



Presented at the NuMat 2012 Conference, 22–25 October 2012, Osaka, Japan

In situ Raman spectroscopic analysis of surface oxide films on Ni-base alloy/low alloy steel dissimilar metal weld interfaces in high-temperature water



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ARTICLE INFO

Article history:

Received 21 March 2013

Accepted 22 March 2014

Available online 29 March 2014

ABSTRACT

In situ Raman spectroscopy has been applied to analyze the surface oxide films formed on dissimilar metal weld (DMW) interfaces of nickel-base alloy/low alloy steel under hydrogenated high-temperature water condition. For the analysis of the oxide films under high temperature/pressure aqueous conditions, an in situ Raman spectroscopy system was developed by constructing a hydrothermal cell where the entire optics including the excitation laser and the Raman light collection system were located at the nearest position to the specimen by means of immersion optics. In situ Raman spectra of the DMW interfaces were collected in hydrogenated water condition at different temperatures up to 300 °C. The measured in situ Raman spectra showed peaks of Cr₂O₃, NiCr₂O₄ and Fe₃O₄ at the DMW interface. It is considered that differences in the oxide chemistry originated from the chemical element distribution inside of the DMW interface region.

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1. Introduction

Dissimilar metal welds (DMWs) have been widely used as a joining technique of key components in nuclear power plants such as in the case of nozzles for reactor pressure vessels and pressurizers or for cold/hot legs of steam generators. A transition zone exists between the bulk low alloy steel (LAS) and the filler metal which has a complicated microstructure and chemical composition compared to the parent materials. Several studies have been performed to analyze the microstructural and mechanical characteristics of DMWs [1–6]. According to previous studies, the existence of a compositional gradient from the base to the weld metal across the fusion boundary was reported, and such a gradient may affect the corrosion resistance, as well as the microstructure and the mechanical properties. In recent years, several cases of cracking in welded joints of nuclear power plants have been reported [7]. However, there exists a wide gap between the actual phenomena occurring in and the mechanistic understanding of DMWs which can be attributed to the conventional ex situ analysis of such incidents [8,9]. In situ investigation can provide a clearer picture of the corrosion mechanism because the removal (ex situ) of material from the corrosion environment that can result in a modification

of the oxide film structure and chemistry. Due to experimental constraints of measurements in aqueous conditions at elevated temperature and pressure, only a limited number of techniques are available for the in situ study of the oxidation or corrosion behavior.

Raman spectroscopy is one of the currently available in situ investigation techniques. Raman spectroscopy is the measurement of the wavelength and intensity of inelastically scattered light due to the excitation of molecules by irradiating a sample with a laser. It is performed by collecting the light that is inelastically scattered by the sample. The inelastically scattered light, which is called Raman scattered light, is shifted in energy compared to the incident light by a discrete amount that is characteristic of the scattering material.

There are several previous studies about in situ Raman investigations of aqueous corrosion which were conducted on pure metals or alloys at elevated temperatures in a high-purity water environment, in air-saturated water or under pressurized water conditions [10–16]. Kumai and Devine [9,10] performed in situ Raman spectroscopic measurements on the aqueous corrosion of iron and iron-base alloys in water at high temperatures. 304 stainless steel and Fe–10Ni alloys with varying chromium content were investigated. Maslar et al. [12–15] have made extensive measurements on pure metals and stainless steels in air-saturated water conditions up to 505 °C by in situ Raman spectroscopy. Kim and

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Hwang [16] developed an optical flow cell for in situ investigations and studied oxide films on the surface of Alloy 600 under primary water conditions of a pressurized water reactor (PWR) with different dissolved hydrogen concentrations and stress [17]. While hydrothermal cells that enable the changeover of the optical path from outside to inside of the hydrothermal cell were designed and manufactured in all previous studies, the results of the measured Raman spectra indicated the need of improvement in the signal-to-noise ratio in several cases.

This study aims at the investigation of the corrosion behavior of Ni-base alloy/low alloy steel DMWs using in situ Raman spectroscopy. For this purpose, a hydrothermal cell was designed and assembled to accommodate immersion probe optics in order to increase the signal-to-noise ratio. In situ surface oxide analyses using Raman spectroscopy were conducted at the interface regions of Ni-base alloy/low alloy steel DMWs in hydrogenated water conditions at high temperatures.

2. Experimental methods

2.1. Specimens

The DMW specimens for in situ Raman spectroscopy were fabricated by the Argonne National Laboratory. The DMW mock-up was made of Alloy 690/Alloy 152/A533Gr.B and its welding procedures have been qualified by ASME Section IX [18]. The chemical compositions of these metals are shown in Table 1. A533Gr.B was buttered with Alloy 152 by shielded metal arc welding, followed by a post welding heat treatment at 607–635 °C for 3 h. After this process, the weld joint of Alloy 690 and A533Gr.B was prepared by the shielded metal arc welding method with Alloy 152 fillers. The welding processes of the specimen are described in detail elsewhere [5]. The samples were 7 mm in diameter and 2 mm in thickness and were mechanically polished up to 1 μm .

