THE INFLUENCE OF ULTRASOUND VIBRATION ON THE PITTING CORROSION OF AISI 316 STAINLESS STEEL

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The influence of ultrasound vibration on pitting corrosion of AISI 316 stainless steel was investigated using galvanostatic polarization and weight-loss techniques in Cl-containing solutions at 20 and 50 °C. Pitting resistance basis was calculated from potential-time dependences and SEM surface analysis was performed after anodic treatment. Both galvanostatic polarization and weight-loss revealed efficient pitting corrosion suppression. The pitting resistance basis increased at least in 100 mV and the weight of dissolved metal decreased in 4-6 times when steel was vibrated with ultrasound. The results obtained are explained in terms of competitive adsorption theory, as increased supply of oxygen.

Pitting corrosion is one of the most widespread and insidious forms of localized corrosion of passive metals, and commonly occurs in a range of aggressive environments. Stainless steels are resistant against general corrosion by forming a passive film, but they are vulnerable to pitting corrosion, which is initiated by the partial breakdown of the protective film on the metal surface [1]. The successful use of stainless steels in chloride-containing environments depends on their ability to resist localized attack.

Various approaches have been utilized to enhance the corrosion resistance of stainless steels. In recent years the pitting corrosion of stainless steel in the ultrasound field was intensively investigated, however the results remain contradictory. The irradiation of water by ultrasonic waves gives rise to the formation of cavitation bubbles [2]. It is frequently reported that the corrosion rate of metal in specific liquids can be accelerated by acoustic cavitation. In the studies [3,4] were investigated the effect of ultrasound frequency, horn distance, temperature and pressure on the corrosion of stainless steel exposed to ultrasound. Ultrasound increased the corrosion rate under all the investigated conditions. However, it was noted, that ultrasound enhances the corrosion rate of a metal if, and only if, the solution is inherently corrosive to it. This also means that stainless steel is completely resistant to ultrasonic erosion. In work [5] ultrasound was found to switch

the metal between active and passive corrosion states. When the metal is corroding actively, sonication increases the corrosion rate by a factor of between 3 and 6. Sonication also encourages passivation to occur earlier than it would have done in the absence of ultrasound. When the metal is passive, sonication promotes the breakdown of passivity and accelerated corrosion proceeds whilst sonication is continued.

On the other hand, it was reported [6] that the pitting corrosion and the crevice corrosion of SUS304 stainless steels were found to be largely suppressed by the application of an ultrasound. US was found to promote repassivation of pits [7,8]. The reason is attributed to the decrease of the enrichment of hydrogen and chloride ions in the pits by removing the corrosion product and stirring the liquid there. So, in general US accelerates corrosion of metal in active state, while promotes passivation for metals in passive state.

Despite positive results being obtained in the works [6–8], in practical application it is not always possible to expand the cavitation field far from US horn. Cavitation field radius usually does not exceed 100-700 mm around horn [9]. However, US vibration of a metal can expand on much higher distances, i.e. US is widely used for nondestructive testing of materials [10]. So, this work was aimed to study the influence of US vibration on pitting corrosion of a stainless steel. The US horn was attached to the stainless steel plate, not immersed in the water, to cause it's vibration on the US frequency.

Research methodology

Commercially supplied heat exchanger plate (thickness: 0.2 mm) was cut into stripes and used as a material in the corrosion tests. Chemical composition of AISI 316 stainless steel was C: 0.08 mass%, Si: 0.28%, Mn: 1.08%, P: 0.040%, S: 0.020%, Cr: 16.1%, Ni: 10.8%, Mo 2.15%, Fe: balanced. In the case of galvanostatic pitting corrosion test, the plate was cut to be 200 mm x 20 mm rectangular shape. The central area of 10 mm x 10 mm in the bottom part was used as the test area and the remaining area was sealed with enamel. The series of NaCl solutions were prepared with different Cl^- concentrations (table 1). Cl^- concentrations lower than 150 mg/l was not used due to low conductivity, while 350 mg/l − is a maximum chloride concentration in potable water according to Ukrainian standards.

