Influence of Octadecylamine Concentration and Temperature on the Organic Film Formation on Alloy 690TT Substrate

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1. Introduction

In nuclear power plants, film forming amine (FFA) addition has positively been considered as a corrosion mitigation strategy during a plant operation or a layup period. The FFA is defined as organic substance with specific functional groups. FFAs are defined by the general formula R_1-[NH-(R_2)-]n-NH_2, where R_1 is an unbranched alkyl chain with 12 to 18 carbon atoms and R_2 is a short-chain alkyl group that generally consists of 1 to 4 carbon atoms and n is an integer between 0 and 7 [1].

The FFA addition could produce a protective hydrophobic film on the exposed surface of secondary feedwater piping and components, thereby isolating the surface from corrosive environments and reducing the corrosion rate of components [2]. In addition, the addition of FFA addition could promote the dropwise condensation and improve the thermal performance of condenser tube [3].

Recently, Electric Power Research Institute (EPRI) selected the FFA chemicals, octadecylamine (ODA), N-oleyl propylene diamine (OPDA), and non-film amine, to focus on a potential EPRI technical evaluation. In particular, ODA, representative of the simplest FFA molecules (n = 0, R_1 = $C_{18}H_{37}$), has been actively studied in secondary water of NPPs [4-7]. In particular, ODACON®, which is ODA-based film forming product (FFP), has been recently used to mitigate the amount of corrosion products at PWR/PHWR units. This FFP has been applied at Embalse (PHWR Unit) in Argentina during a layup period in 2015 and Blayais Unit 1 (PWR Unit) in France in 2018 [8,9].

There are some investigations related to FFA in nuclear power plants [10,11]. However, FFA related researches have mainly focused on the corrosion behavior of vulnerable piping components such as carbon steel and low alloy steel in secondary system. The maintenance effectiveness of carbon steel is enhanced and the corrosion rate is decreased with ODA concentration increase. In addition, 20 mg/kg ODA is strong enough for hydrophobic film formation and corrosion rate mitigation on carbon steel [10]. The formation and the characterization of an ODA film formed on a P275 carbon steel surface at low temperature has been recently studied [11].

To expand FFA application to the all secondary system during the operation, the effects of various secondary water chemistry conditions such as ODA concentration, temperature, substrates, and pH on the film formation and characterization should be investigated.

In this paper, the effects of ODA concentration and temperature on the organic film formed on Alloy 690TT substrate was investigated. The organic film was formed on Alloy 690TT substrate in an autoclave at 90 °C and 230 °C. The film formed on substrate was characterized using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The present work provide the important elements for the understanding of ODA behavior versus concentration and temperature.

2. Methods

2.1 Specimen preparation and film formation

The chemical composition of the Alloy 690TT specimen used in this work is presented in Table I. The specimens were cut into 10 mm x 10 mm x 1 mm for an oxide film analysis.

Table I: Chemical composition of Alloy 690TT tube (wt. %).

Cr	Fe	Si	Mn	Ti	Al	C	Ni
29.3	10.4	0.3	0.3	0.3	0.2	0.02	Bal.

The film-forming solution was used in deionized water containing two ODA concentrations (15 ppm and 500 ppm) with 25 ppm ethanolamine (ETA). The organic film was formed on Alloy 690TT surface in an autoclave at 90 and 230 °C for 10 days.

2.2 Microstructural characterization of organic film

After the film formation, the morphology of organic films formed on Alloy 690 substrate was observed using SEM. The chemical composition of film was analyzed using an energy-dispersive X-ray spectrometer (EDS) attached to the SEM. Cross-section of film was analyzed using a focused ion beam (FIB)-SEM. The depth profile and surface chemical state of the film formed on the SG tube in the solution containing 25 ppm ETA and 500 ppm ODA at 230 °C was also analyzed using a XPS. The XPS analysis was carried out using a Thermo VG scientific sigma probe X-ray photoelectron spectrometer (Thermo VG scientific, USA) with an Al Kα X-ray source (1486.6 eV) operated at 15 kV and 150 W under a base pressure of 2.7×10^{-7} Pa.

