580 °C for five hours and air cooled.

Martensitic samples are induction hardened with the following processing parameters: current frequency  $f = 19 \, \text{kHz}$ , 45 % of the energy potential of the inductor, the temperature of austenitizing of 1 050 °C, while the quenching of samples was conducted in an emulsion.

## Electrochemical testing of corrosive resistance of samples

Testing of resistance of samples to electrochemical corrosion was carried out in a saturated aqueous solution with  $\mathrm{CO_2}$ , pH 5 at 50 °C. Electrochemical tests were conducted in accordance with ASTM G5-94 [9] 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. Measurements have determined the parameters of general corrosion: corrosion potential ( $E_{\mathrm{corr}}$ ), corrosion current density ( $i_{\mathrm{corr}}$ ), corrosion rate ( $v_{\mathrm{corr}}$ ), polarization resistance ( $R_{\mathrm{p}}$ ), pitting potential ( $E_{\mathrm{pit}}$ ) and protective pitting potential ( $E_{\mathrm{Z}_{\mathrm{pit}}}$ ). Table 2 shows the measured corrosion potentials and the results obtained by an examina-

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Table 2 Results of electrochemical testing of samples

Steel/state	E vs SCE / mV	i <sub>corr</sub> / μΑ/cm²	v <sub>corr</sub> / mm/year	$\frac{R_{\rm p}}{\Omega {\rm cm^2}}$
304L nitrided	- 108	6,62	0,067	3 282
316L nitrided	+ 130	6,71	0,069	5 254
440C hardened	- 550	6,10	0,067	5 058
42CrMo4 tempered	- 708	86,62	1,003	250

tion of Tafel curves of surface modified samples of selected materials.

The greatest value of the corrosion potential of the analyzed samples has the nitrided steel AISI 316L, indicating that in the steel leads to spontaneous passivation and reduction of the corrosion rate in comparison to the other samples.

Results obtained by analyzing the Tafel curves shown in Table 2, indicate that the steels AISI 316L, AISI 304L and AISI 440C have substantially higher values of polarization resistance  $R_{\rm p}$  relative to the steel 42CrMo4 that has up to twenty times lower value of polarization resistance. The values of corrosion rate of stainless steels are equal while the steel 42CrMo4 has 14 times higher corrosion rate compared to stainless steels. Cyclic potentiodynamic polarization measurements were carried out in a saturated aqueous solution with CO<sub>2</sub>, the pH value of 5,02 at 50 °C.

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. Diagram of cyclic polarization for the samples of martensitic steel AISI 440C and the control 42CrMo4 shows that these samples have an increased inclination to pitting and crevice corrosion.

# Analysis of the microstructure of test samples

Microstructure of samples was analysed on light microscope Leica 2500 M. Samples of stainless steels

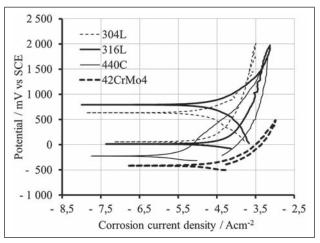
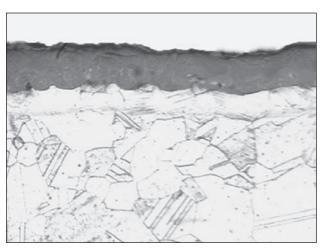


Figure 1 Diagram of cyclical polarization of test samples



Figure 2 Microstructure of nitrided steel 304L, etchingglycergia, 240x



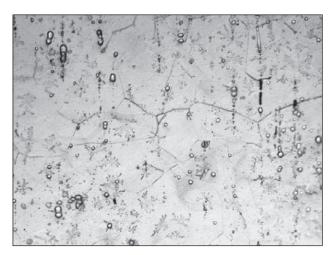
**Figure 3** Microstructure of nitrided steel 316L, etchingglycergia, 240x

were etched with a glycerin mixture. The microstructures of the nitrided samples AISI 304L and AISI 316L were shown in Figures 2 and 3.

Metallographic analysis of samples shows that samples of materials AISI 304L and AISI 316L have an austenitic crystalline structure with strong doubles and finely distributed precipitates. Along the edges of samples there is a clearly visible nitrided layer onto which continues the austenitic structure of the base material. Thickness of the compound layer for the sample AISI 316L is 21 microns, and sample 304L 23 microns. Typical microstructure of hardened martensitic steel AISI 440C is shown in Figure 4. Microstructure of hardened samples of AISI 440C shows that the sample has a martensitic structure with dispersed carbides within the martensitic matrix and some retained austenite.

### Hardness testing of test samples

Tests of micro-hardness of samples of austenitic steels are conducted with the unit DURIMET Leitz, Vickers method HV0,025 and HV1. Hardness results of the samples are shown in Figure 5 and Figure 6. The values of the microhardness on cross-sections of samples of AISI 304L and AISI 316L measured from the



**Figure 4** Microstructure of hardened steel 440C, etchingglycergia, 500x

edge to the core (Figure 5) show that the microhardnesses of samples are equal (1 200 HV0,025 on the surface) and appropriate for the applied procedure for modifying the surface by nitriding. Effective depth of nitration is: NHD = 0,07 mm for nitrided steel AISI 316L and NHD = 0,075 mm for nitrided steel AISI 304L, Figure 5.

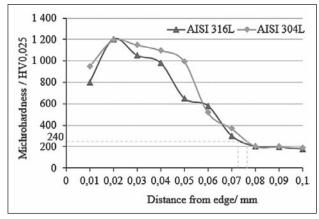
Method of Vickers hardness HV1 was used to measure the hardness on cross-sections of induction hardnesd samples from the edge to the core. The measurement results are shown in the diagram in Figure 6.