All corrosion tests were carried out in a corrosion cell connected to a potentiostat and an ultrasound unit (Fig.1). 28 kHz ultrasound with electrical input power of 50 W was used. The US transducer was attached to the bottom of the steel plate and glass interlayer was placed in between to avoid any electric contact. The specimen was immersed in 200 ml NaCl aqueous solution in the termostated corrosion cell and tested at two temperatures: 20 and 50 °C. A 8 cm^2 platinum plate was

used as the counter electrode and a saturated silver chloride electrode (SSCE) was used as the reference electrode ($E = 0.2$ V/ NHE).

**Table 1.** The concentrations of NaCl solutions for corrosion tests

No	Mass of NaCl, mg/l	Cl^- concentration, mg/l
1	250	150
2	330	200
3	410	250
4	500	300
5	580	350
6	5000	3034
7	10000	6069
8	50000	30340
9	100000	606800
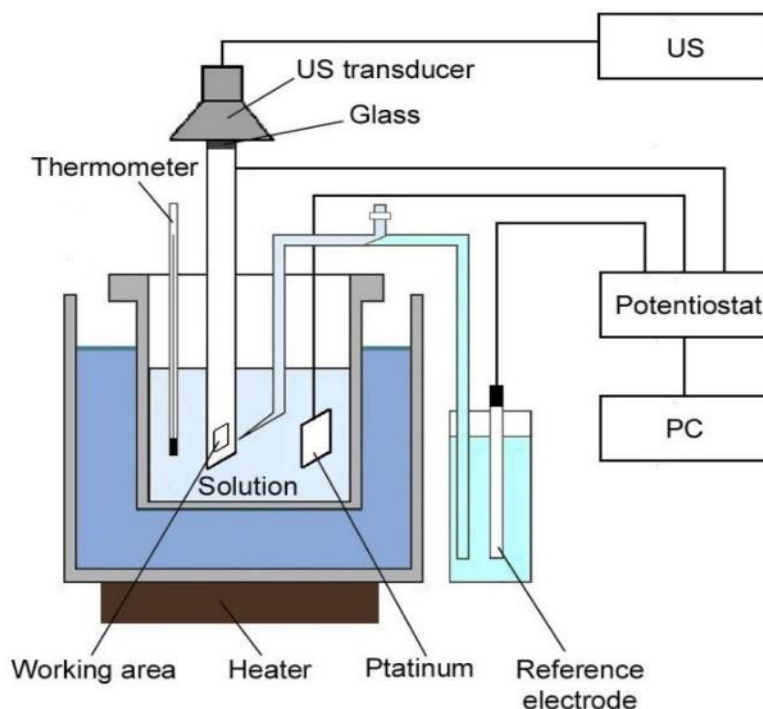
Figure 1. Polarization apparatus for corrosion test.

To test pitting resistance of stainless steel the galvanostatic polarization technique was applied. Typical E-t curve is given in fig. 2. The steel specimen was immersed into the solution (No 1-5, table 1) and kept without any applied polarization for 30 min. After corrosion potential E_{corr} was established a constant anodic current density of 30 μA/cm^2 was applied. The steel electrode potential shifted to positive values, and after pittings were formed – decreased. When a potential reached constant value E_{pc} polarization was turned off. The difference between values of

E_{pc} and E_{corr} gives the pitting resistance basis *PRB*. Higher *PRB* value means higher pitting resistance of the steel. 6 specimens were used for each chloride concentration and data was averaged.
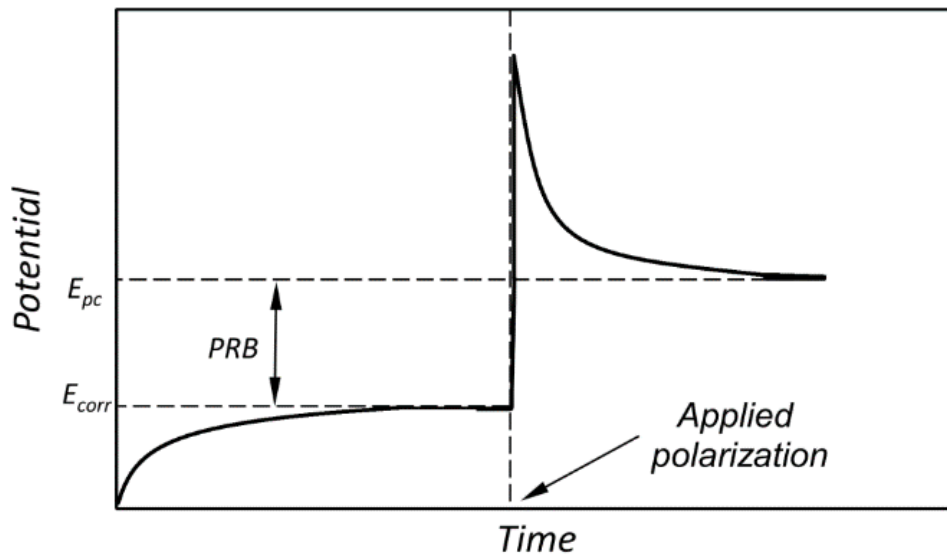

