



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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ABSTRACT

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 H₂/kg H₂O, but absent when exposed under 75 mL H₂/kg H₂O condition. It remains to be verified as to what extent and in which chemical environment this phase would be formed in PWR primary systems.

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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 (Ni₂FeBO₅) 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 H₂/kg H₂O.

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 H₂/kg H₂O. (Dissolved hydrogen concentration, mL H₂/kg H₂O, 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 Me₃O₄ (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 Ni₂FeO₃ 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 Ni₂FeBO₅ 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.

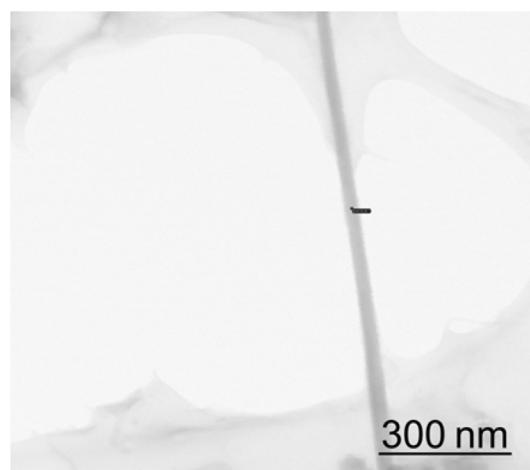


Fig. 1. A threadlike crystal in the fuel CRUD sample.

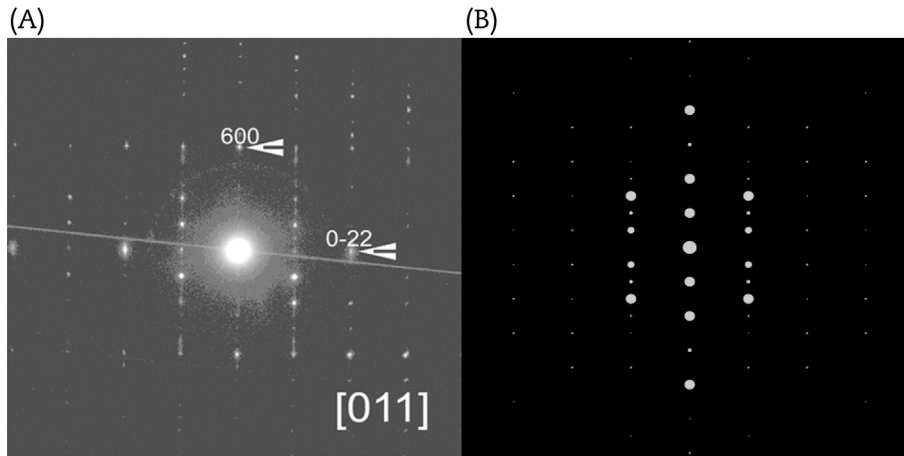


Fig. 2. Diffraction patterns. (A) Electron diffraction pattern obtained for the threadlike crystal in Fig. 1. (B) The corresponding simulated diffraction pattern for bonaccordite.

