

## TRIBOCORROSION TESTS OF DUPLEX STAINLESS STEELS 22-05

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## TRIBOKOROZNÍ ZKOUŠKY ANTIKOROZNÍ DUPLEXNÍ OCELI 22-05

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### Abstrakt

Tribokorozní zkoušky se zabývají procesy vyvolávající poškození kovových materiálů, za společného působení tření a koroze. Pro testy byl použit přístroj typu pin-on-disk, přizpůsobený pro práci v korozním prostředí. Byly studovány především korozní a pasivační reakce v anodické oblasti a jejich ovlivnění třením a to na nerezavějící dvoufázové austeniticko-feritické oceli typu 22-05 a zároveň se sledoval vliv tření na elektrochemickou reaktivitu třených povrchů. Měřením mikrotvrdosti ve třecí stopě bylo zjištěno zpevnění povrchu vyvolané třením. Prokázalo se, že toto zpevnění neovlivňuje citelně reaktivitu povrchu zkoušené duplexní oceli. Dále bylo pozorováno, že destrukce povrchových vrstev třením, urychluje korozní rozpouštění kovů. Zároveň bylo experimentálně dokázáno, že přítomnost těchto korozních a pasivačních vrstev ovlivňuje podmínky tření, a to zejména koeficient tření. Prováděné práce ukázaly nutnost detailnějšího popisu: elektrochemických parametrů, mechanického kontaktu a strukturních vlastností materiálu na lokální úrovni a zároveň na nutnost popisu interakce mezi třeným a netřeným povrchem kovu (galvanických článků, distribuce potenciálů a proudů).

### Abstract

The effects of combined damage processes of friction and corrosion on metallic materials were studied by tribocorrosion tests. A pin-on-disk type apparatus modified to corrosion environment was used for these tests. The study was focused especially on the influence of friction on corrosion and passivation reactions in the anodic region. An austeno-ferritic duplex stainless steel was used for the tests. Hardening of surface was determined by measuring the micro-hardness in a friction trace as a result of wear. It was found that hardening of the surface, caused by the friction, does not significantly influence the surface reactivity of the metallic material. Acceleration of corrosion dissolution by destruction of the surface layers by friction was observed as another result. Concurrently, it was

experimentally proved that presence of these corrosion and passivation layers influences the friction conditions, particularly values of friction coefficients. The results show that there is a need of precise description of the following characteristics: electrochemical parameters, mechanical contact and structural properties of materials at the point of friction, as well as interactions (galvanic cells, potential and current distributions) between different locations on the surface of metal.

## 1. INTRODUCTION

Corrosion is an important degradation process leading to damage of metallic materials. In order to decrease or completely eliminate this negative phenomenon, a proper material selection is needed such as using of high alloyed anticorrosion steels. These steels form a protection layer, the so-called, passive film, on the metal-environment interface. This barrier, mainly consisting of chromium oxide, protects against corrosion and decreases or eliminates the corrosion rate [1,2]. An external load or friction can damage these protective layers and, though a process of regeneration of the film follows, the surface of the steel is exposed to the aggressive environment for a certain time.

Tribocorrosion describes the processes leading to degradation of the properties of metallic materials by a combination of friction (from Greek *tribos* = friction) and corrosion. Processes of tribocorrosion include a number of parameters: mechanical and electrochemical, which are involved in a complex interaction [3, 4]. The understanding of this interaction requires the analysis of tribocorrosion processes and real time analysis of their variations. Studies are focused especially on the normal and tangential (response of system) forces, and corrosion rates. Among others, following parameters have to be included: the characteristics of the contact, properties of contact surfaces (hardness, structure, stresses), chemical composition (passive layers and corrosion products) and wear.

The aim of this work is to study and explain these interactions, particularly the corrosion and passivation reactions on anodic area, their influence on friction and the influence of friction on the electrochemical activity. The emphasis was put on the hardness and structure of the friction trace as well.

## 2. EXPERIMENTAL MATERIAL

For experiments, a duplex stainless steel (DSS) supplied by Vítkovice a.s was used. The chemical composition of the steel is shown in Table 1. Due to its mechanical properties and good corrosion resistance, this steel is suitable for wide range of uses (chemical plants, nuclear reactors, food industry, transport, mining, oil and gas processing) [5].

Table 1 Chemical composition of duplex stainless steel 22-05

It is a two-phase steel consisting of 50% of ferrite ( $\alpha$ ) and 50% of austenite ( $\gamma$ ). The exact ratio of the phases depends on previous heat treatment and on orientation in respect to the rolling direction (Figure 1a). Theoretically, it is possible to obtain 100% of ferrite in structure by water quenching from temperature of approx. 1300°C [6,7]. For the tests, cylindrical samples (25 mm in diameter, 25 mm high) were prepared from a plate with thickness of 80 mm. In order to ensure homogenous structure, the samples of dimensions 30 x 30 x 200 mm were prepared from the top and bottom part of the plate (i.e. without the central part, which may contain defects). These samples were consequently submitted to the following heat treatment at 1050°C/2 hours/water quenching

Due to the elongation of the structure in the rolling direction, the tests of mechanical properties were carried out in the two perpendicular directions. The results of the tension tests showed minimal differences in mechanical properties in these two directions (see Table 2). In order to ensure a uniform distribution of ferrite and austenite, the specimens were prepared in the orientation parallel to the rolling direction and thus points of friction are on the plane perpendicular to the rolling direction (see Figure1).

