Corrosion and Cavitation Erosion Behaviours of Cast Nickel Aluminium Bronze in 3.5% NaCl Solution with Different Sulphide Concentrations

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Abstract

The effect of sulphide (Na_2S) concentration (SC) on the corrosion and cavitation erosion behaviours of a cast nickel aluminium bronze (NAB) in 3.5% NaCl solution is investigated in this study. The results show that when the SC exceeds 50 ppm, the hydrogen evolution reaction dominates the cathodic process, and a limiting current region appears in the anodic branch of the polarisation curve due to the formation of a copper sulphide film, which is a diffusion-controlled process. After long-term immersion, the increased mass loss rate of NAB with the sulphide additions of 20 and 50 ppm is attributed to the less protective films, which contains a mixture of copper oxides and sulphides. Moreover, NAB undergoes severe localised corrosion (selective phase corrosion, SPC) at the β' phases and eutectoid microstructure $\alpha + \kappa_{\text{III}}$. By comparison, NAB undergoes general corrosion and a copper sulphide film is formed in 100 and 200 ppm sulphide solutions. Cavitation erosion greatly increases the corrosion rate of NAB in all solutions and causes a negative potential shift in 3.5% NaCl solution due to the film destruction. However, a positive potential shift occurs in the solutions with SC higher than 50 ppm due to the accelerated mass transfer of the cathodic process. The cavitation erosion mass loss rate of NAB increases with the increase of SC. The occurrence of severe SPC decreases the phase boundary cohesion and causes brittle fracture under the cavitation impact. The corrosion-enhanced erosion is the most predominant factor for the cavitation erosion damage when the SC exceeds 50 ppm.

Keywords Nickel aluminium bronze · Sulphide · Corrosion · Cavitation erosion · Synergy

1 Introduction

Nickel aluminium bronze (NAB) is widely used for marine applications, including making marine pumps, ship propellers, valves and fittings because of its good mechanical properties and excellent corrosion resistance to seawater [1–3]. It contains approximately 9–12 wt% Al, 6 wt% each of Fe and

Ni and 1 wt% Mn. In seawater, a corrosion product film with Al_2O_3 in the inner layer and Cu_2O in the outer layer quickly forms and keeps the corrosion rate of NAB at a very low value [2, 4]. The Fe and Ni ions incorporate into the Cu_2O crystal lattice and further increase the ion and electronic conductivities of the film [5, 6]. However, copper and its alloys suffer aggravated corrosion damage in pollutants-containing seawater environments.

Sulphide is a common pollutant in seawater and introduced from industrial waste discharge, metabolism of marine cultures and sulphate reduction process by sulphate-reducing bacteria (SRB). It has a significant influence on the corrosion behaviour of marine components. Sulphide concentration (SC) varies in different seawater environments, and high SC can be detected in harbours, coastal regions and near off-shore oil platforms [7, 8]. Hamdy et al. reported that the pitting and erosion–corrosion resistance of a mild steel decreased with the increase of SC in NaCl solution [8]. The Na_2S addition tremendously promoted active dissolution and corrosion damage of 2205 duplex stainless steel in HCl

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solution [9]. Yang et al. reported that when the SC was lower than 2 mmol/L in deoxygenated simulated seawater environment, the increased SC promoted the formation of TiO_2 , which then enhanced the corrosion resistance of the film on Ti alloy TA2. However, when the SC exceeded 2 mmol/L, the corrosion resistance of the film decreased because of the increased TiOS/TiS_2 and decreased TiO_2 inside the film [10]. The effect of sulphide on the corrosion behaviour of copper and its alloys had also been investigated. With sulphide addition in chloride-containing solutions, the corrosion product films, which were formed on pure copper [11, 12], copper–nickel alloy [13–15] and aluminium bronzes [16], developed a loose and defective structure and became less protective. Elselstein et al. [14] found that the synergistic effect of sulphide and oxygen inhibited the formation of a protective cuprous oxide film and resulted in a very high corrosion rate of Cu–10Ni. The localised corrosion rate of Cu–10Ni in aerated sulphide-polluted seawater was approximately 155 times greater than that in aerated unpolluted seawater. In anaerobic simulated seawater, the average pit depth on Cu–Ni alloy in the presence of SRB was almost twice deeper than that in the absence of SRB [17]. Hazra et al. [18] also reported that the highly polluted seawater with sulphide induced severe selective phase corrosion (SPC) and pitting corrosion of NAB, and it was a key factor for the failure of NAB canned motor pump impeller. Li et al. [19] found that the sulphide resulted in embrittlement wear of Al brass and Cu–Ni alloy in seawater. The corrosion rates of Cu10Ni and Al brass, as well as the stress cracking corrosion susceptibility of Al bronze increased with the increase of SC in aerated 3.5% NaCl solution [15, 20]. Taniguchi et al. [21] also reported that in deaerated synthetic seawater, pure copper was susceptible to selective dissolution and intergranular attack at low SC (less than 0.005 M), whereas it underwent stress cracking corrosion at high SC (0.01 M).

