Corrosion Science 87 (2014) 265–277

Contents lists available at ScienceDirect

Corrosion Science

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

Semiconductivity conversion of Alloy 800 in sulphate, thiosulphate, and chloride solutions

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ARTICLE INFO

Article history:
Received 20 April 2014
Accepted 11 June 2014
Available online 21 June 2014

Keywords:
A. Alloy
B. EIS
B. SIMS
B. SEM
C. Anodic films
C. Passivity

ABSTRACT

Passive films formed on Alloy 800 in sulphate, thiosulphate, and chloride solutions were investigated using electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), secondary ion mass spectrometry (SIMS), and Mott–Schottky analysis. Experimental results revealed that the p-type or n-type semiconductivity of the passive film depended significantly on the solution chemistries. In a chloride–sulphate system, competitive adsorption of these two ions was believed to determine the type of semiconductivity. However, in a thiosulphate–chloride solution, the type of semiconductivity was attributed to the electrochemical reduction of the sulphur in thiosulphate and the subsequent adsorption of reduced sulphur species in the passive film.

1. Introduction

The extensive use of Fe–Cr–Ni alloys as engineering materials has led to numerous studies of the properties of their passive films. The composition, structure, thickness, and resistance of such passive films dictate the behaviour of these alloys [1–3]. Alloy 800, one of the Fe–Cr–Ni alloys, is a preferred material used in CANDU™ (CANada Deuterium Uranium) reactors and steam generators (SGs) in some pressurised water reactor (PWR) systems [4]. Pitting of SG tubing in SG second side crevice environments is a potential concern in nuclear power generating systems, however, no failure occurred and only a few flaws were recently detected in the tube sheet area of two Siemens designed plants [5]. Film degradation is found mostly at the heat-transfer crevices associated with the tube supports, where impurities such as sulphate and chloride ions in the SG feed water are highly concentrated. Hydrazine is intentionally added to the secondary side of SGs to minimise the oxygen content and avoid an elevated corrosion potential of SG alloys which causes the reduction of sulphate to HS^- or H_2S and $S_2O_3^{2-}$ (S valences being −2 and +4, respectively) depending on the pH [6–9]. Thiosulphate and chloride ions are recognised as the primary contributors to the passivity degradation of SG tubing materials whereas sulphate can inhibit corrosion degradation to some extent [10–12]. Previous investigations revealed that chloride and thiosulphate have a combined effect on the passivity degradation of Alloy 690 [13], type 304 stainless steel [14,15], Alloy 800 [7,8,15], and Alloy 600 [15].

Studies of the physicochemical properties of passive films have aimed to elucidate the mechanisms governing the surface reactivity and to explain the nature of the passive state [16,17]. To understand the properties of the passive film and their impact on corrosion resistance, many ex situ and in situ surface analysis techniques are used, such as X-ray photoelectron spectroscopy (XPS) [18,19], scanning tunnelling microscopy (STM) [20–22], scanning electron microscopy (SEM), secondary ion mass spectrometry (SIMS) [23,24], X-ray absorption near edge structure [25], and X-ray scattering [26]. Electrochemical methods are also widely used such as the scanning Kelvin probe (SKP) [27], electrochemical impedance spectroscopy (EIS) [28,29], Mott–Schottky analysis [30,31], scanning electrochemical microscopy (SECM) [32,33], and photoelectrochemistry [3,34–36]. An electrochemical equivalent circuit (EEC) model can be used to process EIS data related to high impedance systems like passive metals [37–41], but it can be difficult to clarify the physical meaning of each element in the EEC model [42]. In recent years, the point defect model (PDM) [43–45] and the kinetic model [7,46,47] have been successfully used to model EIS data. Recently, Marcus et al. proposed a "generalised model" for oxide film growth kinetics on metals and alloys [48,49]. In general, the passive film formed on Fe–Cr–Ni

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http://dx.doi.org/10.1016/j.corsci.2014.06.036
0010-938X/

alloys was interpreted in terms of its p-type or n-type semiconductivity. Capacitance measurements and photoelectrochemistry are often utilised to study the conducting behaviour of passive films. The donor densities and the flatband potential are often obtained through the analysis of Mott–Schottky curves. It is believed that degradation of the passive film is related to the electron structure of the film. The electronic properties of the passive film are determined by ionic movements in the film driven by the electric field, which is in turn affected by the electronic properties and structure of the passive film [50]. Many studies have explored the relationship between the electronic structure of passive film and its electrochemical and corrosion properties. For example, Gerischer [51] related the transpassive potential of iron to the electronic structure of its passive film. Schmuki and Bohni [52] modified the electronic structure of an iron passive film by illumination and improved its pitting resistance. Yang et al. [53] found that the presence of hydrogen in 310 SS caused an inversion of the conductivity type of a surface film from p-type to n-type, and p-type exhibited a lower susceptibility when there was a high content of chromium and nickel oxides. Zhong et al. [54] investigated the semiconducting behaviour of the temporarily protective oil coating on the surface of AISI 304 stainless steel in 5% Na_2SO_4 solution under corrosion potential: At the early stage of immersion, an anodic process was predominant at the metal/oil-coating interface, and the oil coating behaved as a p-type semiconductor. However, with the lapse of time, a cathodic reaction became dominant and the metal/oil-coating interface changed from p-type to n-type. Nevertheless, as of this writing, investigations of the mechanism of p-type/n-type semiconductivity conversion in different materials, and the effect of sulphate, chloride, and thiosulphate on the semiconductivity of the passive film formed on Alloy 800 have not been conducted.

