Materials Science & Engineering A 671 (2016) 118–126

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

Responses of the corroded surface layer of austenitic stainless steel to different corrosive conditions under cavitation

Xingyue Yong *, Ning Xiao, Hanjie Shen, Yili Song

State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China

ARTICLE INFO

Article history:
Received 18 March 2016
Received in revised form
8 June 2016
Accepted 9 June 2016
Available online 10 June 2016

Keywords:
Nanoindentation
X-ray diffraction
Austenite
Martensite
Interfaces
Phase transformation

ABSTRACT

Nanoindentation was used to measure the nano-mechanical properties of the corroded surface layer of austenitic stainless steel after cavitation corrosion tests. The phase structures and chemical compositions of the corroded surface layer were analysed using X-ray diffraction and X-ray Photoelectron Spectroscopy. The results show that corrosion caused a decrement of the nano-mechanical properties of the corroded surface layer. Once corrosion was weakened, the formation of a work-hardened layer resulted from the transformation of austenite into martensite. The synergistic effect caused the more rapid dissolution of Fe hydroxides, resulting in the enrichment of Cr and property changes of the corroded surface layer under cavitation.

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1. Introduction

Cavitation corrosion, which has also been called cavitation erosion-corrosion in the literature [1], often occurs in a severe manner on metallic components in industrial services. Cavitation corrosion is caused by the synergistic effect between cavitation erosion (mechanical factor) and corrosion (electrochemical factor) [1–3]. Cavitation erosion was defined as the progressive loss of original material from a solid surface due to continued exposure to cavitation [4]. Therefore, the cavitation corrosion resistance of metals depends not only on their corrosion resistance but also on their mechanical properties, such as the yield properties (hardness and rate of straining hardening), elastic properties (elastic modulus, resilience and super elasticity) and surface topography [1,5]. For example, hardness, tensile strength, engineering strain and grain size are significant parameters for the cavitation corrosion resistance of duplex structure alloys [6]. The excellent cavitation erosion resistance of Fe-Mn-Si-Cr shape memory alloys was found to be mainly attributed to their excellent elasticity in the local micro-zone of the corroded surface layer. In addition, the local elasticity of the corroded surface layer was one of the predominant factors characterising the cavitation erosion resistance of stainless steels and shape memory alloys [7,8]. The total recovery/deformation ratio (F_t), which reflects both super-elasticity and pseudo-plasticity, had also been found to correlate well with the cavitation erosion resistance of heat-treated NiTi [9]. Furthermore, C. Godoy et al. [10] found that a linear relationship between cavitation corrosion resistance and the ratio of the square of the hardness to the elastic modulus of the surface layer (H^2/E) could be established. For the cavitation erosion resistance of a hard coating, the derived parameter was proportional to the plasticity index, the ratio of the hardness to the Young's modulus (H/E), the adhesion force (L_{C2}), and the ratio of the thermal conductivity of the coating to that of the substrate. The derived parameter was inversely proportional to the number of phases in the coating phase composition, the ratio of the thermal expansion of coatings to that of the substrate, and the coating thickness [11–14]. Among these parameters, the mechanical parameters, for example H/E, had a close relationship to the cavitation corrosion resistance of the materials under cavitation [14,15].

Corrosion often causes a degradation of the mechanical properties of the corroded surface layer [16]; this degradation can accelerate corrosion on the corroded surface layer of metals under cavitation, resulting in the formation of a corrosion-induced soft layer [17] and a decrease in the thickness of the metals [15,18]. This type of degradation would also further lead to the degradation of the structural mechanical properties of metals [19], resulting in disastrous accidents and permanent failures of metallic components. In addition, when austenitic stainless steel in a 3.5% NaCl solution under cavitation was polarised at different potentials, the nano-mechanical properties of the corroded surface layer

* Corresponding author.
E-mail address: yongxy@mail.buct.edu.cn (X. Yong).

http://dx.doi.org/10.1016/j.msea.2016.06.019
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List of symbols

E	the averaged value of nano-elastic modulus, GPa
E_{nano}	nano-elastic modulus, GPa
H	the averaged value of nano-hardness, GPa
H_{nano}	nano-hardness, GPa
H/E	ratio of hardness to elastic modulus
$(H/E)_{nano}$	corroded surface layer nano-mechanical property
h	indentation depth, nm
h_1	a maximum of indentation depth, nm
M_{d30}	transformation temperature of austenite
Me^{n+}	metallic ion
$(Me)_2O_n$	metallic oxides
$Me(OH)_n$	metallic hydroxides
MeOOH	hydroxyl metallic hydroxides

were changed and the cavitation corrosion mechanism of the austenitic stainless steel was different [20]. To date, there are few articles available regarding the relationship of the properties of the corroded surface layer of metals with their corrosion resistance [7,8,18,21,22]. Thus, it is very important to study the corroded surface layer properties of metals, including the mechanical properties of the corroded surface layer, to understand the close relationship of these properties to the cavitation corrosion resistance of metals under cavitation.

