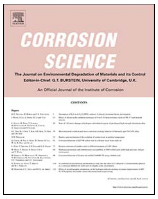
Corrosion Science 131 (2018) 386–403

Contents lists available at ScienceDirect

Corrosion Science

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



Characterization of oxide scales formed on alloy 82 in nominal PWR primary water at 340 °C and in hydrogenated steam at 400 °C

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ARTICLE INFO

Keywords:
Nickel
Welding
Alloy 82
XPS
TEM
Passive film

ABSTRACT

Alloy 82, used as weld metal in Pressurized Water Reactor (PWR), was exposed to hydrogenated steam at 400 °C and to simulated primary water at 340 °C. A comparative study of the oxide layer formed on the alloy surface in both environments was performed to confirm that steam conditions were representative of accelerated primary water conditions. For this purpose, the oxidation products were investigated at a nanometer scale using Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectrometry (XPS) and Transmission Electron Microscopy (TEM). Results obtained in both conditions are compared and the influences of heat treatment, test duration and surface preparation are studied.

1. Introduction

Nickel-based austenitic alloys are widely used in nuclear primary water reactors (PWR) either as wrought materials or as weldments. Although Alloy 600 (Ni-15Cr-10Fe) is known since the late 1950s to be susceptible to primary water stress corrosion cracking (PWSCC) [1], the first crack initiations in its weld material Alloy 182 were detected in 1994 [2]. To date, more than 300 cases have been reported mostly in Alloy 182 (13–17 wt.% Cr) but few events of cracking have also been documented for Alloy 82 (18–22 wt.% Cr) [3–5]. In addition, only welds that are not stress-relieved by the thermal treatment applied to the adjacent low carbon steel components are affected and cracking occurs in regions with high residual stresses [2,6].

The properties of the oxide scale that forms at the surface of nickel-based alloys in primary water are likely to play a key role in the SCC mechanism [7]. Although detailed descriptions of the oxide layers formed at the surface of Alloys 600 and 690 in primary water were extensively reported in the literature [8–13], fewer data exist for nickel-based welds [14–21] most probably because their oxidation behavior is quite similar to that of the wrought alloys. Oxidation of Alloy 600 in PWR conditions leads to the formation of a duplex oxide layer with a discontinuous outer layer covering a continuous Cr-rich inner layer. The outer layer consists of nickel ferrite ($NiFe_2O_4$) crystallites coming mainly from the saturation of the water in Fe and Ni cations. The presence of nickel hydroxide $Ni(OH)_2$ is sometimes reported [8,10,22]. The inner layer is constituted of mixed nickel and iron chromite $Ni(Fe,Cr)_2O_4$. Some authors also report the existence of Cr_2O_3 either as a thin continuous layer [11] or as discontinuous nodules [8] at the oxide/alloy interface. Besides, Cr depletion of the alloy may be observed below the alloy/oxide interface [23,24].

In addition, during laboratory tests, initiation of stress corrosion cracks in Alloy 82 in simulated primary water may require long exposure times of several thousand of hours, even at 360 °C [25]. One way to accelerate the SCC tests is to perform them at a higher temperature in hydrogenated steam. Indeed, Economy et al. [26] showed that a tenfold decrease in PWSCC initiation time is obtained in Alloy 600 by performing SCC tests in hydrogenated steam at 400 °C instead of primary water at 360 °C, without any significant modification of the SCC mechanisms.

The aims of this work are to provide a detailed description of the oxide scales formed on Alloy 82 welds and to estimate the representativeness of the hydrogenated steam environment to simulate oxidation in primary water conditions. For this purpose, oxidation tests are carried out in hydrogenated steam at 400 °C and in simulated

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https://doi.org/10.1016/j.corsci.2017.11.029
Received 3 December 2016; Received in revised form 6 November 2017; Accepted 8 November 2017

Table 1
Chemical composition (wt.%) of Alloy 82.

C	Ni	Cr	Fe	Co	Nb	Ti	Si	Mn	P	S	Cu
0.025	71.7	19.12	3.07	0.04	2.41	0.1	0.07	2.57	0.004	< 0.001	< 0.01

primary water at 340 °C. The oxide layers are characterized using X-ray Photoelectron Spectroscopy (XPS) and analytical Transmission Electron Microscopy (TEM). The effects of post-welding thermal treatment and surface finish on the oxide layer are also studied.

2. Materials and experimental procedures

2.1. Materials and specimens

Butt welds of Alloy 82, manufactured by Fouré-Lagadec using Gas Tungsten Arc Welding (GTAW), were deposited between two plates of 304L stainless steel. The chemical composition of Alloy 82 after welding is given in Table 1. One butt weld was studied in the as-welded conditions while the other one underwent a heat treatment of 7 h at 600 °C. This heat treatment simulated the stress relief treatment applied in service to the components next to the weld. More details on the welding process conditions, weld's geometry and microstructure are given in [27,28]. In particular, it was shown that the heat treatment favors chromium carbide precipitation at the grain boundaries.

