



Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

Characteristics of Oxidation and Oxygen Penetration of Alloy 690 in 600 °C Aerated Supercritical Water

Xiangyu Zhong^{*}, Xinqiang Wu^{*}, En-Hou Han

CAS Key Laboratory of Nuclear Materials and Safety Assessment, Liaoning Key Laboratory for Safety and Assessment Technique of Nuclear Materials, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

ARTICLE INFO

Article history:

Received 17 June 2016

Received in revised form

22 September 2016

Accepted 14 October 2016

Available online

Key words:

Ni-based alloy

XPS

Supercritical water

High temperature corrosion

High temperature oxidation

Oxide film

The oxide films formed on Alloy 690 exposed to 600 °C supercritical water were characterized using mass measurement, X-ray diffraction, Raman spectroscopy, scanning electron microscopy equipped with energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. It was found that the mass gain of the alloy in supercritical water decreased with increasing exposure time. The oxide films have a double-layer structure, with an inner layer rich in Cr and outer layer rich in Ni and Fe after short time and long time exposure. The penetration of the oxide along the grain boundaries was observed, and the penetration depth increased with increasing exposure time. The grain boundaries and voids are the short-path of oxygen diffusion into the metal.

Copyright © 2016, The editorial office of Journal of Materials Science & Technology. Published by Elsevier Limited.

1. Introduction

The aim of the modern power plant is high thermal efficiency and low release of carbon dioxide. Supercritical water (SCW) as coolant has attracted increasing attention for its potential to satisfy both energy conservation and environmental protection requirements. To obtain higher efficiency, modern power plants are expected to operate at temperatures up to 650 °C or even higher, and pressures up to 34.5 MPa. Because of its high thermal efficiency and plant simplification, supercritical water cooled reactor (SCWR) is one of the most promising advanced reactor concepts for Generation IV nuclear reactors^[1,2]. However, under such an elevated temperature and pressure environment, the structural materials used in nuclear reactors and fossil power plants are much more prone to be corroded. Therefore, for the safety of the nuclear power plant, the corrosion performance of candidate materials used in such an aggressive environment needs to be investigated. Nickel-based alloys such as Inconel 625, Inconel 617, 718 and Hastelloy C-276 have been considered as candidate materials for SCWR because of their good corrosion resistance at high temperature water^[3–8]. These literatures

revealed that the oxides formed on nickel-based alloys at SCW environments have a multilayer structure where Ni is enriched in the outer layer and Cr is enriched in the inner layer. Weight gains in low conductivity SCW have been conducted and show that some nickel-based alloys do not have definite trend with temperature and exposure time, but instead manifest some form of erratic behavior. Tan et al.^[8], Was et al.^[9] and Cook et al.^[10] assumed that the fluctuation of mass change of Inconel 625 and Hastelloy C-276 exposed to SCW is due to the competition between the oxidation and pitting or spalling of the oxide films. But a mass gain behavior of the Alloy 625 and C-276 exposed to SCW was reported by Sun et al.^[6] and Zhang et al.^[7] Chang et al.^[11,12] found that the mass change of Alloy 625 were slight and fluctuated in 400 °C and 500 °C SCW with 8.3 ppm (by weight) O₂, and the mass gain followed a parabolic law in 600 °C and 700 °C SCW. In our previous work^[13] we found that general corrosion, pitting corrosion and nodule corrosion are observed on the Alloy 690 in 400–550 °C aerated SCW, and the mass change is fluctuated and a mass loss is observed with increasing exposure time, which could be attributed to the pitting. Therefore, there are some contradictory results on the corrosion behavior of nickel based alloys in SCW environment. On the other hand, intergranular oxidation of nickel based alloys was observed in high temperature air^[14–19] and high temperature water (T < 360 °C) environments^[20–25]. However, there are only a few investigations on intergranular corrosion of nickel based alloys in SCW environments^[4,13,26]. Thus the

^{*} Corresponding authors. Fax: +86 24 2389 4149.

E-mail addresses: xyzhong@alum.imr.ac.cn (X. Zhong); xqwu@imr.ac.cn (X. Wu).

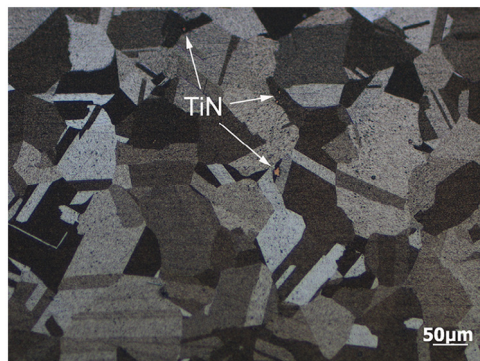


Fig. 1. Metallographic image of as-received Alloy 690.

intergranular oxidation mechanism of nickel based alloys in SCW is not fully understood, and more in-depth investigations are needed.

In the present work, the initial stage oxidation and long term oxidation of Alloy 690 were investigated. The specimens were exposed to 600 °C/25 MPa supercritical water containing 8 ppm (by weight) O₂ for different duration times from 1 h to 494 h. Mass change, phase composition, surface morphology, cross-section structure and chemical composition of oxide film were investigated by using various technologies, and the intergranular oxidation mechanism was also discussed.