Some marine hydraulic components, such as ship propellers, rotate at high speeds in seawater and suffer both corrosion and cavitation erosion. Cavitation erosion damage is induced by cavitation, which is related to the formation and collapse of bubbles because of the pressure fluctuation in fluid. The collapsing bubbles result in violent mechanical compact on the component surface. In a corrosive medium, the electrochemical corrosion effect and mechanical impact induced by cavitation erosion always work synergistically and facilitate the degradation of marine components. The mass loss caused by the synergistic effect between cavitation erosion and corrosion was reported to reach 22.24% of that of the cumulative mass loss for cast NAB in 3.5% NaCl solution [22], 18.17% for high-nitrogen stainless steel in 0.5 mol/L NaCl solution [23] and even 66% for mild steel in 3.5% NaCl solution [24].

The presence of sulphide aggravates the corrosion damage of marine components, and it will further enhance the

synergistic effect between cavitation erosion and corrosion, thereby resulting in increased mass loss. It was reported that the cavitation erosion damage of stainless steels increased gradually with the increase of SC in 3.5% NaCl solution [25]. The presence of sulphide also increased the cavitation erosion damage of both the cast NAB and manganese–aluminium bronze in 3.5% NaCl solution [16]. However, the effect of SC on the corrosion and cavitation erosion behaviours of NAB is lack of systematic studies. Moreover, the effect of SC on the cavitation erosion–corrosion synergy, which is the key to reveal the cavitation erosion degradation mechanism, is also rarely mentioned.

In this research, the corrosion and cavitation erosion behaviours of the cast NAB in 3.5% NaCl solutions with various SCs were investigated by conducting electrochemical measurements, long-term gravimetric tests and ultrasonically vibrating cavitation erosion tests. The corrosion product film and synergistic effect between cavitation erosion and corrosion were analysed and discussed.

2 Experimental

2.1 Materials and Test Media

A cast NAB with 9.30 wt% Al, 4.50 wt% Ni, 4.88 wt% Fe, 0.97 wt% Mn and balance Cu was selected as the test material. The test media for corrosion and cavitation erosion tests were aerated 3.5% NaCl solutions with various SCs. The 3.5% NaCl solution was prepared by using analytical sodium chloride and distilled water. Analytical sodium sulphide nonahydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) was added in 3.5% NaCl solution to prepare sulphide-polluted solutions with Na_2S concentrations of 20, 50, 100 and 200 ppm. The SC referred to the Na_2S concentration in 3.5% NaCl solution.

2.2 Corrosion Tests

Electrochemical tests were performed using a Gamry Interface 1000E potentiostat. A saturated calomel electrode (SCE) acted as the reference electrode, which was connected to the solution through a salt bridge. All potentials stated in this paper were measured versus SCE. A platinum plate served as the counter electrode. The working NAB electrode with an exposure area of 1 cm^2 was firstly immersed in the solution for 1 h to obtain a stable open circuit potential (OCP). Afterwards, the polarisation curve was recorded from -0.5 V versus OCP to approximately 1.2 V , and the scanning rate was 0.5 mV/s .

Moreover, long-term immersion tests were conducted. At least three samples with dimensions of $14\text{ mm}\times 10\text{ mm}\times 2\text{ mm}$ were prepared for each immersion period and in each solution. The sulphide-polluted solutions

were entirely replaced daily in consideration of the gradual SC decrease when exposed to air. The sample weight was recorded before immersion (m_0), after immersion for a certain immersion period (m_1) and after pickling off the corrosion products (m_2). The corrosion product on the NAB surface was removed by immersing in a pickling solution of 500 mL HCl + 500 mL distilled water for 2 min. This pickling method caused negligible mass loss of the NAB substrate. The mass loss of the sample was equal to ($m_0 - m_2$), and the film weight was equal to ($m_1 - m_2$).

2.3 Cavitation Erosion Tests

Cavitation erosion tests were performed using an ultrasonically vibrating device according to the ASTM G32 standard [26]. The test sample was immersed 15 mm deep from the liquid level of the medium. The vibrating horn was held 0.5 mm right above the sample surface with a working frequency of 20 kHz and an amplitude of 60 μ m. The medium temperature was maintained at approximately 20 °C by cycling cooling water. The mass loss of NAB was recorded after cavitation erosion for 5 h. Electrochemical measurements were also conducted under cavitation erosion conditions, as schematically presented in Fig. 1. The OCP of the cast NAB under alternate conditions of quiescence and cavitation erosion was monitored in different solutions, and the lasting duration of each condition was 20 min. Polarisation curves were recorded from -0.25 V versus OCP to approximately 0 V with a scanning rate of 0.5 mV/s, and the electrochemical parameters were obtained using the CView 3.2 software.

Scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS, JEOL JSM-6360LA, acceleration

voltage 15 kV) was used to characterise the morphology and chemical composition of the corroded samples. Glancing X-ray diffraction (XRD) analysis of the corrosion product films was performed using an X-ray diffractometer (X'Pert PRD, PANalytical, Holland) with Cu $K\alpha$ radiation. The incidence angle ranged from 10° to 90°, and the inclining angle was 0.6°.

3 Results and Discussion

Figure 2 shows the optical microstructure of the cast NAB. It consists of lightly etched coarse α , grey κ and darkly etched β' phases. The κ phases comprise various intermetallic compounds, including rosette-shaped κ_I , globular κ_{II} , lamellar κ_{III} and fine κ_{IV} phases. The κ_I , κ_{II} and κ_{IV} phases are Fe₃Al-based intermetallics, and κ_{III} is a NiAl-based intermetallic [27, 28].

3.1 Electrochemical Results

Figure 3 shows the polarisation curves of the cast NAB in different solutions. The following points can be obtained. Firstly, in the presence of sulphide, the corrosion potential, E_{corr} , of the cast NAB moves forward in the negative direction and decreases with the increase of SC. This phenomenon is caused by the adsorption of HS⁻ on the NAB surface [29, 30], as also reported in other studies [13, 29, 30]. Secondly, both the anodic and cathodic branches of the polarisation curves change distinctly when the SC exceeds 50 ppm. Thirdly, in the solutions with SC higher than 50 ppm, a limiting current region appears in the anodic branch and the limiting current density increases with the increase of SC.

Fig. 1 Schematic diagram of the ultrasonically vibrating equipment for cavitation erosion test. 1: water inlet; 2: cooling system; 3: Pt electrode; 4: reference electrode; 5: amplitude transformer; 6: transducer; 7: horn; 8: sample; 9: water outlet; 10: ultrasonic generator

Fig. 2 Optical microstructure of the cast NAB

Fig. 3 Polarisation curves of NAB in 3.5% NaCl solutions with different SCs

For copper and its alloys, the oxygen reduction in Eq. (1) is the main cathodic process in near neutral and alkaline chloride-containing solutions [31, 32]:

Other cathodic reactions will proceed in the presence of sulphide. In the solutions with SC higher than 50 ppm, the E_{corr} decreases to approximately -1.0 V. The cathodic branch of the polarisation curve indicates the occurrence of a charge transfer-controlled process, which corresponds to the following hydrogen evolution reaction [11, 29, 30]:

Additionally, the limiting current region, which appears in the anodic branch near the corrosion potential, demonstrates the occurrence of a diffusion-controlled process. In the presence of sulphide, copper sulphide forms on NAB through the following reactions [30, 33]:

Chen et al. reported that at short periods before a coherent copper sulphide film was established on the copper surface, the film growth was controlled by the diffusion of HS^- in solution [30, 34, 35]. Therefore, the limiting current density of NAB increases with the increase of SC. When the applied potential exceeds -0.3 V, the Cl^- -induced copper dissolution occurs, and soluble cuprous dichloride anion complexes form through the following reaction [32]:

Therefore, the current density increases distinctly with the increase of the applied potential. The retained polarisation curves overlap with that in 3.5% NaCl solution, because the Cl^- -induced copper dissolution is also the main anodic process for NAB in the absence of sulphide. In 20 ppm sulphide solution, the anodic and cathodic processes of NAB are similar with those in 3.5% NaCl solution, and the E_{corr} decreases slightly, probably because of the low SC.

3.2 Long-Term Immersion Results

3.2.1 Gravimetric Measurements

The electrochemical results above can reflect the initial and short-term corrosion behaviour of NAB in different solutions. In order to evaluate the long-term corrosion behaviour of NAB, gravimetric measurements are also conducted. Figure 4 presents the mass loss and film weight results. The mass loss rates of NAB after immersion for 15 days are 0.0091, 0.0067, 0.0081 and 0.0040 $\text{mg cm}^{-2} \text{h}^{-1}$ in the solutions with SCs of 20, 50, 100 and 200 ppm, respectively. In comparison with the result in 3.5% NaCl solution (0.0010 $\text{mg cm}^{-2} \text{h}^{-1}$), the addition of 20, 50, 100 and 200 ppm sulphide remarkably

Fig. 4 **a** Mass loss, **b** film weight results of NAB after immersion for different periods in 3.5% NaCl solutions with different SCs

accelerates the mass loss rate of NAB by a factor of 8.1, 5.7, 7.1 and 3.0, respectively. Notably, the film weight is lower than the mass loss in the solutions with SC less than 50 ppm, but it is larger in 100 and 200 ppm sulphide solutions (Fig. 4b). The mass loss of NAB in different solutions is mainly caused by the formation of soluble metal ions and ion complexes, loose insoluble corrosion products that are easily detached from the NAB surface, and compact insoluble corrosion products that are deposited on the surface as a film. In the solutions with SC lower than 50 ppm, the corrosion product films with loose structures might form and detach easily from the NAB surface, and soluble metal ions/ion complexes might dissolve into the solutions during immersion.

