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Original Article

EELS and electron diffraction studies on possible bonaccordite crystals in pressurized water reactor fuel CRUD and in oxide films of alloy 600 material

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A B S T R A C T

Experimental verification of boron species in fuel CRUD (Chalk River Unidentified Deposit) would provide essential and important information about the root cause of CRUD-induced power shifts (CIPS). To date, only bonaccordite and elemental boron were reported to exist in fuel CRUD in CIPS-troubled pressurized water reactor (PWR) cores and lithium tetraborate to exist in simulated PWR fuel CRUD from some autoclave tests. We have reevaluated previous analysis of similar threadlike crystals along with examining some similar threadlike crystals from CRUD samples collected from a PWR cycle that had no indications of CIPS. These threadlike crystals have a typical [Ni]/[Fe] atomic ratio of ~2 and similar crystal morphology as the one (bonaccordite) reported previously. In addition to electron diffraction study, we have applied electron energy loss spectroscopy to determine boron content in such a crystal and found a good agreement with that of bonaccordite. Surprisingly, such crystals seem to appear also on corroded surfaces of Alloy 600 that was exposed to simulated PWR primary water with a dissolved hydrogen level of 5 mL H_2/kg H_2O, but absent when exposed under 75 mL H_2/kg H_2O condition. It remains to be verified as to what extent and in which chemical environment this phase would be formed in PWR primary systems.

1. Introduction

CRUD-induced power shifts (CIPS), also called axial offset anomaly (AOA), is caused by boron deposition in fuel CRUD promoted by local subcooled nucleate boiling on fuel surfaces. It impacts shutdown margin and can potentially lead to plant power derating. Therefore, it has been an area of intense technical assessments and root cause examinations by many researchers. Although there are various ideas about which boron containing chemical species might be formed in fuel CRUD, lines of experimental evidence are scarce. One of the prime suspects, threadlike bonaccordite (Ni_2FeBO_5) crystals, was examined by Sawicki [1] using fuel CRUD samples from a severely CIPS-affected Callaway Cycle 9 fuel deposit. The samples were examined first with Mössbauer spectroscopy [1,2] and later by Sawicki and Woo [3] with electron diffraction in transmission electron microscopy (TEM). In these studies, however, no direct determination of boron content in the crystals was performed.

In this paper, we have applied both electron diffraction and electron energy loss spectroscopy (EELS) in TEM to study some threadlike crystals collected from a pressurized water reactor (PWR) unit without any CIPS indications. We have also examined some similar threadlike crystals that were present on a corroded Alloy 600 material exposed in autoclave under simulated PWR primary water conditions with a dissolved hydrogen level of 5 mL H_2/kg H_2O.

2. Experimental

2.1. Materials

2.1.1. Fuel CRUD

The fuel CRUD sample examined in this paper was from Ringhals unit 4, which is a Westinghouse-built PWR and has been long

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operated at a modified pH of 7.24 at 300°C with a $[Li]_{max}$ of 2,200–3,500 ppb at the beginning of cycle (BOC) until the refueling outage of 2007, when it was further increased to 4,200 ppb. In 2011, steam generator replacement (SGR) from Alloy 600MA to Alloy 690TT tubing was performed. Prior to and after SGR, Ringhals launched large CRUD scrape/ultrasonic fuel cleaning campaigns to collect and analyze fuel CRUD samples. Some of the results were presented in Ref. [4]. The CRUD sample as analyzed in this paper was from a once-burnt (14.63 MWd/kgU) fuel rod from Ringhals unit 4 in 2011 prior to SGR, and it was scraped in a pool at an axial level of 2,403 mm (measured from the top of the bottom plate) and collected using a membrane disk filter with an average pore size of 0.45 μm. The history of water chemistry conditions of Ringhals unit 4 was described by Bengtsson et al [5].

2.1.2. Corroded Alloy 600 material

Another examined specimen was a compact tension (CT) specimen made of Alloy 600MA that had been subjected to crack growth measurement under constant load in simulated PWR primary water with a dissolved hydrogen level of 5 mL H_2/kg H_2O. (Dissolved hydrogen concentration, mL H_2/kg H_2O, calculated with standard temperature and pressure of 100 kPa and 273.15 K.) The detailed sample description and the experimental conditions can be found in Ref. [6]. Following the crack growth rate measurement, the sample was first embedded in epoxy and the corroded surface was then cut with focused ion beam (FIB) to lift out a TEM lamella containing corrosion products in the crack tip region (approximately 30 μm from the crack tip).