Figure 2. Typical E-t dependence of a galvanostatic pitting corrosion test.

To tests pitting resistance in terms of metal dissolution the weight loss technique was used. Both vibrating and non-vibrating steel specimens were anodically polarized with 50 mA/cm^2 current density for 10 min in concentrated NaCl solutions (No 6-9 table 1). Vibrating plate was attached to US transducer, 28 kHz, 230 W. The weight loss was determined with 0.0001 g accuracy. The data for 3 specimens were averaged. The surface of the specimens after dissolution in 100 g/l NaCl was investigated with SEM.

Results and Discussion

The values of E_{corr}, E_{pc} and *PRB*, calculated from corresponding E-t curves obtained at 20 °C are given in fig. 3a-c. The E_{corr} values for non-vibrating specimen appeared to be dependent on Cl$^-$ content. The E_{corr} decreased from 300 to 150 mV when Cl$^-$ concentration increased from 150 to 350 mg/l (fig. 3a). When US vibration was applied to the specimen E_{corr} values reduced to 0-30 mV and appeared to be less dependent on Cl$^-$ concentration (fig. 3a). Under the applied polarization the electrode potential E_{pc} for both vibrating and non-vibrating specimens established between 300-400 mV showing no dependence on chloride concentration (fig. 3b). Calculated values of *PRB* for vibrating specimen are at least 200 mV higher comparing to non-vibrating (fig. 3c). Thus, the application of US vibration to the stainless steel increases pitting resistance basis in 200 mV at 20 °C in tested Cl$^-$ concentration range.
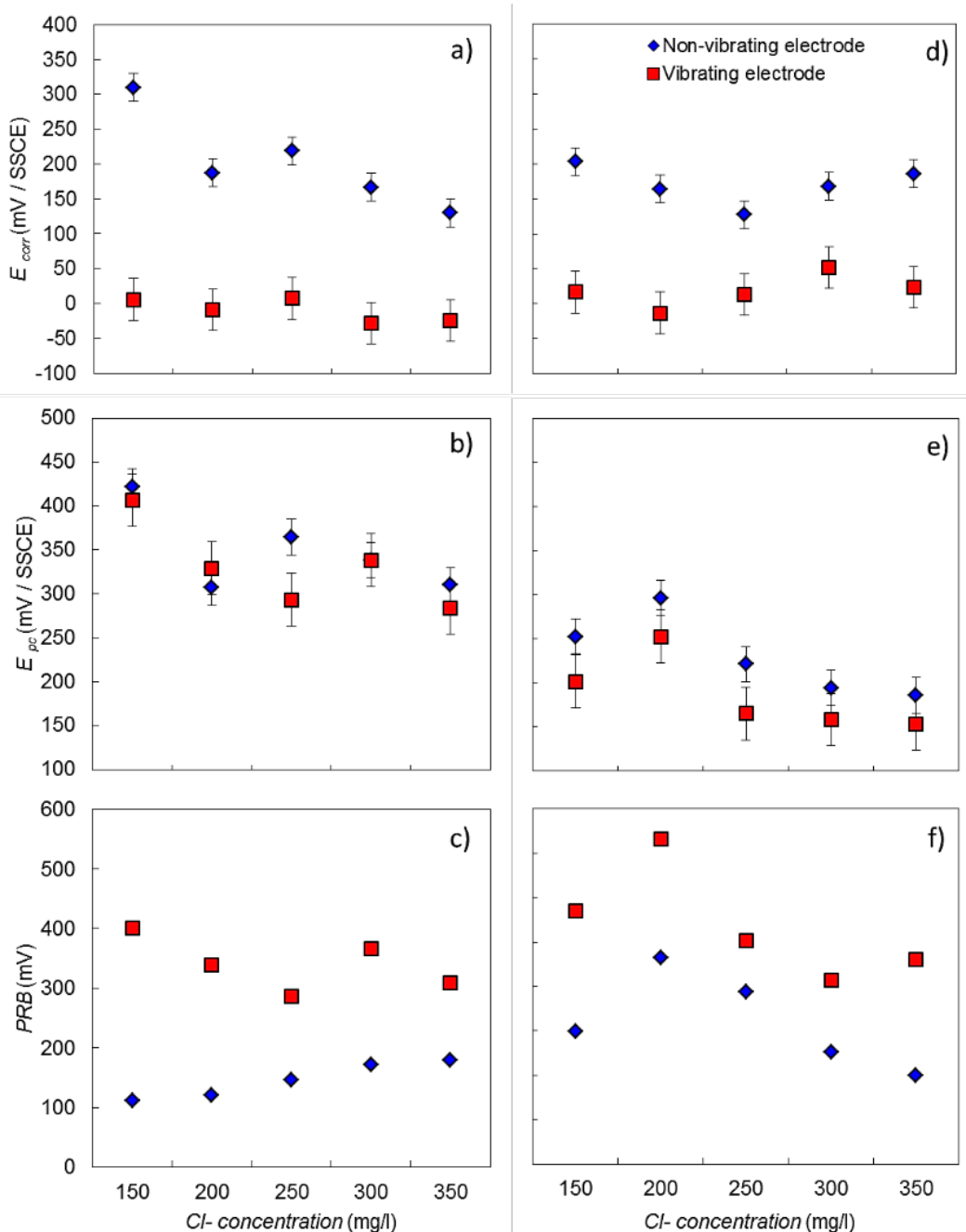
Figure 3. Cl⁻ concentration dependences of corrosion potential E_{corr}(a, d), potential under polarization E_{pc} (b, e) and pitting resistance basis *PRB* (c, f) of AISI 316 stainless steel. Temperature: a, b, c – 20 °C; d, e, f – 50 °C. Applied current density i = 30 μA/cm².