3.2.2 Surface Morphology and Corrosion Product Film Analysis

Figures 5 and 6 show the surface morphologies of the cast NAB after immersion for 7 days, and the EDS analysis of the corrosion products is presented in Table 1. As shown in Fig. 5a, b, some piles of floccus corrosion products (areas 2 and 3), which possess relatively high chloride content, are dispersed on the surface. After long-term immersion in chloride-containing solutions, copper hydroxychlorides, including $\text{Cu}_2(\text{OH})_3\text{Cl}$ and $\text{Cu}(\text{OH})\text{Cl}$, are formed in the outer layer of the film (areas 2 and 3 in Fig. 5a) for copper and its alloys. The inner layer of the film mainly consists of copper oxides (area 1 in Fig. 5a) [2, 4, 32, 36]. The XRD result presented in Fig. 7 also confirms the existence of copper hydroxychlorides in the film. The chemical composition and structure of the film on NAB change remarkably after the sulphide addition. In 20 ppm

Fig. 5 Surface morphologies of NAB after immersion for 7 days in 3.5% NaCl solutions with SCs of **a, b** 0 ppm, **c, d** 20 ppm, **e, f** 50 ppm

Fig. 6 Surface morphologies of NAB after immersion for 7 days in 3.5% NaCl solutions with SCs of **a, b** 100 ppm, **c, d** 200 ppm

Table 1 Chemical compositions of the corrosion products located on different areas in Figs. 5 and 6 (wt%)

Solutions (SC)	Areas	O	Al	Ni	Fe	Mn	Cu	Cl	S
0 ppm	1	1.84	8.44	13.53	10.28	0.57	64.56	0.48	–
	2	3.60	9.48	9.10	8.61	1.44	66.51	1.27	–
	3	12.40	14.01	4.42	3.04	0.30	63.40	2.43	–
20 ppm	4	5.03	2.31	7.56	3.38	0.10	72.42	4.82	4.37
	5	2.36	2.27	4.64	4.49	0.77	81.39	0.81	3.26
50 ppm	6	11.89	1.42	1.86	1.42	0.57	67.84	–	15.00
	7	7.59	–	1.68	3.35	0.77	71.85	–	13.94
	8	8.47	2.47	3.80	4.53	1.86	69.59	–	9.28
100 ppm	9	–	–	–	1.08	0.58	78.12	–	20.22
	10	–	–	–	1.10	0.89	76.66	–	21.35
200 ppm	11	–	–	0.59	1.25	1.27	77.65	–	19.24
	12	–	–	–	0.87	–	80.30	–	18.83

sulphide solution, the film is composed of granulated corrosion products (area 4) and some clusters of corrosion products, which are discontinuously distributed in the outermost layer (area 5), as shown in Fig. 5c, d. In 50 ppm sulphide solution, large piles of corrosion products (area 6) are dispersed in the outermost layer of the film. Flake-shaped (area 7) and needle-like (area 8) corrosion products are also presented in Fig. 5e, f. Both oxygen and sulphur are detected in the films on NAB in 20 and 50 ppm sulphide solutions. The XRD result (Fig. 7) reveals that the film contains Cu_2O , FeO and Cu_2S in 20 ppm sulphide solution, whereas oxides are not detected in the film formed in 50 ppm sulphide solution probably because of their

limited content. By comparison, the films are more homogeneous in the solutions with high SCs (100 and 200 ppm), and corrosion products with well-developed crystals are found on the NAB surface, as shown in Fig. 6. In 200 ppm sulphide solution (Fig. 6c, d), strip-shaped corrosion products (area 12) seem to distribute along the scratches, which are introduced during sample preparation on the NAB surface. They possess similar chemical composition with the surrounding small-sized crystals (area 11) according to the EDS results. The atomic ratio of Cu and S in the corrosion products is close to 2:1 at areas 9–12. Furthermore, the percentage of mass loss to film weight is 80–88% after a certain immersion period,

Fig. 7 XRD patterns of NAB after immersion for 7 days in 3.5% NaCl solutions with different SCs

which is also close to the mass fraction value (80%) of Cu in Cu_2S . These results indicate that Cu_2S is the main component of the films in 100 and 200 sulphide solutions, as also revealed by the XRD result in Fig. 7.