This paper presents insight into the p-type/n-type semiconductivity conversion of Alloy 800 in sulphate, thiosulphate, and chloride solutions at 21 °C. The effects of these three ionic species on the semiconductivities and compositions of passive films were studied. A correlation between semiconductivity and passivity degradation was established. The factors that control sulphur-induced corrosion are basic to the design of a practical inspection schedule for plant maintenance.

2. Experimental procedures

2.1. Materials and electrolytes

A specimen of the nickel-based Alloy 800 was cut from tubing (Sandvik, heat number 516809) with an outer diameter (OD) of 15.88 mm and an average wall thickness of 1.13 mm, as shown in Fig. 1a. Samples were connected with copper wires and the inner surface and cross section were sealed with epoxy, therefore, while the outer surface of the tube was used for surface testing, the other surfaces were insulated from the testing solution. Prior to each experiment, the exposed surface was ground in the following sequence: 320, 600, 800, and 1200 grit, rinsed copiously with deionized water, acetone, and ethanol, then dried in air for 24 h. The exposed area for electrochemical tests was about 3.118 cm^2. The composition of Alloy 800 used in the experiments is listed in Table 1. The microstructure of Alloy 800 as determined by transmission electron microscopy (TEM) is shown in Fig. 1b where dislocation lines and angles that result from the cold rolling can be seen.

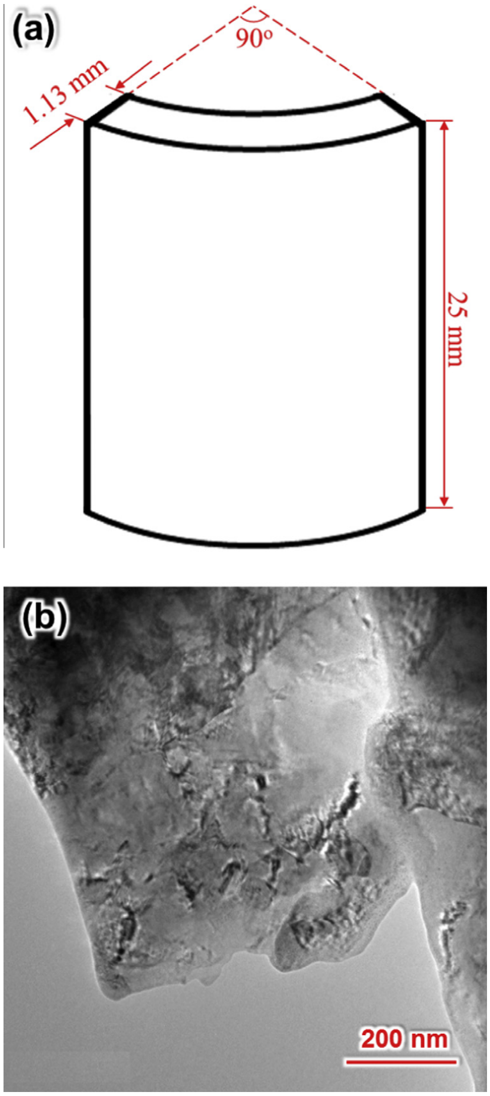

Fig. 1. Alloy 800 sample (a) schematic diagram of a sample cut from an Alloy 800 tube, (b) TEM micrograph of an Alloy 800 sample.

Table 2 lists the composition of the test solutions simulating the SG secondary side crevice chemistry conditions. Solutions R1 and R2 were reference solutions containing either sulphate (R1) or thiosulphate (R2). Solutions NC0, NC1, and NC2 contained chloride, chloride/sulphate, and chloride/thiosulphate, respectively. All chemicals used in the experiments were reagent grade (ACS reagent, +99%, Aldrich). The test solution was freshly prepared with deionized water (Milli-Q, Millipore, 18.2 MΩ resistance) prior to each test.

2.2. Experimental methods

Before electrochemical experiments were performed, the solutions were deaerated with high purity (99.99%) N_2 for 1 h. Nitrogen flow was kept constant throughout electrochemical measurements using a Gamry (PC-750) electrochemical workstation. Duplicate experiments were conducted on separate specimens.

2.2.1. Potentiodynamic polarisation

Each specimen was placed in a deaerated solution and constant-cathodic polarisation ($-1.0\ V_{SCE}$) was applied for 15 min as an initial conditioning step to reduce the oxide film (formed by ambient air) on the specimen surface. The specimens were then kept at an open-circuit potential for an hour before beginning the experiments. While the initial cathodic pretreatment was probably unable to completely reduce the air-formed film on high