3. Results

3.1 Surface characteristics of the organic film by using SEM analysis

Fig. 1 shows the surface morphology of the film formed on Alloy 690TT substrate under various ODA concentration and temperature conditions by using SEM analysis. In the cases at low temperature (15 ppm ODA and 500 ppm ODA at 90 ºC), the film was not formed on the entire surface, but was formed intensively on only some parts. Compare to 15 ppm ODA at 90 ºC, the film-formed surface was much larger and evenly distributed under high ODA concentration. In the case of 500 ppm ODA at 230 ºC, the film was uniformly distributed on the entire surface of Alloy 690TT substrate. The film had a petal-like morphology. Based on the results, the ODA concentration and temperature affect the efficiency of film formation. In particular, temperature has a greater influence on film formation than ODA concentration.

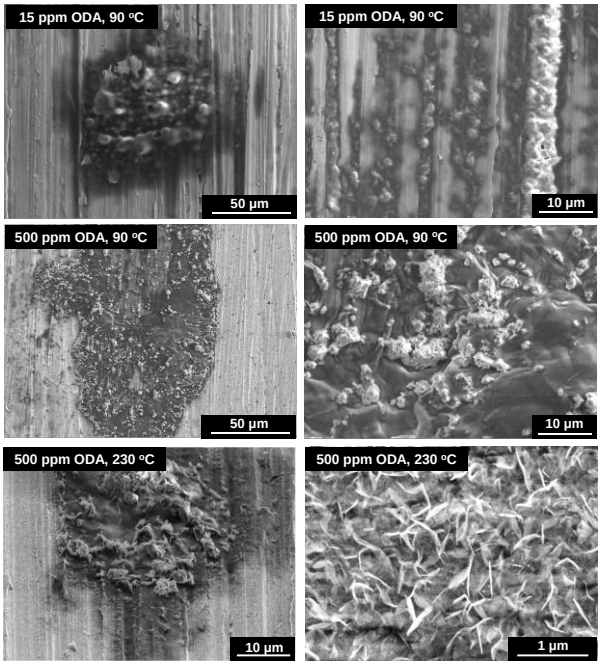
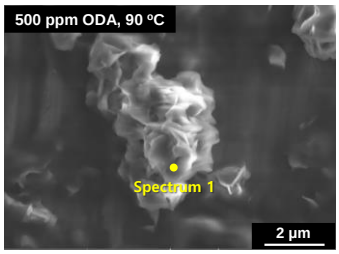
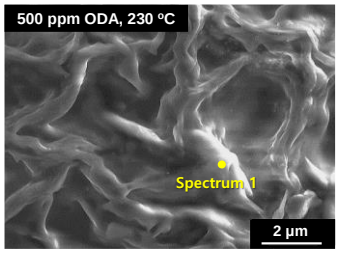


Fig. 1. SEM image of the surface of film formed on Alloy 690TT substrate under various ODA concentration and temperature.

Fig. 2 shows the chemical composition of the film in the two conditions (500 ppm ODA at 90 ºC and 230 ºC) by using SEM-EDS analysis. In both cases, it was mainly composed of C (about 85~88 wt. %) and N and O amounted to (6~7 wt. %) and (4 wt. %), respectively. Metallic elements such as Cr, Ni, and Fe were detected in trace amount. Compare to 500 ppm ODA at 90 ºC, the amount of metallic elements in 500 ppm ODA at 230 ºC was relatively high. The reason for this is that the corrosion rate of Alloy 690TT is much faster at high temperature. Based on the results, temperature does not effect on the content of main elements of organic film.



Element	wt. %
C	87.37
N	7.33
O	3.92
Cr	0.89
Fe	0.10
Ni	0.43



Element	wt %
C	85.06
N	6.25
O	4.4
Cr	2.37
Fe	0.41
Ni	1.51

Fig. 2. SEM-EDS analysis of the film formed on Alloy 690TT substrate under different conditions.

Fig. 3 shows the SEM images of cross-sectional part of organic film formed on the substrate. In the cases at low temperature (15 ppm ODA and 500 ppm ODA at 90 ºC), the thickness of the films is about 1.5~5.0 µm. These films were not formed evenly on the surface and exists in some agglomerated form. In the case of 500 ppm ODA at 230 ºC, the film thickness is approximately 0.2~0.25 µm. This film was uniformly formed on entire surface. Under all conditions, no defects such as pores and cracks were observed in the film. Furthermore, no gap or hole can be observed at the interface between film and Alloy 690TT substrate, which confirms that film tightly bonded to the substrate.