Notably, the SC in the polluted solutions decreases with exposure time to air. In the sulphide solutions, both HS^- and Cl^- participate in copper dissolution and film growth. In 100 and 200 ppm sulphide solutions, the SC is probably sufficiently high during a solution refreshing duration (i.e., 1 day). HS^- mainly reacts with the NAB substrate, resulting in the formation of adsorbing $\text{Cu}(\text{HS})_{\text{ads}}$ and Cu_2S through Eqs. (3) and (4). Therefore, a weight gain phenomenon is exhibited and the film weight is larger than the mass loss. The mass loss rate of NAB is very high despite the formation of a copper sulphide film (Fig. 4), indicating that the film exhibits an inferior corrosion resistance. After a coherent copper sulphide film is established on the NAB surface, the HS^- content decreases to a low value at the Cu_2S film/NAB interface because of the consumption by film formation. Then, soluble CuCl_2^- is formed via the following reaction under high Cl^- and low HS^- contents [30, 37]:

This reaction will not be expected to cause remarkable dissolution of copper. Dissolution in the form of CuCl_2^- can realise the transport of Cu^+ throughout the film. After CuCl_2^- reaches the Cu_2S film/solution interface, where the HS^- content is higher, Cu_2S formation occurs through the following reaction [30, 34]:

Thus, the film growth is controlled by a solid-state diffusion of Cu^+ through the film. This transport–deposition

process promotes the copper sulphide film growth and continuous corrosion of NAB in 100 and 200 ppm sulphide solutions. More HS^- shortage sites at the Cu_2S film/NAB interface are expected to exist in 100 ppm sulphide solution because of the relatively low SC. Thus, more CuCl_2^- forms and transfers to the film/solution interface, resulting in increased copper corrosion and Cu_2S film growth rates. Therefore, the mass loss of NAB is much higher in 100 ppm sulphide solution.

In 50 ppm sulphide solution, the SC is sufficiently high at the early stage of a solution refreshing period to support the formation of copper sulphides, as confirmed by the limiting current region in the anodic branch of the polarisation curve (Fig. 3). With prolonged immersion time, the corrosion potential of NAB moves to the positive direction because of the gradually decreased SC. As a result, the Cl^- -induced copper dissolution proceeds through Eq. (5), and the hydrolysis reaction of CuCl_2^- further promotes the formation of cuprous oxide (Cu_2O) through Eq. (8) [32]:

Consequently, the sulphides and oxides coexist in the film, where the sulphides have a larger proportion. In 20 ppm sulphide solution, the SC is very low and decreases quickly. The anodic processes (Eqs. (5) and (8)) of NAB are similar to those in 3.5% NaCl solution (Fig. 3). Thus, the film is composed of copper oxides and a small proportion of sulphides. The films with a mixture of oxides and sulphides exhibit loose structures and inferior protectiveness [12, 13, 38]. Therefore, the mass loss rate of NAB increases obviously after the sulphide additions of 20 and 50 ppm in 3.5% NaCl solution. In the solutions with SC lower than 50 ppm, soluble corrosion products, such as CuCl_2^- , are partially dissolved into the solutions. In addition, some corrosion products, including $\text{Cu}_2(\text{OH})_3\text{Cl}$ in 3.5% NaCl solution and the mixture of oxides and sulphides in 20 and 50 ppm sulphide solutions, possess loose structures and are detached easily from the NAB surface. Corrosion product detachment is also observed in the solutions during immersion. Therefore, the mass loss is larger than the film weight in these solutions.

3.2.3 Cross-Sectional Morphology

Figure 8 shows the cross-sectional surface morphologies of NAB after immersion in different solutions for 7 days. In 3.5% NaCl solution, a very thin film is formed on the NAB surface (Fig. 8a), and a pit with a depth of approximately $3.1 \mu\text{m}$ is found at the eutectoid microstructure $\alpha + \kappa_{\text{III}}$ (Fig. 8b), as also reported in other studies [39–41]. In the sulphide solutions, the β' phase and eutectoid microstructure also undergo SPC. In 20 and 50 ppm sulphide solutions, deep pits are found beneath the corrosion products (Fig. 8c, d). As shown in Fig. 8c, the pits with a maximum depth of

Fig. 8 Cross-sectional morphologies of NAB after immersion for 7 days in 3.5% NaCl solutions with SCs of **a, b** 0 ppm, **c** 20 ppm, **d** 50 ppm, **e** 100 ppm, **f** 200 ppm

23 µm extend along the β' and $\alpha + \kappa_{III}$, and the coalescence of the pits results in huge mass loss of NAB in 20 ppm sulphide solution. In 100 and 200 ppm sulphide solutions, the NAB surface is covered by a relatively homogeneous film with a thickness of approximately 2 µm, and only small-sized pits are found (Fig. 8e, f). These results reveal that NAB undergoes severe localised corrosion (i.e., SPC) in the solutions with SC lower than 50 ppm, but general corrosion in the solutions with SCs of 100 and 200 ppm.