2.2. Experimental system

The in situ Raman spectroscopic system developed in this study mainly consisted of a hydrothermal optical cell, a high-temperature–high-pressure water loop, and a Raman spectroscopic system.

2.2.1. Hydrothermal optical cell

A hydrothermal optical cell was developed for the in situ observation at high temperature and pressure aqueous conditions. The 19.05 mm (3/4 in.) union cross of a compression fitting made of alloy 600 was used as the main part of the optical cell, which was connected to a 19.05 mm union tee for the simulated primary water circulation of a PWR. The 19.05 mm union tee served as a water inlet and outlet in a coaxial configuration with 6.35 mm (1/4 in.) inner tubing. The sample holder and the immersion probe optics were inserted through the left and right arm of the union cross, respectively. The union cross was fully covered by a main heater and thermal insulation, thus leading to a maximum working temperature of around 350 °C. The sample holder was made of an oxidized Zr rod to avoid the formation of a galvanic couple, and the cap was made of Alloy 718. To achieve a maximum temperature of

350 °C, the flowing-in water was heated in multiple stages: through the coaxial heat exchanger, a cable-type preheater, and finally a main heater covering the union cross.

2.2.2. Test loop

The test loop was designed and assembled in order to simulate PWR primary water conditions for the oxidation of DMW samples. The test loop enabled the heating of water up to a temperature of 350 °C at 15 MPa by the pre and main heater. The water chemistry conditions were maintained in such a way that the dissolved hydrogen content was around 30 cm^3/kg and the dissolved oxygen content was less than 10 ppb.

2.2.3. Raman spectroscopic system

The Raman spectroscopy system, RamanRXNTM manufactured by Kaiser optical systems, Inc., was employed in this work, and the system is mainly composed of an excitation laser, a spectrometer and optical components including mirrors and filters. A continuous krypton ion laser operating at 532 nm was used for the excitation of in situ spectra. Unwanted plasma lines from the laser were removed by a holographic laser bandpass filter that consisted of a volume transmission grating located between two prisms. Volume-phase holographic gratings used in Raman spectrographs had dispersions as high as 5000 grooves/mm. It was possible to construct compact, high-resolution spectrographs using these holographic transmission gratings. The reflectivity of the notch filter could be quite high and the bandwidth can be quite narrow. The transmission at the center of the notch was less than 0.0001%, equivalent to optical density greater than 6.0. The half width at the half maximum (HWHM) of the notch corresponds to about 175 cm^{-1} . The spectral resolution of the Raman system was 5 cm^{-1} . Direct-contact immersion optics with a sapphire window at the tip was used to collect the Raman reflected signal from the specimen. The power density at the specimen was less than 10 mW/cm^2 and the beam size of the laser was 100 μm . The body of the immersion optics was made of Alloy-C276 and was compatible with 12.7 mm (1/2 in.) compression fittings. The temperature range of the immersion optics was –30 to +450 °C and the pressure was up to 20 MPa. Fig. 1 shows the in situ Raman spectroscopic system, the assembled immersion optics, as well as the sample stage and the specimen inside the hydrothermal optical cell. An appropriate holographic notch filter was placed in the collected, collimated radiation. Reference Raman spectra at ambient conditions were measured on oxide powder samples such as nickel and chromium oxides and their spinels.

2.3. Experimental procedure

In situ Raman spectroscopy was performed on DMW interfaces in hydrogenated water environment. The test temperature was increased from 25 °C to 300 °C. The exposure temperature was measured by a thermocouple placed in the interior of the cell through the bottom arm of the 19.05 mm union cross described above. The duration of the exposure at each temperature is summarized in Table 2. The data for all in situ and ex situ Raman spectra were post-treated with baseline correlation by line correction method

Table 1
Chemical composition of dissimilar metal weld used in this study.

Material	Composition (wt%)													
	C	Al	Si	P	S	Cr	Mn	Fe	Co	Ni	Cu	Nb + Ta	Mo	Ti
Alloy 690	0.03		0.07		<0.001	29.5	0.2	9.9		59.5	0.01			
Alloy 152	0.04	0.24	0.46	<0.003	<0.001	29.04	3.56	9.36	<0.01	55.25	<0.01	1.84	0.01	0.15
A533 Gr.B	0.22		0.19	0.01	0.012	0.18	1.28	Bal.		0.51			0.48	

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