Coupons with dimensions of 50 × 9 × 1.5 mm^3 were cut by electro-discharge machining with the weld in the middle of the sample. In order to study the influence of surface preparation on oxidation, the samples were polished to mirror finish either with 1 μm diamond paste or with colloidal silica suspension.

2.2. Corrosion test procedure

The corrosion experiments in pure hydrogenated steam were performed in a 23L stainless steel autoclave at 400 °C and under a pressure of 200 bar with a partial pressure of hydrogen of 800 mbar. The hydrogen content was controlled by a silver-palladium probe. The corrosion experiments in simulated primary water were carried out in a 380 mL stainless steel autoclave at 340 °C and with a total pressure of 144 bar. The solution contained 2 ppm lithium (as LiOH) and 1000 ppm boron (as H_3BO_3) and was in equilibrium with a hydrogen partial pressure of 200 mbar (dissolved hydrogen content = 37 cc/kg H_2O). The exposure times for both tests were 1500 h and 2500 h. The effects of the metallurgical state (as-welded/heat treated), environment (hydrogenated steam/primary water), test duration (1500 h/2500 h) and surface state (1 μm/colloidal silica suspension) were then studied.

2.3. Experimental characterizations

2.3.1. SEM and TEM observations

Scanning Electron Microscopy (SEM) observations of the oxidized surfaces were performed using a field emission gun (FEG) Zeiss Ultra 55 microscope. Observations were realized in backscattered-electron mode to better distinguish the oxide from the material.

TEM observations were performed on cross-section samples. The latter were prepared by ion milling or Focused Ion Beam (FIB) techniques. FIB preparation allowed the observation of large (20 × 10 μm) and thin (~100 nm) areas. Ion milling preparation allowed the observation of smaller areas but with very thin zone (< 50 nm) at the extreme surface, which was more suitable for High-Resolution TEM (HRTEM) observations. More details on the ion milling preparation are given elsewhere [8]. FIB preparation was carried out by SERMA Technologies (Grenoble, France) on a dual beam FEI Strata DB400 apparatus equipped with an omniprobe. Sample surfaces were first protected by a tungsten coating.

TEM investigations were realized on a FEI TECNAI F20-ST field emission gun microscope equipped with an Energy Dispersive X-ray (EDX) device, a Scanning TEM (STEM) system and High-Angle Annular Dark Field (HAADF) detector. STEM-HAADF combination allowed obtaining chemical contrast (Z-contrast) images with a high spatial resolution. Elemental EDX analysis was performed in both positional and line-scan modes using a nanometer-sized probe (1–2 nm). Crystallographic structure of oxides was investigated using HRTEM imaging. Local area fast Fourier transforms (FFT) were calculated on HRTEM images and indexed as electron diffraction patterns. Electron diffraction was also carried out when possible, especially on large particles. A systematic combination of lattice imaging (HRTEM) and chemical analysis (EDX) was applied in order to clearly identify oxides structure and composition.

2.3.2. XPS analysis

X-ray Photoelectron Spectroscopy (XPS) analyses were carried out using a Thermo-Fischer K-alpha spectrometer with a monochromatic Al Kα source. The analyses were performed on all the 1 μm-finished samples oxidized in hydrogenated steam (in the as-welded state after 1500 h and 2500 h exposure, heat-treated after 2500 h). No XPS characterization of the oxide layers formed in primary water were carried out.

Depth profiles were obtained by sputtering the surface with a monoatomic Ar^+ ion beam. An ellipsoid surface of 300 × 600 μm^2 was analyzed in the center of the 1 × 2 mm^2 sputtered surface. The crater depth was measured using a Dektak 8 stylus profilometer. The mean sputtering rate, measured on 8 different craters, was estimated to 0.6 nm s^{-1}. The sputtering rates of the oxide and the alloy were assumed to be similar. During XPS analysis, a low energy flood-gun was used in order to reduce the charge effect that can be present on the less conductive oxide layer on surface. The pass energy was 40 eV for the detailed spectra.

3. Results

3.1. Oxidation in hydrogenated steam

3.1.1. SEM observations

SEM investigations of the surfaces of coupons exposed to hydrogenated steam show that the oxide layer is composed of a continuous layer on which a variety of crystallites are dispersed (Fig. 1). The latter are of different shapes and sizes but may be divided into two families: (i) large pyramidal particles which can reach one micrometer in size and (ii) platelet-like particles with relatively smaller sizes.

The comparison between the different samples shows that the density of crystallites varies from one sample to another whereas the continuous compact layer seems to be similar on all of them. Considering the as-welded sample exposed 2500 h (Fig. 1a) as a reference, it can be noticed that the heat treatment reduces the platelet-like particle density whereas it increases the density of the pyramidal ones (Fig. 1b). For a shorter exposure time, we notice an increase of both platelet-shaped and pyramidal crystallite density (Fig. 1c). At last, an increase of the number and the size of the pyramidal crystallites is observed after colloidal silica suspension finish (Fig. 1d) compared to a 1 μm diamond paste finish. The effect of the final polishing on the platelet-shaped crystallites is less obvious.