3.3 Cavitation Erosion Results

3.3.1 Mass Loss

Figure 9 shows the mass loss results of NAB after cavitation erosion in different solutions for 5 h. The mass loss rate

is $1.4722 \text{ mg cm}^{-2} \text{ h}^{-1}$ in 3.5% NaCl solution, and 1.9611, 3.9611, 5.2278 and $8.0778 \text{ mg cm}^{-2} \text{ h}^{-1}$ with the sulphide addition of 20, 50, 100 and 200 ppm, respectively. In contrast, the mass loss rate in distilled water, which is merely caused by the mechanical attack under cavitation erosion, is much lower ($0.9111 \text{ mg cm}^{-2} \text{ h}^{-1}$). In a corrosive medium, a synergistic effect exists between corrosion and cavitation erosion. The corrosion effect increases the surface roughness, weakens the cohesion among different phases, facilitates the crack propagation and thus intensifies the damage under the mechanical attack. Meanwhile, the mechanical attack damages the film, activates the surface, accelerates the mass transfer process and thus increases the corrosion rate [22, 24, 42–45]. As a result, the cumulative mass loss in a corrosive medium (T) is higher than the sum of mass loss caused by pure corrosion (C) and pure mechanical attack

Fig. 9 Cumulative mass loss results of NAB after cavitation erosion in 3.5% NaCl solutions with different SCs for 5 h

(*E*). The mass loss caused by the corrosion–cavitation erosion synergy (*S*) can be evaluated by using the following equation [24]:

$$S = \Delta E + \Delta C = T - E - C, \quad (9)$$

where ΔE and ΔC are the mass loss caused by corrosion–enhanced erosion and erosion–enhanced corrosion, respectively.

3.3.2 Electrochemical Measurements Under Cavitation Erosion

Figure 10 shows the OCP results of NAB under alternate conditions of quiescence and cavitation erosion. Different OCP results are exhibited in different solutions when the quiescence and cavitation erosion conditions are switched. Cavitation erosion has two competing effects on the corrosion behaviour of the studied material. On the one hand, the cavitation impact damages the protective film on the material surface and accelerates the anodic process. On the other hand, cavitation accelerates the mass transfer of the reactants and reaction products [24, 42]. A negative potential shift occurs if the former effect dominates, whereas a positive shift is presented if the latter effect plays a key role (especially the mass transfer of the cathodic process is enhanced). In either case, the corrosion rate is increased because cavitation accelerates the anodic and cathodic processes of the studied material. The increased current density caused by cavitation erosion was also reported for 0Cr13Ni5Mo and CrMnB in either 0.5 M NaCl or 0.5 M HCl solutions [43]. The effect of cavitation erosion on the corrosion potential and current density can be revealed by the schematic diagrams shown in Fig. 11.

Fig. 10 OCP results of NAB under alternate quiescence and cavitation erosion conditions in 3.5% NaCl solutions with different SCs

In 3.5% NaCl solution, the OCP shifts to the more negative direction by 50–60 mV when cavitation erosion starts. Similar potential shift results were reported for CrMnN and 0Cr13Ni5Mo in 0.5 mol/L NaCl solution [42] and brass, SS 304, SS Zeron 100 and SS 316L in 3.5% NaCl solution [24]. During sample preparation, an oxide film is formed on the NAB surface and continues to grow after quiescent immersion in 3.5% NaCl solution. The cavitation impact damages the protective oxide film, accelerates the anodic process and decreases the OCP, as revealed by Fig. 11a. When cavitation erosion is terminated, the corrosion product film is rebuilt on the NAB surface and the OCP increases. In the sulphide solutions with SC higher than 50 ppm, the OCP shifts to the more positive direction by approximately 100 mV when cavitation erosion starts. In these solutions, a copper sulphide film with inferior protectiveness is rapidly formed on the NAB surface, as discussed above. Cavitation accelerates the anodic (copper dissolution, Eqs. (3) and (4)) and cathodic (hydrogen evolution, Eq. (2)) processes, especially the cathodic process, by enhancing the mass transfer of HS^- . Therefore, a positive OCP shift occurs under the cavitation erosion condition, as revealed by Fig. 11b. Similar phenomenon was reported for nickel-free high-nitrogen steel in 0.5 mol/L HCl solution [44], 20SiMn in 0.5 mol/L NaCl solution [42] and 1050 mild steel in 3.5% NaCl solution [24].