2.2. Sample preparation

2.2.1. CRUD particles on TEM grid

To transfer CRUD particles on the membrane filter material to a grid used in TEM, a small piece of the filter material was placed in acetone in a laboratory test tube. The filter material was then quickly dissolved, and the solid CRUD particles were centrifuged onto a custom-made Teflon set holding a TEM grid. Thereafter, the acetone in the test tube was removed with a pipette and the CRUD-deposited TEM grid was removed from the tube and dried in air.

2.2.2. TEM lamella liftout from a crack tip

A dual-beam system of the Nova 600 NanoLab (FEI Company) was used to prepare the TEM lamella from the crack tip region of the sample. The system, combining a high-resolution field emission gun scanning electron microscopy with FIB, was used to search for and to accurately identify the locations of crack tips on the abovementioned sample surfaces. To protect the metal surface from Ga^+ ion beam damage, two protective Pt layers were deposited on the metal surface subsequently, first using an electron beam induced deposition followed by an ion beam induced deposition of Pt. The thinning of the lamella was made progressively until its thickness became approximately 50 nm or less. The final low-energy polishing step was performed at ion acceleration voltage and current of 5 kV and 70 pA, respectively.

2.3. TEM instrumentation

A field emission type TEM (JEOL model, JEM 2100F), operated at 200 kV and equipped with energy-dispersive X-ray spectroscopy (EDS) and EELS detectors, was used to examine fuel CRUD particles that were collected on TEM grids and the TEM lamella prepared from the crack tip regions of the CT specimen. The microscope is equipped with both bright field and dark field scanning transmission electron microscopy detectors. EDS and EELS were used, where appropriate, to determine local elemental compositions. Quantification of EELS data was done using the standard procedure of the Digital Micrograph Suite (GATAN). Leading background was removed using a power law function, and effects of plural scattering are estimated and removed from the element spectral range. Electron diffraction was used to determine the crystal structures of interest. Simulated electron diffraction patterns were calculated using Web-EMAPS, emaps.mrl.uiuc.edu [7].

3. Results and discussion

3.1. Threadlike crystals in fuel CRUD

Among the main phase compositions of fuel CRUD in PWRs, such as NiO and mixed spinel of Me_3O_4 (Me: e.g., Ni, Fe, Cr), some threadlike crystals have been reported in the literature (e.g., [3,8–10]). There was one kind of threadlike crystals with a nickel/iron atomic ratio close to 2. As mentioned above, these materials could correspond to either bonaccordite possessing an orthorhombic structure [3], or the previously characterized tetragonal Ni_2FeO_3 phase [9]. The threadlike crystals, as mentioned in both studies, were from different PWR units. A strict comparison between the different studies was not possible, even though the crystals look rather similar in morphology and in their atomic ratio of nickel to iron. In this paper, two threadlike crystals (one is shown in Fig. 1) were chosen for examination with EDS, electron diffraction, and EELS in TEM. In particular, EELS was applied to provide a direct evidence of the presence of boron in such crystals.

Fig. 2 shows an electron diffraction pattern measured on a threadlike crystal and a simulated electron diffraction pattern based on the bonaccordite Ni_2FeBO_5 crystal structure found in Ref. [11]. The experimental and measured patterns agree well with each other. For example, measured *d* values for the two crystal planes, *hkl* (6 0 0) and (0 −2 2), as represented by the indicated spots in the electron diffraction pattern, agree up to the second decimal (1.53 and 1.46 Å, respectively). Fig. 3 shows a tilting experiment in which the simulated diffraction patterns are compared with the experimental ones at various tilting angles. The calculated and experimental tilting angles also agree with each other within the experimental error, and therefore it can be said that the measured crystal structure is in good agreement with that of bonaccordite.

In Fig. 4, EEL spectra, in raw data and with the background removed, are shown together. In the energy loss region for boron, an increased intensity can be seen. The elemental compositions of the crystal as determined with EELS are presented in Table 1.

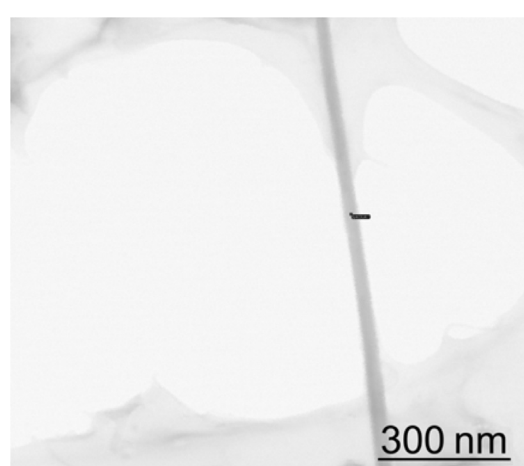

Fig. 1. A threadlike crystal in the fuel CRUD sample.

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