Short Communication

Effect of Passive Film on Cavitation Corrosion Behavior of 316L Stainless Steel

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Received: 5 October 2019/ Accepted: 11 November 2019 / Published: 30 November 2019

The effect of passive film on the cavitation erosion-corrosion of 316L stainless steel (316L SS) was investigated via pulse and continuous cavitation modes, open circuit potential (OCP) measurements and scanning electron microscope (SEM). Results demonstrate that the passive film healed rapidly within seconds during pulse cavitation in 3.5 wt. % NaCl solution and played an important role in resisting the cavitation erosion–corrosion. 316L SS exhibition negative synergistic characteristic between cavitation erosion and corrosion due to its optimal repassivation performance in the absence of cavitation erosion.

Keywords: 316L stainless steel; cavitation erosion-corrosion; synergism; electrochemical; passive film

1. INTRODUCTION

316L stainless steel is an engineering alloy widely used in liquid handling systems and hydraulic machinery, especially for manufacturing turbine blades, marine propellers and acid resistant pumps, due to its excellent corrosion resistance, good processability and relative low cost [1].

Cavitation erosion damage is a serious problem faced by engineering components face during service conditions. It refers to the generation and collapse of bubbles induced by the fluctuation of liquid pressure [2]. Shock waves and micro–jets generating as bubbles collapse, and apply fierce pressure pulses to nearby propeller solid surfaces, thus leading to reduction in their working efficiency and service life [3]. In marine environments, however, cavitation erosion rarely occurs alone and constantly coexists with corrosion, the phenomenon called as cavitation erosion–corrosion [4]. In recent years, numerous research studies have been carried out on the cavitation erosion–corrosion behavior of 316L stainless steel. Wan reported that stainless steel suffered more severe cavitation damage in solution with high concentration of Cl⁻ due to dissolution of the surface passive film by Cl⁻[5]. Montemor [6] and Ferreira

[7] proposed that the oxide film formed on the surface of 316LSS contained iron oxide and chromium oxide in the outer and the inner parts of the film respectively. The stability of the film was reduced by cavitation, and the film was destroyed after a certain period of cavitation erosion. Zheng [8] reported that cavitation accelerated the anode reaction rate, and the passive film on the surface of the sample was partially destroyed, followed swift repassivation of damaged surface. Kwok [9] studied the self-corrosion potential of 316L stainless steel in NaCl solution as well as the effect of cavitation on the passive film. The indicated that cavitation caused the potential to move in the active direction and the passive film was destroyed. As cavitation stopped, the surface of stainless steel has been reported to play an important role in the process of cavitation erosion–corrosion.

Though there are many studies concerning the cavitation erosion–corrosion behavior of 316L stainless steel, the effect of oxide film generated in a short period of time has been rarely studied. In work conditions, the mechanical impact of the bubble on the steel surface is random and discontinuous and the passive film is repaired immediately at cavitation intermittent, which will inevitably impact the cavitation erosion–corrosion behavior of stainless steel [10]. Therefore, it is of immense importance to study the passive film generated during short durations on the cavitation erosion–corrosion behavior of stainless steel.

2. EXPERIMENTAL

2.1 Material

The test substrate in this study was 316L stainless steel, and the chemical composition is listed in Table 1.

Table 1. Chemical composition (wt. %) of 316L stainless steel

material -	Chemical composition (wt. %)							
	С	Si	Mn	Р	Cr	Ni	Cu	Fe
316L	0.02	0.33	1.01	0.03	17.52	9.41	0.28	71.40

Fig. 1 shows the microstructure and X-ray diffraction (XRD) pattern of 316L stainless steel. The microstructure was observed to be homogeneous (Fig. 1a). Combined with the XRD results (Fig. 1b), it can be concluded that the metallographic structure of the material conformed to austenite.



Figure 1. Microstructure (a) and XRD pattern (b) of 316L stainless steel.

2.2 Cavitation erosion-corrosion tests

The cavitation erosion–corrosion tests were performed using ultrasonic vibratory apparatus following ASTM G32 standard [11]. Ultrasonically vibrating device was operated in either continuous or pulse cavitation mode [12, 13]. The former mode produced successive cavitation shock with a higher frequency than the actual flow field. The latter, recommended by ASTM G32 standard to study the cavitation erosion–corrosion behavior of the materials, produced an intermittent pressure field, thus inducing the periodic growth and collapse of the cavitation bubbles.