2. Experimental

Exposure experiments were performed with a static SCW testing system maintained at 600 °C/25 MPa and exposure time up to 494 h. An alloy 800H autoclave with a volume of 200 mL was used in the present work, and the test solution was aerated pure water (8 ppm O₂). The Alloy 690 used in this study was solution annealed at 1060 °C for 0.5 h. Fig. 1 shows the metallurgic microstructure of Alloy 690 before SCW testing. The figure also shows that some TiN inclusions (arrows) exist in the grains and grain boundaries. Coupons (10 mm × 12.5 mm × 2 mm) were prepared by grinding with SiC papers to 2000 mesh and subsequently polished with diamond paste down to 2.5 μm. The specimens were cleaned with ethanol and ultrasonically rinsed with deionized water for 30 min before the tests. Table 1 is the chemical composition of the alloy.

After exposure, all the coupons were cleaned and dried, and were characterized by mass gain measurement, surface analysis and cross section analysis. The Sartorius BP211D microbalance (with a resolution of 10⁻⁵ g) was used to measure the mass of all coupons before and after exposure. X-ray diffraction (XRD) analysis was performed with a D/Max 2400 X-ray diffractometer using copper radiation. The Raman system (Horiba Jobin-Yvon LabRam HR 800) used in the present work contains a powerful laser at 532 nm⁻¹. INSPECT F and Phillips XL30 scanning electron microscopy (SEM) equipped with energy-dispersive X-ray analysis (EDX) system were used to analyze the surface and cross section morphologies and chemical compositions of oxide scales. X-ray photoelectron spectroscopy (XPS) measurements were performed with ESCALAB250 X-ray photoelectron spectrometer. Photoelectron emission was excited by monochromatic AlK_α source. The C1s peak from

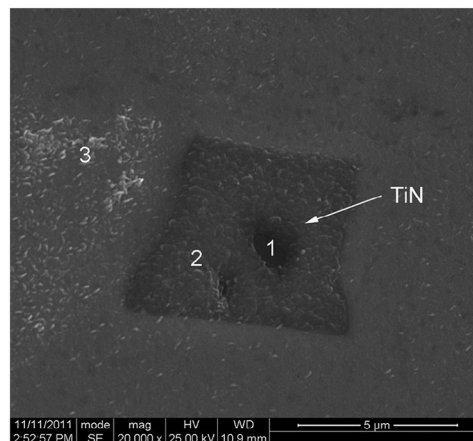


Fig. 2. SEM morphologies of oxides and TiN inclusions after exposure in 600 °C SCW for 1 h.

adventitious carbon at 285 eV was used as a reference to correct the charging shifts. Depth profile was performed under 2 keV Ar-ion sputtering and sputtering rate was determined to be about 0.2 nm/s (vs. Ta₂O₅). XPS spectra are quantified in terms of peak intensities and peak positions. The peak intensities show how much of a material is at the surface, and the peak positions indicate the elemental and chemical composition. The full width at half maximum (FWHM) is a useful indicator of chemical state changes and physical influences. The basic assumption of quantifying XPS spectra is that the number of electrons recorded is proportional to the number of atoms in a given state^[27]. Detailed cross-section characteristics were investigated using a transmission electron microscopy (TEM). Thin-foil specimens for TEM observations were prepared using a focused ion beam (FIB, FEI Helios NanoLab 600i) with Ga ion sputtering after a protective Pt strap was deposited on the oxide scale. Selected area electron diffraction (SAED) and TEM observations were performed with a CM121 STEM instrument operating at 200 kV.

3. Results

3.1. Initial oxidation behavior of alloy 690

Fig. 2 shows the surface morphologies of the Alloy 690 sample exposed at 600 °C for 1 h. It can be seen that the specimen surface is not fully covered by oxides. There are only a few flake-like oxides formed in some local area on the surface (Area 3 in Fig. 2). There is a TiN inclusion on the surface, and the EDS results (Table 2) show that the content of O is higher in the TiN inclusion than that of inclusion surrounding metal matrix, indicating that the oxidation of the TiN occurred first. In our previous work^[13], it was also found that some selective oxidation of the TiN inclusions resulted in some pits and nodules on the surface of Alloy 690 in 450–550 °C aerated SCW environment.

Fig. 3 shows XPS depth profiles of the oxide formed on alloy 690 exposures to supercritical water for 1 h. It is clear that Cr content first increases from the outermost surface and then decreases gradually, while Ni content first decreases from the outermost surface

Table 1
Chemical compositions of Alloy 690 (wt%)

C	N	Cr	Fe	Mn	P	Si	Al	Ti	Cu	Nb	Co	Ni
0.013	0.01	29.15	9.19	0.21	0.01	0.02	0.26	0.305	0.01	0.01	0.01	Bal.

Download English Version:

<https://daneshyari.com/en/article/7952056>

Download Persian Version:

<https://daneshyari.com/article/7952056>

[Daneshyari.com](https://daneshyari.com)