The flow of hardness HV1 by depth of the layer measured at the reference direction, shows an effective hardening depth SHD = 1,25 mm for the sample (material AISI 440C), diagram on Figure 6.

Measured hardness values of the quenched and tempered sample of cast steel (material 42CrMo4) are ranging from 230 to 280 HV 0,5.

### Testing samples in real conditions of tribocorrosion wear

After analyzing the test results of corrosive resistance of samples, austenitic steels AISI 304L and AISI 316L in nitrated state have showed better resistance to



**Figure 5** Display of the flow of hardness for the tested samples, nitrided 304L and 316L

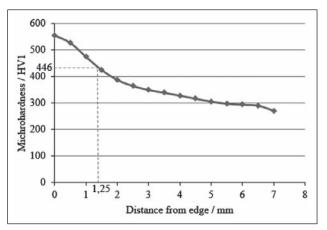


Figure 6 Display of the flow of hardness for the tested sample

pitting corrosion and crevice corrosion unlike hardened martensitic steel AISI 440C and the control 42CrMo4.

Therefore, austenitic steels were selected for the implementation of the wear resistance tests under real conditions, where they were exposed to abrasive wear-adhesion effect with an acidic medium of pH around 5,0 in the presence of abrasive particles  $SiO_2x$  nH<sub>2</sub>O hardness  $\approx$  6 Mohs.

Semi-rings were made from the test material (AISI 304L and 316L) with nitrided surfaces. After the semirings were used for two work cycles of a screw press with the final pressing capacity  $\approx 100$  t/day, according to a previous agreement, the press was dismantled in order to remove the tested semi-rings. Dimensional control using a movable scale has found that there was no decrease in the thickness of either semi-ring, and the measured thickness for all was 7 mm, except for the damage caused by dismantling, Figure 7. There was also a detailed review of the external and internal surfaces of test semi-rings under scanning electron microscope (SEM), Figure 8. The same mechanisms of wear were determined at semi-rings made of various materials, whereby there was no evidence of significant difference in intensity, both of abrasion and adhesion, as well as corrosion, irrespective of the differences in chemical composition. The first two mechanisms of wear are more present on the outside of the semi-ring, while the third mechanism is more present on the inside.



Figure 7 Test semi-ring after use

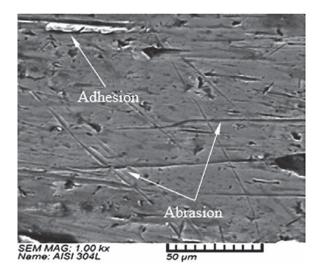


Figure 8 SEM display of outer surface of test semi-ring

The reasons for the appearance of abrasion wear should be sought within the sunflower cake content, more precisely in SiO<sub>2</sub> x nH<sub>2</sub>O from the sunflower shell as the main vehicle of abrasive properties of sunflower shells. The occurrence of pitting corrosion can be explained by the presence of the so-called "acid humidifying".

By detailed examination of the exterior surfaces of all semi-rings, observed under scanning electron microscope, it was found that we can find traces incurred as a result of abrasive wear by fine grind particles, then adhesion due to the contact of the semi-ring of the gearbox door with the semi-ring of the fitting surface, but also corrosion damage.

### **DISCUSSION AND CONCLUSION**

After the examination and analysis of the results obtained, it can be concluded that the tested samples of steel AISI 316L and 304L have equal depth of the nitrided layer. The values of hardness at the cross-section of both test samples are uniform, and are in the range  $800-1\ 200\ HV$ , which represents good prerequisites

for the use in the tribosystem of the screw press. AISI 316L has a slightly higher corrosion resistance, but from an economic standpoint, taking the price of the base material into account, AISI 304L is 45 % cheaper than 316L, so it is recommended to use the steel AISI 304L for parts under tribocorrosion conditions present in the vegetable oil screw press.

### **REFERENCES**

- S. Mischler, S. Debaud, D. Landolt, Wear-accelerated corrosion of passive metals in tribocorrosion systems, Journal of the Electrochemical Society 145 (1998) 3, 750–758
- [2] J. P. Celis, P. Ponthiaux, F. Wenger, Tribo-corrosion of materials: interplay between chemical, electrochemical, and mechanical reactivity of surfaces, Wear 261 (2006) 9, 939–946
- [3] A. Nasery Isfahanya, H. Saghafiana, G. Borhanib, The effect of heat treatment on mechanical properties and corrosion behavior of AISI 420 martensitic stainless steell. Journal of Alloys and Compounds 509 (2011) 9, 3931–3936
- [4] S. Dodds, A. H. Jones, S. Cater, Tribological enhancement of AISI 420 martensitic stainless steel through friction-stir processing, Wear 302, (2013) 1-2, 863-877
- [5] H. Arabnejad, S. A. Shirazi, B. S. McLaury, H. J. Subramani, L. D. Rhyne, The effect of erodent particle hardness on the erosion of stainless steel, Wear 332 (2015) 1098–1103
- [6] T. Kumar, P. Jambulingam, M. Gopal, A. Rajadurai, Surface hardening of AISI 304, 316, 304L and 316L using cyanide free salt bath nitriding process, International Symposium of Research Students on Materials Science and Engineering, Chennai India, 2004, pp. 1-11
- [7] ASTM A240 Standard Specification for Chromium and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Pressure Vessels and for General Applications, 2004.
- [8] EN 10083-1 Steels for quenching and tempering, General technical delivery conditions, 2006.
- [9] ASTM G5-94 Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements, 1999.

Note: The responsible translator for English language is prof. Martina Šuto, University of Osijek