Table 2 Mechanical properties of the used austeno-ferritic duplex stainless steel

a)

b)

Fig.1 Microstructure of duplex stainless steel 22-05 after heat treatment 1050°C/2 hours/water  
a) in the rolling direction b) perpendicularly to the rolling direction

### 3. EXPERIMENTAL EQUIPMENT AND TECHNIQUES

No standard tribocorrosion test exists, but the testing unit, the so-called tribocorrosimeter, designed and constructed in the first part of the work, was a classical pin-on-disk tribometer modified to work in corrosive environment and to implement electrochemical methods for corrosion testing (see Figure 2).

Similar arrangement was used previously by [8]. Compared to this arrangement, the new device enables continual regulation of normal force. The tribocorrosimeter is based on a modified hydraulic-mechanical testing device manufactured by the company DARTEC. The conventional jaw has been replaced by a special electrically isolated component with friction pin holder. In this work, the friction pin is made of sintered  $Al_2O_3$ , so as it does not form a galvanic cell with the tested sample. In addition, it is inert in the used environment ( $H_2SO_4$  0.5M) and it is moreover sufficiently strong ( $E = 400$  GPa) in order that its deformation and wear can be neglected. Various friction pins can be used with this tribometer. In this study, a pin with a spherical end, 10 mm in diameter, was used. The rotation of the pin generates a 16 mm diameter friction trail on the surface of the specimen.

Electrochemical tests are carried out in a working cell made of Perspex 160 mm in diameter and 80mm high, with platinum counter-electrode (diameter 140mm). The tested specimen is connected as working electrode. Standard SSE (Hg/Hg<sub>2</sub>SO<sub>4</sub>/sat. K<sub>2</sub>SO<sub>4</sub>) is used as a reference electrode. Potentiostat of EG&G society is used for application of voltage. All polarisation curves presented in this paper are corrected from the ohmic drop due to the electrolyte resistance. Normal ( $F_n$ ) and tangential ( $F_t$ ) forces, electrochemical potential (E) and current (I) are recorded continuously and processed simultaneously with help of computer card for data processing, that calculates the friction coefficient ( $\mu = F_t/F_n$ ). A computer controls the potentiostat. The rotation speed of the pin is also controlled and recorded by the computer. Different experimental techniques are used: wear determination by weight losses measurements, observation of surface by optical microscopy or scanning electron microscopy, measurement of microhardness and observation of the transversal profiles of the wear trail.

#### 4. RESULTS AND DISCUSSIONS

To separate the influence of corrosion and friction, the electrochemical tests with and without application of friction were carried out under similar electrochemical conditions. In addition, electrochemical tests with only rotation of friction pin end approximately 1 mm above the surface were carried out to study the effect of electrolyte convection on the electrochemical behaviour.

##### *Tests without friction:*

The tests with rotation of the pin but without application of friction were carried out mainly to show the influence of stirring on electrochemical parameters in the anodic region. When the rotation speed of the pin increased, the anodic current in the active dissolution potential domain (between +500 and +1200 mV/SSE) increased too (see Fig.3). At the same time, no change of potential of maximum current (+870mV/SSE) was observed and the potential did not depend on the rotation speed of the friction pin. This behaviour indicates that mass transfer limits the dissolution current. The increase in the rotation speed increases the rate of mass transfer and, as a result, the dissolution current. In the passivation domain (between the rest potential and +500mV/SSE), no variations of the passive current were observed when the rotation speed was changed.

##### *Tests under friction:*

The dependence of the  $E_{free}$  potential  $E_{free}$  on time with and without friction is shown in Figure 4. The value of the free potential is characteristic of the development of a passive film. The initial value (-830 mV/SSE) corresponds to the initial material state without any passive film. Before the experiment, this film is removed by polishing the surface up to 1  $\mu$ m diamond paste. The value of  $E_{free}$  stabilised at -250 mV/SSE. In the corrosive environment, the passive film forms.

The passive film, consisting of Cr<sub>2</sub>O<sub>3</sub>, formed a barrier against dissolution and its formation was accompanied by a rapid change of potential to values of specimens without friction, about -750 mV/SSE (see Figure 4, graph without friction).

Further, it was observed that the passive current increased with  $\omega$  in the passive domain of the polarisation curve under friction. This indicates the destruction of the passive film by the motion of the pin on the friction trail. On the areas where the passive film is destroyed, dissolution occurs with high anodic current density, increasing the total current.