Thus, the current study carried out the pulsed cavitation erosion tests by employing $3-\sec-on/3$ sec-off time cycle (3–3). And NaCl solution (3.5 wt. %) and deionized water were used as testing solutions. NaCl solution was employed to explore the cavitation erosion-corrosion behavior of NAB, while deionized water was used to evaluate the cavitation erosion action. The continuous erosion tests were also carried out lasting 8 h, while the period of the pulse cavitation erosion tests were 16 h to ensure same effective cavitation erosion time. The samples were fastened 1 mm below a horn vibrating with a frequency of 20 kHz and amplitude of 65 µm. The temperature of test solution was maintained at $25 \pm$ 1°C using cycling cooling water. Prior to the tests, each sample was ground with silicon carbide abrasive paper up to 1200 grit and polished with 1 µm diamond paste, followed by ultrasonic cleaning, drying and weighing by an electronic balance with the accuracy of 0.01 mg. Each test was repeated at least five times to ensure the reliability of the test results. The surface morphology after cavitation erosion tests was observed using scanning electron microscope (SEM).

2.3 Electrochemical measurements

Electrochemical measurements were conducted by emoloying a CHI 660E electrochemical system using a three-electrode cell (specimen as working electrode (WE), a saturated calomel electrode (SCE) as reference electrode (RE) and a platinum electrode as counter electrode (CE)). Open-circuit

potential (OCP) was measured to investigate the effect of cavitation erosion on the electrochemical behavior of 316L SS. Polarization resistance (R_p) was determined by linear potentiodynamic sweep in the range of \pm 10 mV_{OCP} at a rate of 0.5 mV/s. Correspondingly, potentiodynamic polarization curves were measured at same rate to acquire anodic and cathodic Tafel slopes (b_a and b_c). Subsequently, the corrosion current density (i_{corr}) was calculated by using the Stern-Geary relation [14].

$$i_{corr} = \frac{b_a \ b_c}{2.303 \times R_P (b_c - b_a)} \tag{1}$$

The electrochemical measurements were repeated at least thrice to verify the reliability of the test data.

3. RESULTS AND DISCUSSION

3.1. Cavitation erosion-corrosion behaviors

The cumulative mass loss as a function of effective cavitation erosion time for 316L SS in NaCl solution and deionized water is shown in Fig. 2, and the corresponding results were listed in Table 2. In NaCl solution (Fig. 2a), the values for 316L SS exposed to continuous cavitation erosion-corrosion were observed to be higher than the pulse mode. For cavitation erosion for 8 h, the mass loss caused by the continuous cavitation was 17.19 ± 0.65 mg, which was almost 1.2 times the mass loss observed for pulse mode (14.43 \pm 0.67 mg). In deionized water (Fig. 2b), the weight loss for pulse cavitation erosion-corrosion was similar to the continuous mode, which indicated that the mechanical damage to the NAB alloy was nearly the same. It also implied that there was no difference in the cavitation strength between the two modes of the ultrasonically vibrating device in this case. Thus, the damage caused to steel by the pulse cavitation erosion in NaCl solution was lighter than the continuous cavitation mode. It could be inferred that the passive film, formed immediately by the corrosion reaction during the absence of cavitation erosion for 3 s under pulsed mode, reduced the cavitation erosion damage to the substrate. [15].



Figure 2. Cumulative mass loss of 316L SS as a function of cavitation erosion–corrosion time in (a) NaCl solution and (b) deionized water.

Solution	Continuous mode			Pulsed mode (effective time)		
	4h	6h	8h	4h	6h	8h
NaCl	6.40	12.02	17.19	4.74	10.70	14.43
	(±0.52)	(±0.62)	(±0.65)	(±0.82)	(±0.58)	(±0.67)
Deionized	5.60	11.56	16.69	5.10	11.87	15.93
water	(±0.74)	(±0.86)	(±0.63)	(±0.81)	(± 0.57)	(±0.69)

Table 2. Cumulative mass loss of 316L SS for different test durations under continuous and pulse cavitation erosion–corrosion

3.2 Electrochemical properties

Fig. 3 shows the OCP of steel for quiescent, continuous and pulse cavitation erosion–corrosion in NaCl solution. It was observed that cavitation erosion induced the negative shift of OCP, in both continuous and pulsed modes. During cavitation erosion, the OCP of 316L SS was affected by two competing factors, the increase of mass transport (oxygen) and the corrosion film detachment [9, 16]. Vigorous stirring under cavitation erosion enhances the oxygen supply to the substrate surface, thus, accelerating the cathodic polarization reaction and the resulting positive shift of OCP, whereas the corrosion film detachment shifts the potential in the active direction by exposing the fresh base metal. [17]. In the case of continuous cavitation (Fig. 3a), OCP was stabilized at a more negative value of -0.25V than in stationary NaCl solution (around -0.18V), which was consistent with the results reported before [18]. It was owing to the fact that the film destruction was dominant as compared to the accelerated mass transport. The surface of steel was always bare under continuous mechanical shock, thus, the corrosion potential was stabilized around -0.25V in continuous mode. Under pulse cavitation erosion in NaCl solution, the potential of 316L SS rose to -0.235 V and subsequently decreased to -0.26V periodically (Fig. 3b). This phenomenon was observed due to the rapid formation of the passive film as cavitation erosion stopped, along with shedding of the passive film as cavitation erosion appeared.