However, in 20 ppm sulphide solution, the OCP first decreases when cavitation starts, but continues to decrease even under the following quiescence condition. The OCP shift phenomenon in the first quiescence–cavitation erosion period is similar to that in 3.5% NaCl solution, indicating that a protective film exists on the NAB surface in the primary quiescent immersion condition. The oxide film, which is formed on the NAB during sample preparation, transforms into a mixture of oxides and a small proportion of sulphides

Fig. 11 Schematic diagrams for OCP and current density evolution under alternate conditions of quiescence and cavitation erosion: **a** with, **b** without a protective film on the material surface under quiescence condition

in 20 ppm sulphide solution. This film is expected to be protective. The abrupt negative OCP shift under cavitation erosion condition is induced by the film destruction. The OCP increases gradually with the cavitation erosion time, probably because of the enhanced mass transfer of both oxygen and HS^- in the solution. Once the cavitation impact is stopped, the OCP further shifts to a more negative value, and the following OCP result is similar to that in the solutions with SC higher than 50 ppm. The negative OCP shift from the cavitation erosion condition to the second quiescence condition is caused by the slowing-down cathodic process. With prolonged quiescent immersion time, the OCP increases gradually because of the formation of a new film and the repressed anodic process. However, the new rebuilt film is less protective than the film formed in the first quiescent immersion condition, because it is formed under a highly negative potential (-700 to -600 mV) and contains of a large proportion of sulphides inside. The second cavitation erosion condition again damages the rebuilt film and accelerates the mass transfer of the cathodic processes, and the latter effect is the dominated factor. Therefore, a positive OCP shift is caused by cavitation.

Figure 12 presents the polarisation curve results of NAB under quiescence and cavitation erosion conditions. The electrochemical parameters obtained from Fig. 12 are shown in Table 2. In comparison with the results under quiescent conditions, the cavitation impact increases the current density, i_{corr} , of NAB by nearly one order of magnitude in 3.5% NaCl solution and approximately two orders of magnitude in the sulphide solutions. In the solutions with SC higher than 50 ppm, a limiting current region is presented under both quiescence and cavitation erosion conditions. This phenomenon is related with the HS^- transfer in the anodic process through Eqs. (3) and (4). Under the cavitation erosion condition, the diffusion process of HS^- is accelerated remarkably

Fig. 12 Polarisation curves of NAB under quiescence and cavitation erosion conditions in 3.5% NaCl solutions with different SCs

and the corrosion rate of NAB is determined by the reaction process. Therefore, the limiting current densities of NAB are very close in the solutions with different SCs.

3.3.3 Synergistic Effect Between Cavitation Erosion and Corrosion

The synergy results between corrosion and cavitation erosion in different solutions are listed in Table 3. T is the mass loss after cavitation erosion in a specific corrosive solution. E is the mass loss induced by pure mechanical attack, which is obtained by conducting cavitation erosion tests in distilled water. The corrosion rates under quiescence (C) and cavitation erosion (C') conditions are calculated from the current density results (Table 2) according to the Faraday's law, as provided by Eq. (10):

Table 2 Electrochemical parameters obtained from the polarisation curves in Fig. 12 for NAB in 3.5% NaCl solutions with different SCs

Conditions	3.5% NaCl solution + x ppm Na_2S				
	0	20	50	100	200
Quiescence					
I (A cm^{-2})	6.8175×10^{-6}	3.1426×10^{-6}	2.7630×10^{-6}	2.5147×10^{-6}	7.0212×10^{-6}
E_{corr} (mV)	−277	−341	−950	−963	−962
Cavitation					
I (A cm^{-2})	3.0678×10^{-5}	2.6561×10^{-4}	5.5525×10^{-4}	8.1464×10^{-4}	8.6688×10^{-4}
E_{corr} (mV)	−290	−364	−746	−790	−837

Table 3 Cavitation erosion–corrosion synergy results for NAB in 3.5% NaCl solutions with different SCs

Solutions (SC)	Mass loss rate ($\text{mg cm}^{-2} \text{h}^{-1}$)						Percentages (%)					
	T	E	C	ΔE	ΔC	S	E/T	C/T	S/T	$\Delta E/T$	$\Delta C/T$	
0 ppm	1.4722	0.9111	0.0163	0.4879	0.0570	0.5448	61.89	1.11	37.01	33.14	3.87	
20 ppm	1.9611	0.9111	0.0075	0.4154	0.6266	1.0420	46.46	0.38	53.16	21.21	31.95	
50 ppm	3.9611	0.9111	0.0066	1.7226	1.3189	3.0415	23.00	0.17	76.83	43.54	33.30	
100 ppm	5.2278	0.9111	0.0060	2.3713	1.9387	4.3100	17.43	0.11	82.46	45.37	37.08	
200 ppm	8.0778	0.9111	0.0168	5.0994	2.0527	7.1521	11.28	0.21	88.51	63.10	25.41	

$$\text{Corrosion mass loss Rate} = 37.3 \times M \times i_{\text{corr}}/n. \quad (10)$$