Galvanostatic tests were also performed at elevated temperature – 50 °C. The series of E-t curves were measured and corresponding parameters of E_{corr}, E_{pc} and *PRB* are given in fig. 3d-f. The temperature had little influence on E_{corr} values for both vibrating and non-vibrating specimens (fig. 3d) at 50 °C. The values of E_{corr} were located between 150-200 mV without ultrasound application and between −20 and +50 mV with US. At applied anodic current for both cases similar dependences were obtained, however with applied US the E_{pc} values are

50 mV lower. Calculated values of *PRB* are found to be at least 100 mV higher for vibrating plate (fig 3f). So, the application of US was found to increases the pitting resistance of stainless steel on 100 mV, however the rise of temperature reduces the pitting suppression efficiency of US vibration.

Galvanostatic polarization tests clearly showed the increase of pitting resistance when US vibration is applied to the stainless steel. In addition, the efficiency of US pitting suppression was tested with weight-loss technique. The steel specimen was polarized in series of concentrated NaCl solutions (No 6-9, table 1). The weight loss data is reported in fig. 4.
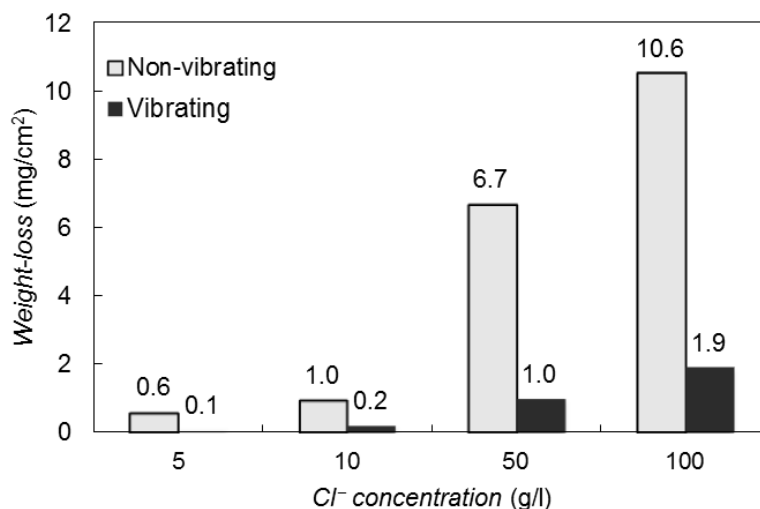
Figure 4. The weight-loss of stainless steel after anodic polarization in chloride-containing solution. Applied current density $i = 50$ mA/cm^2.