Figure 3. OCP of 316L stainless steel measured in NaCl solution under (a) continuous cavitation erosion and (b) pulse cavitation erosion conditions.

Therefore, it can be concluded that in the process of continuous cavitation erosion, the steel surface was subjected to continuous mechanical shock, and the passive film on the surface of the material could not be formed or formed at a rate lower than being peeled off, thus, the steel surface was always bare. As the pulse cavitation erosion occurred, the passive film healed quickly in the absence of cavitation erosion, which protected the matrix from damage. Thus, the mass loss in the case of pulse cavitation erosion of stainless steel is observed to be lower than the continuous mode

3.3 Synergistic effect of cavitation erosion and corrosion

The total mass loss (T) of 316L stainless steel caused by cavitation erosion–corrosion in NaCl solution is contributed by three components: pure corrosion (C), pure erosion (E) and the synergy (S) between the both, which can be expressed by the following equation [19]:

$$\Gamma = C + E + S \tag{2}$$

Among these, T and E are obtained by gravimetric measurements, while C is evaluated from polarization and Faraday conversion techniques [20]. In more detail, the values of T and E in this study were measured through cavitation erosion tests in NaCl solution and distilled water, respectively. C was calculated from the corrosion current density (i_{corr}) according to the Faraday's law:

Mass loss rate =
$$\frac{I_{corr} \times Atomic mass of corroding elemnet \times exposed area}{number of electrons freed \times Faraday's constant}$$
(3)

The corroding element was Fe, number of free electrons (n) was 3 and Faraday's constant = 96485 C mol⁻¹.



Figure 4. Potentiodynamic polarization curve (a) and linear polarization plots (b) of 316L stainless steel measured in NaCl solution.

Table 3. Electrochemical parameters of 316L stainless steel in NaCl solution under quiescent condition

Solution	$R_p \left(\Omega \cdot cm^2 \right)$	ba	bc	i _{corr}	
		$(mV \cdot dec^{-1})$	$(mV \cdot dec^{-1})$	$(\mu A/cm^2)$	
NaCl	122370.60	0.033	-0.071	0.079	

The exposed area was calculated as 1.94 cm^2 according to the size of the horn, whereas i_{corr} was calculated according to equation (1). The corresponding electrochemical parameters are summarized in Table 3, evaluated from the potentiodynamic polarization curve and linear polarization plot shown in Fig. 4.



Figure 5. Mass loss contributed by pure corrosion (C), pure erosion (E), cavitation erosion-corrosion (T), and synergy (S) as well as the corresponding contribution of synergy on T for 316L stainless steel after effective cavitation erosion for 8 h in NaCl solution.

Table 4. Mass loss related to cavitation erosion-corrosion (T), pure erosion (E), pure corrosion (C) and synergy (S) between corrosion and cavitation erosion as well as the contribution of S on T (S/T) for 316L stainless steel for cavitation erosion-corrosion for 8 h in NaCl solution

Test solution Te	st	Т	Е	С	S=T-(E+C)	(S/T) x 100
3.5wt. % NaCl Contin	iuous (17.19 (±0.65)	16.69 (±0.63)	0.0006	0.49	2.90
Pul	se (14.43 (±0.67)	15.93 (±0.69)	0.0012	-1.50	-10.40

The values of T, C, E and S as well as the contribution of S on T for cavitation erosion duration of 8 h are shown in Fig. 5 and Table 4. In NaCl solution, the value of T under continuous cavitation erosion–corrosion was higher (17.19 mg) than the pulse mode (14.43 mg). The mass loss from E for continuous (16.69 mg) and pulsed (15.93 mg) modes was observed to be almost similar. As observed from Table 4, the value of C was 0.0006 mg for continuous cavitation erosion which was less than 0.0012 mg for pulsed mode, attributed to the shorter duration for the samples exposed to NaCl solution in continuous mode. In addition, the value of synergy in the continuous mode was 0.499 mg, while a negative value of -1.50 mg was obtained in the pulse mode .Moreover, 316L SS exhibited negative synergistic (S/T of -10.40%) characteristics of cavitation erosion and corrosion in pulse cavitation mode, while presented a typically positive synergistic (S/T of 2.90%) for continuous mode. The similar result was reported in the micro–abrasion–corrosion behavior of S32760 stainless steel due to excellent repassivation performance in NaCl solution. It pointed out that the large negative synergies produced by the two-body wear mechanism may be a reflection of the differences in repassivation kinetics and/or composition of the passive films reducing the overall level of two–body abrasion [21]. Compared with continuous cavitation erosion–corrosion, passive film formed by corrosion reaction during pulse cavitation erosion–corrosion enabled the matrix to resist the damage of cavitation erosion, thus, exhibiting negative synergistic characteristics.