where M is the atomic mass of the corroding element (Cu, 64 g mol^{-1}), and n is the number of electrons freed (+1 for Cu). The Faraday's constant is equal to $96,485 \text{ C mol}^{-1}$. The mass loss is in $\text{mg cm}^{-2} \text{h}^{-1}$, and i_{corr} is in A cm^{-2} . Then, ΔC and ΔE can be obtained using Eqs. (11) and (12):

$$\Delta C = C' - C, \quad (11)$$

$$\Delta E = S - \Delta C. \quad (12)$$

The E/T value reaches 61.89% in 3.5% NaCl solution, indicating that the mechanical attack dominates the cavitation erosion degradation. The corrosion-enhanced erosion ($\Delta E/T$, 33.14%) is much more prominent than the erosion-enhanced corrosion ($\Delta C/T$, 3.87%). However, the E/T value remarkably decreases in the sulphide solutions. The cavitation erosion–corrosion synergy is the key component that causes cavitation erosion damage. The S/T value increases with the increase of SC and reaches 88.51% in 200 ppm sulphide solution. The $\Delta C/T$ reaches a maximum value of 37.08% in 100 ppm sulphide solution. In the sulphide solutions with SC higher than 50 ppm, $\Delta E/T$ is higher than $\Delta C/T$, demonstrating that the corrosion-enhanced erosion is the most predominant factor for the cavitation erosion damage, and the erosion-enhanced corrosion is also an important factor.

3.3.4 Eroded Morphology

The surface morphologies of NAB after cavitation erosion in different solutions are shown in Fig. 13. In distilled water, craters spread all over the surface, indicating the plastic

deformation under cavitation erosion (Fig. 13a) [45]. In the corrosive solutions, galvanic corrosion occurs among different phases of the multi-element NAB alloy. The β' phases and eutectoid microstructure $\alpha + \kappa_{\text{III}}$ undergo SPC. As shown in Fig. 13b, c, the corrosion effect is relatively low in 3.5% NaCl and 20 ppm sulphide solutions. Some eutectoid microstructures with high hardness protrude on the surface, and the surrounding soft α phase is severely eroded. In the solutions with SC higher than 50 ppm, the NAB exhibits a brittle fracture mode and large pieces of materials are detached, resulting in large-sized and even groove-shaped cavities on the surface (Fig. 13d–f). At the bottom of the cavities, the eutectoid $\alpha + \kappa_{\text{III}}$ collapses and the κ phase falls off (arrows in Fig. 13e). In 200 ppm sulphide solution, the eutectoid microstructures and β' phases undergo severe corrosion damage, and cracks extend along the boundaries between the α matrix and β' phase/eutectoid microstructure (Fig. 13f). These results demonstrate that the presence of sulphide aggravates the SPC and decreases the phase boundary cohesion of NAB. The corrosion-enhanced erosion contributes largely to the remarkable mass loss increase of NAB in the sulphide solutions with SC higher than 50 ppm.

4 Conclusions

1. The electrochemical results show that when the SC exceeds 50 ppm, the cathodic process is dominated by the hydrogen evolution reaction because of the highly negative corrosion potential of the cast NAB. A limiting current region appears in the anodic branch of the polarisation curve, and it corresponds to the formation

Fig. 13 Surface morphologies of NAB after cavitation erosion for 5 h in **a** distilled water and 3.5% NaCl solutions with SCs of **b** 0 ppm, **c** 20 ppm, **d** 50 ppm, **e** 100 ppm, **f** 200 ppm

of a copper sulphide film, which is controlled by the diffusion of HS^- .

2. After long-term immersion, the mass loss rate of NAB is remarkably increased in the presence of sulphide. In 20 and 50 ppm sulphide solutions, the corrosion product films comprise a mixture of oxides and sulphides, which exhibits loose structures and inferior protectiveness. The severe SPC results in deep corrosion pits at the β' phases and eutectoid microstructure. In 100 and 200 ppm sulphide solutions, NAB suffers general corrosion, and the

films, which mainly consist of copper sulphides, are formed on the NAB surface.

3. Cavitation erosion greatly increases the corrosion rate of NAB in all solutions. It causes a negative OCP shift in 3.5% NaCl solution, but a positive OCP shift in the solutions with SC higher than 50 ppm. The cavitation erosion mass loss rate of NAB increases with the increase of SC. In 3.5% NaCl solution, the mechanical attack mainly contributes to the cavitation erosion damage. However, the cavitation erosion–corrosion syn-

ergy dominates the cavitation erosion degradation in the sulphide solutions. The corrosion-enhanced erosion is the most predominant factor for the cavitation erosion damage when the SC exceeds 50 ppm. The presence of sulphide aggravates SPC at the β' phases and eutectoid microstructure $\alpha + \kappa_{III}$ and weakens the phase boundary cohesion, thus resulting in brittle fracture mode and remarkable mass loss.

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