Fig.3 Influence of stirring on the anodic domain of the potentiodynamic polarisation curves.

The potential was increased at a scan rate of 100mV/min.

Fig.4 Evolution of the free potential  $E_{\text{free}}$  without ( $\omega = 0$  revs/min.,  $F_n = 0$  N)  
and with friction ( $\omega = 40$  revs/min.,  $F_n = 20$  N).

### **Synergy:**

Tribocorrosion tests clearly showed synergy between the electrochemical state of the metal and the tribological conditions, characterised by the friction coefficient  $\mu$ . Figure 5 shows the evolutions of normal force and free potential during one revolution of the friction-pin. Long period variations of  $F_n$  and  $E_{\text{free}}$  are associated to perturbations of hydraulic regulation of the normal force generated by instabilities of the contact conditions during friction. These instabilities, due to microwelds, microcutting, and plastic deformation processes, occurring during friction, generate also the rapid fluctuations observed in figure 5. These processes provoke short time halting of friction pin and increase in normal and tangential forces at the same time.

Fig.5 Fluctuations of the normal force and free potential during one turn of the friction pin.  
(Conditions:  $F_n = 50$  N,  $\omega = 40$  revs/min.)

It must be noticed that fluctuations of  $E_{\text{free}}$  are generated by the local damages generated on the contact area by the above-mentioned mechanical processes (microwelds, microcutting, plastic deformation...), that destroy the passive film.

The next figure (see Figure 6) shows the evolution of the friction coefficient together with the evolution of the current during the potentiodynamic sweep from -1200 mV/SSE to +1200 mV/SSE, i.e. the influence of electrochemical parameters on the friction coefficient. The diminution of the friction coefficient in the first stage of the potentiodynamic scan (up to -1100 mV/SSE) is a result of two phenomena:

accommodation of the surfaces in contact by plastic deformation of the metal in the friction trail during the first revolutions of the pin,

hydrogen evolution : hydrogen seems to act as a lubricant.

The vanishing of hydrogen evolution and the change from cathodic to anodic current above -750 mV/SSE corresponds to a moderate increase of the friction coefficient followed by a stabilisation between -500 and +450 mV/SSE, where the dissolution of tested metal commences. From this potential value up to +1200 mV/SSE, the corrosion products form a lubricating film between pin and metal, which results in the decrease of the friction coefficient.

Fig.6 Evolution of friction coefficient  $\mu$  under potentiodynamic polarisation ( $F_n = 20$  N,  $\omega = 10$  revs/min)

### ***Influence of tribocorrosion on structure and hardness:***

Duplex stainless steels offer benefits over austenitic stainless steels and carbon steels because of their higher strength, good toughness and ductility, in combination with equivalent resistance to

general corrosion. Problem with duplex is in their selective dissolution of ferrite in anodic region [9], so that only austenite remains in friction trail. By using a scanning electron microscope and local chemical analysis (EDS) the friction trail was observed. By measuring the content of Cr, Ni and Mo in ferrite and austenite, the trace was found to contain 100% of austenite. Figure 7a present the global view at surface with attacked ferrite, figure 7b internal side of friction trail. In friction trail, only austenite is present. It is very important to take in account this evolution of the metal surface for industrial applications, if the DSS is used in aggressive environment under friction, because the resistance of austenite and ferrite to corrosion are different.

a)

b)

Fig.7 Photos of surface after the tribocorrosion test. Global view at surface on the left hand-side and internal side of friction trace on the right-hand side. Conditions of test  $\omega = 60$  revs/min.,  $F_n = 75$  N.

Among other parameters, the change of microhardness was influenced by friction. In the friction trail, the microhardness increased significantly from about 250 HV<sub>0,02</sub> at the edge to 1000 HV<sub>0,02</sub> in the centre. By comparing with the curve of hardening after rolling, it can be deduced that deformation up to 100% or more can be obtained in the present case [6].

## 5. CONCLUSIONS

For tribocorrosion tests no standards exists and thus every laboratory dealing with this subject uses different methods. The advantage of our pin-on-disk system with hydraulic regulation of normal force is stable electrochemical conditions. It is a result of constant speed of friction head and continuous contact between pin and surface. The present work showed the relationship between different parameters (I, E,  $\mu$ , structure) included in the tribocorrosion measurements. The necessity of observation of solution convection caused by the rotation of friction head was shown. This convection changes the kinetics of electrochemical reactions involved in the corrosion process. It seems to be evident that, there is a synergy between electrochemical conditions and mechanical response of the system: the influence of corrosion products on the friction coefficient was clearly pointed out as well as a strong effect of the damage to the passive film, caused by friction, with the result of an increased electrochemical activity. The investigation of structural mechanical and electrochemical changes in the friction trail is of prime necessity for materials selection in industry.

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