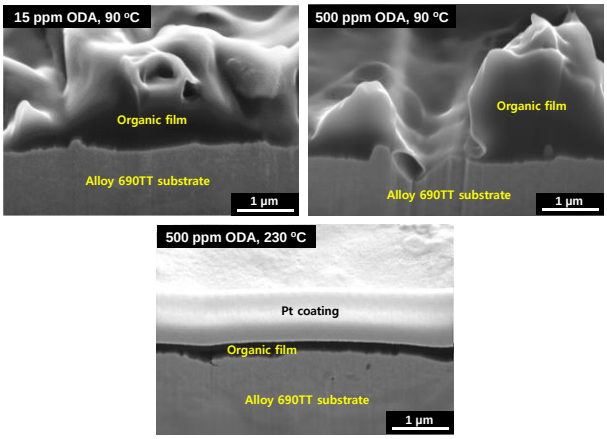


Fig. 3. Cross-section SEM image of the film under various ODA concentration and temperature.

3.2 XPS analysis of the organic film

Fig. 4 shows the XPS survey spectra for the surfaces of the film-formed specimens in 500 ppm ODA at 90 ºC

and 230 ºC. C, N, and O peaks were observed on both specimens confirming a homogenous coverage of specimen surface by the ODA molecules. In special, the small N peak and the intense C peak are associated with the presence of the ODA molecules. In the case of 500 ppm ODA at 90 ºC, the relatively high amount of Ni is due to the exposure of Alloy 690TT matrix.

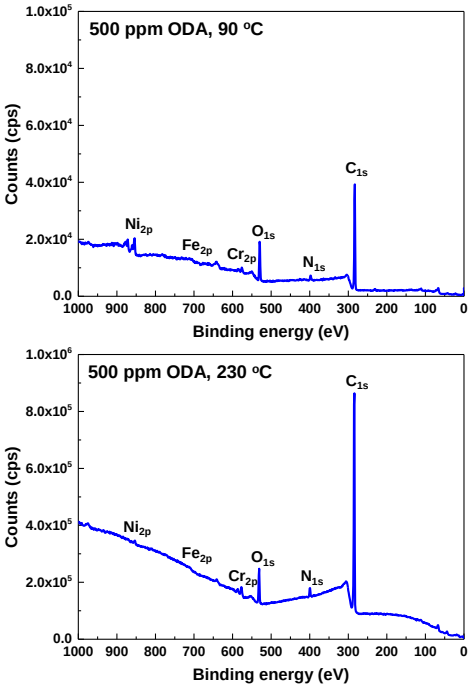


Fig. 4. XPS survey spectra of the film formed on Alloy 690TT substrate in the solution containing 500 ppm ODA at 230 ºC.

Fig. 5 presents the XPS depth profile of chemical composition with sputtering time for the organic film formed on Alloy 690TT substrate in the solution containing 500 ppm ODA at 230 ºC. The outermost part of the film is rich in C, O, and N. As the sputtering time increased, the content of C, N, and O decreased and the Ni, Cr, and Fe concentrations increased. It also shows the similar tendency under low temperature conditions.

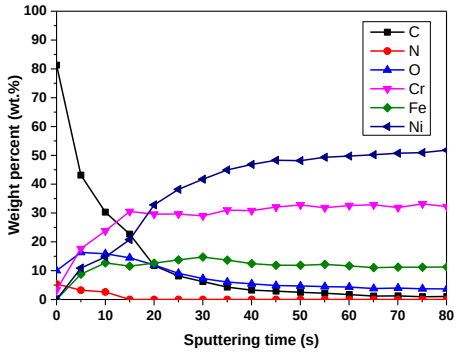


Fig. 5. XPS depth profile of the film formed on Alloy 690TT substrate in the solution containing 500 ppm ODA at 230 ºC.

In addition, deconvolution data of XPS spectra will be presented at the presentation.

4. Conclusions

1) Under low temperature conditions, the film was not formed on the entire surface, but was formed intensively on only some parts. However, under high temperature and ODA concentration condition, the film had a petal-like morphology and uniformly formed on the entire surface of Alloy 690TT substrate.

2) Based on the SEM-EDS results, temperature does not effect on the content of main elements of organic film. Regardless of ODA concentration and temperature, no defects were observed in the film and at the interface between film and substrate.

3) Among the three conditions, the optimal condition for the film formation on Alloy 690TT substrate was determined to be 500 ppm ODA at 230 ºC. However, the effects of other water chemistry parameters (fluid velocity, pH, and oxygen concentration) on film formation by ODA addition should be considered. In addition, it will be necessary to determine the behavior of ODA thermal degradation products. Currently, our research group is ongoing to study the thermal stability of organic film formed on various secondary materials.

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