Nanoindentation technology is a powerful tool for quantitatively measuring the surface layer nano-mechanical properties [10,15,23–25]. In the present paper, nanoindentation technology was used to quantitatively measure the corroded surface layer nano-mechanical properties of austenitic stainless steel in corrosive media without cavitation and after cavitation corrosion exposures. The phase structures and chemical compositions of the corroded surface layer without cavitation and under cavitation were analysed using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. The relationship of the nano-mechanical properties of the corroded surface layer to its phase structures and chemical compositions was studied to understand the relationship of the corroded surface layer properties to cavitation corrosion resistance.

2. Experimental materials and methods

The material used in this study was S30400 austenitic stainless steel (wt%: C, 0.07; Cr, 18.8; Ni, 8.9; Si, 1.0; Mn, 2.0; S, 0.03; P, 0.035; Fe, balance) in the form of a bar with a diameter of 19 mm. All specimens, which were solution annealed at 1050 °C for 30 min and subsequently quenched in water, were manufactured in accordance with ASTM G32 [4], wet polished with SiC paper up to 800 grit, cleaned using the ultrasonic method, degreased with ethanol, and finally dried in desiccators.

Cavitation corrosion exposures were performed using an ultrasonic cavitation corrosion apparatus [18,20]. The vibration frequency and vibration amplitude were 20 kHz and approximately 50 μm, respectively. The probe was mounted vertically with the specimen immersed in the test medium contained in an 800-ml glass beaker. To perform electrochemical tests, each specimen was first fixed on the top of the PTFE block. Next, the specimen was placed co-axially relative to the horn of the ultrasonic probe and was held still at a distance of 0.6–0.8 mm from the horn tip. The horn tip was immersed at a maximum depth of 10 mm, as shown Fig. 1.

Specimens made of S30400 stainless steels were used as the working electrodes. Platinum wire and saturated calomel electrodes (SCE) were used as the counter and reference electrodes, respectively. Specimens were subjected to a series of cavitation corrosion exposures in a 3.5% (wt%) pH 6.0–8.0 NaCl solution at 30 °C for 1.0 h. The test media were saturated with air. At the same time, some specimens were subjected to cavitation corrosion

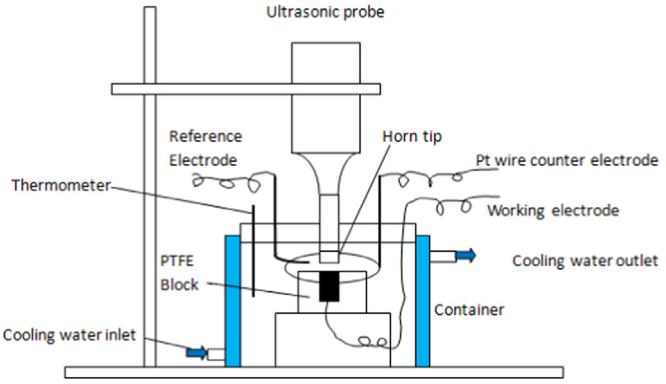

Fig. 1. A diagram of the ultrasonic cavitation corrosion apparatus with the specified electrochemical test cell.

exposures in the same media for 1.0 h while they were polarised at a −0.80 V (SCE) potential. The other specimens were subjected to cavitation corrosion in pH 4.5–6.5 distilled water at 30 °C for 1.0 h. For comparing the specimens under cavitation, specimens were also only immersed in a 3.5% (wt%) pH 6.0–8.0 NaCl solution at 30 °C for 1.0 h without cavitation.

The measurements of the nanohardness (H_{nano}) and nanoelastic modulus (E_{nano}) of the corroded surface layer were made on specimens without cavitation and after cavitation corrosion exposure. Before taking the nanoindentation measurements, the corrosion products on the corroded surfaces of specimens were removed by ultrasonic cleaning to reduce the effects of corrosion product films [16]. Based on the nanoindentation continuous stiffness measurement technique, all of these measurements were performed using a MTS Nano Indenter XP in accordance with ISO 14577-1:2007 and GB/T22458-2008 [25,26]. A maximum indentation depth was 2.0 μm. The Berkovich indenter was a three-sided pyramid [27]. Five indents were made per specimen. The nanohardness (H_{nano}) and the nanoelastic modulus (E_{nano}) were determined using the initial unload slope, contact area and peak load according to the method of Oliver and Pharr [28,29]. Thus, the profiles of H_{nano} and E_{nano} for the corroded surface layer with indentation depth (h) can be obtained first. The averages (H, E) of H_{nano} and E_{nano} were then calculated using the following formulas:

$$H=\frac{1}{h_1}\int_0^{h_1} H_{nano}(h)\cdot dh \quad (1)$$

$$E=\frac{1}{h_1}\int_0^{h_1} E_{nano}(h)\cdot dh \quad (2)$$

The nano-mechanical property of the corroded surface layer was comprehensively defined as $(H/E)_{nano}$, which is a dimensionless function [18]. The profiles of $(H/E)_{nano}$ with indentation depth (h) were then obtained. Similarly, the average (H/E) of $(H/E)_{nano}$ can be calculated using the following formula:

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