3.5 Effect of oxide film on the cavitation erosion–corrosion behavior

The excellent corrosion resistance of 316L stainless steel was mainly due to the dense passive film formed on the surface, which blocked the transmission of ions between the metal surface and corrosive solution, thereby, reducing the corrosion rate. Fig.6 and Fig.7 demonstrate the full and narrow XPS spectra of the passive film after 7 days of immersion in 3.5 wt. % NaCl solution. Obvious Cr_{2p} , Fe_{2p} and O_{1s} peaks as well as a weak Ni_{2p} peak were observed in the spectrum, indicating that the main constituent elements of Cr and Fe in the passive film existed in the oxide form. The binding energy of the Cr_2O_3 and Fe_2O_3 peaks was 576.4 eV and 710.4 \pm 0.1 eV respectively [17]. It was consistent with the conclusion that the passivation film was composed of chromium oxide as the inner component and iron oxide as the outer component [22, 23].



Figure 6. Full XPS spectra of the passive film on the surface of 316L stainless steel after immersion in NaCl solution for 7 days.



Figure 7. XPS spectra of Cr, Fe and Ni in passive the film on the surface of 316L stainless steel after immersion in NaCl solution for 7 days.

Cavitation morphology was carried out to gain further insights into the cavitation erosion– corrosion behavior of 316L stainless steel, as shown in Fig.8. The pulsed cavitation erosion–corrosion behavior of 316L stainless steel was observed to be different from the continuous mode in NaCl solution, which was mainly related to the passivation film. The corresponding mechanism has been proposed in Fig.9. Prior to the initiation of cavitation (Fig.9a), the stainless steel surface in NaCl solution was quickly passivated to form a double-layer passivation film, wherein the inner layer was Cr_2O_3 and the outer layer was Fe_2O_3 .On initiation of cavitation, the passive film on the steel surface became thin and eventually ruptured under the mechanical impact [24]. After passive film was destroyed, the fresh substrate was directly subjected to mechanical impact, and the surface of the material underwent plastic deformation (Fig. 8). With time, the fatigue cracks sprouted at the grain boundaries and penetrated into the interior of the material (Fig. 8 and Fig.9b). As the cavitation erosion stopped, the steel surface was rapidly repassivated to form an oxide film thinner than before, which protects the substrate from subsequent cavitation damage (Fig.9c). [25].



Figure 8. Damage morphology of 316L stainless steel after cavitation erosion in NaCl solution for 15 min.

During pulse cavitation erosion–corrosion, the passive film was periodically formed and destroyed. In the continuous process, the surface of 316L SS was constantly mechanically impacted by the bubbles, and the surface could not form a passive film, thus, keeping it in bare state. Therefore, the passive film formed intermittently in pulse behavior alleviated the cavitation damage to the substrate.



Figure 8. Schematic of the cavitation erosion–corrosion behavior of 316L stainless steel in NaCl solution.

4. CONCLUSION

The effect of passive film on the cavitation erosion–corrosion behavior of NAB alloy was investigated in this study and the conclusions are as follows:

1. During cavitation erosion-corrosion tests, the passive film on the alloy surface healed rapidly during the absence of cavitation erosion, thus, resisting the cavitation erosion damage and thus resulting in reduced mass loss in the pulsed mode.

2. Stainless steel showed negative synergistic characteristics between cavitation erosion and corrosion during pulse cavitation erosion–corrosion with the protection of passive film while presented typically positive synergistic behavior for continuous cavitation erosion–corrosion.

3. The effect of cavitation erosion on the electrochemical properties, investigated by OCP tests, was influenced by corrosion film detachment and enhanced mass transport. Under pulse cavitation erosion in NaCl solution, the potential of 316L SS rose and fell periodically. The observed phenomenon was due to the rapid formation of the passive film as the cavitation erosion stopped and its shedding as the cavitation erosion appeared.

ACKNOWLEDGEMENTS

This research was financed by the National Key Research and Development Program of China (2016YFE0205700) and the National Natural Science Foundation of China (No.51601114).

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