From the results obtained it is clearly seen, that the application of US vibration prevents dissolution of steel. The specimens, treated in 100 g/l NaCl solution were investigated with SEM. The microphotographs are given in fig. 5. The surface of non-vibrating plate is heavily damaged with corrosion, however, no signs of dissolution is visible on vibrated specimen.
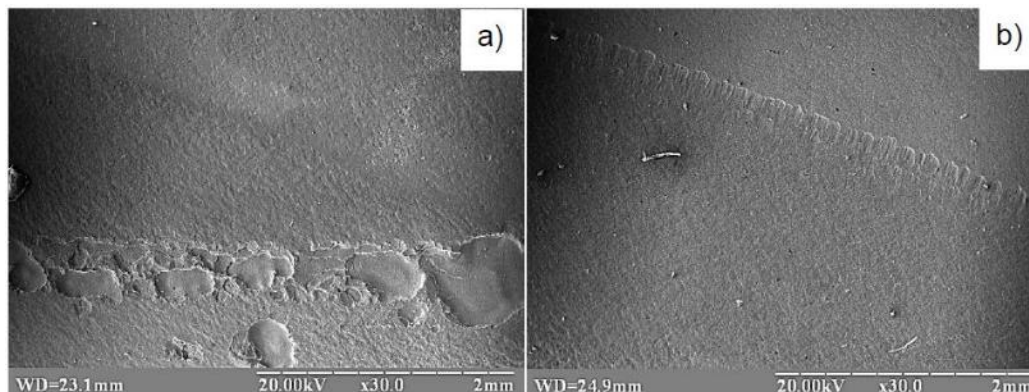
Figure 5. SEM images of AISI 316 stainless steel after 10 min anodic polarization at 50 mA/cm^2 in 100 g/l NaCl: a) – non-vibrating, b) – vibrating (28 kHz, 230 W).

Analyzing the results obtained pitting corrosion of stainless steel is efficiently suppressed when US vibration is applied. According the last concepts the pitting of stainless steel occurs in three consecutive stages. The first stage is nucleation, a microscopically violent and unstable process. Nucleated pit enters the second stage, that of metastable growth. Second stage is also unstable, and if the pit survives, grows enters the third stage and grows becomes stable [11,12]. The main reason of pitting suppression in a cavitation field was found to be the removal of corrosion products from pits, which leads to fast repassivation, presumably in metastable and stable stages. However, when US is applied to the metal, no cavitation occurs, so this mechanism cannot fully explain the observed phenomenon. This leads to the assumption, that pitting suppression occurs on the pit nucleation stage. According to the competitive adsorption theory of pitting corrosion [13–15] Cl^- are adsorbed on to the passive film and compete with oxygen in the film. The application of US vibration leads to the acceleration of oxygen supply, due to diffusional layer thinning. Thus, the amount of oxygen at the surface increases as well as its amount in the adsorbed film, so the pitting resistance of stainless steel increase. However, further investigation of adsorption on vibrating electrode is required to prove this hypothesis.

Conclusions

Summarizing, in this work, the application of ultrasound vibration (28 kHz) was tested for pitting corrosion prevention of AISI 316 stainless steel. It was found that pitting resistance basis, determined as a difference between corrosion potential and stable pitting potential, increases in 200 mV at 50 °C and in 100 mV at 20 °C when 50 W US is applied. The weight-loss of anodically polarized steel is 4-6 times lower in Cl-containing solution and no signs of pitting were observed on the vibrated steel plate with SEM. The results obtained are explained in terms of competitive adsorption theory, as increased supply of oxygen.

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