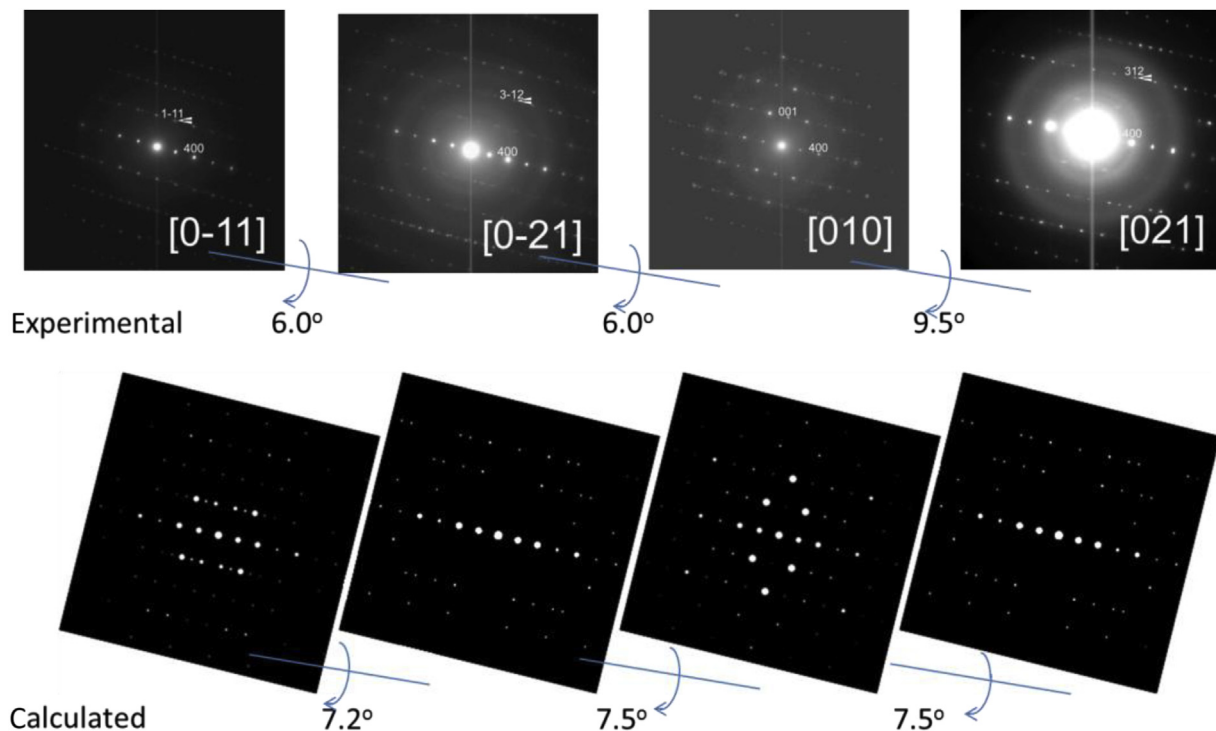


Fig. 3. Electron diffraction patterns obtained in a tilting experiment for the Fig. 1 crystal and the corresponding simulated patterns with similar tilt angles for bonaccordite.

Similar EELS measurements were performed on many such threadlike crystals. Fig. 5 shows another EEL spectrum (background removed) from the measurements. The elemental compositions are listed in Table 2. The threadlike crystals on average contained 7 at.% chromium. The mineral bonaccordite belongs to a family of compounds (ludwigite structure-type) known to crystallize with varying concentrations of other +2 and +3 metal cations. It is therefore likely that in the primary coolant these crystals were formed with some amount of $\text{Ni}^{2+}/\text{Cr}^{2+}$ substitution. However, the somewhat ambiguous results concerning the Cr content might also be attributable to the difficulty of measuring chromium in oxides. This is because the Cr edge at 575 eV can be hidden in the tail of the oxygen signal. It should be noted though that not all analyzed crystals contained chromium, and hence a chromium concentration was calculated from the EELS data for the second crystal

(Table 2) but not for the first crystal (Table 1). Generally, the measured elemental compositions for the two threadlike crystals are close to that for bonaccordite.

3.2. Threadlike crystals on a corroded Alloy 600 material

In an earlier experimental work performed at Studsvik, some threadlike crystals were also observed on the surfaces of corroded Alloy 182 and Alloy 600 materials only at a dissolved hydrogen level of 5 mL $\text{H}_2/\text{kg H}_2\text{O}$ [6,12]. At the higher dissolved hydrogen levels of 15, 25 and 75 mL $\text{H}_2/\text{kg H}_2\text{O}$, however, no such threadlike crystals appeared [6,12]. The threadlike crystals had an approximate atomic ratio of $[\text{Ni}]/[\text{Fe}]/[\text{Cr}] = 2:1:0.54$ [12]. Fig. 6 shows an electron diffraction pattern taken on several threadlike crystals as shown in the TEM image of a corroded Alloy 600 material surface, which was

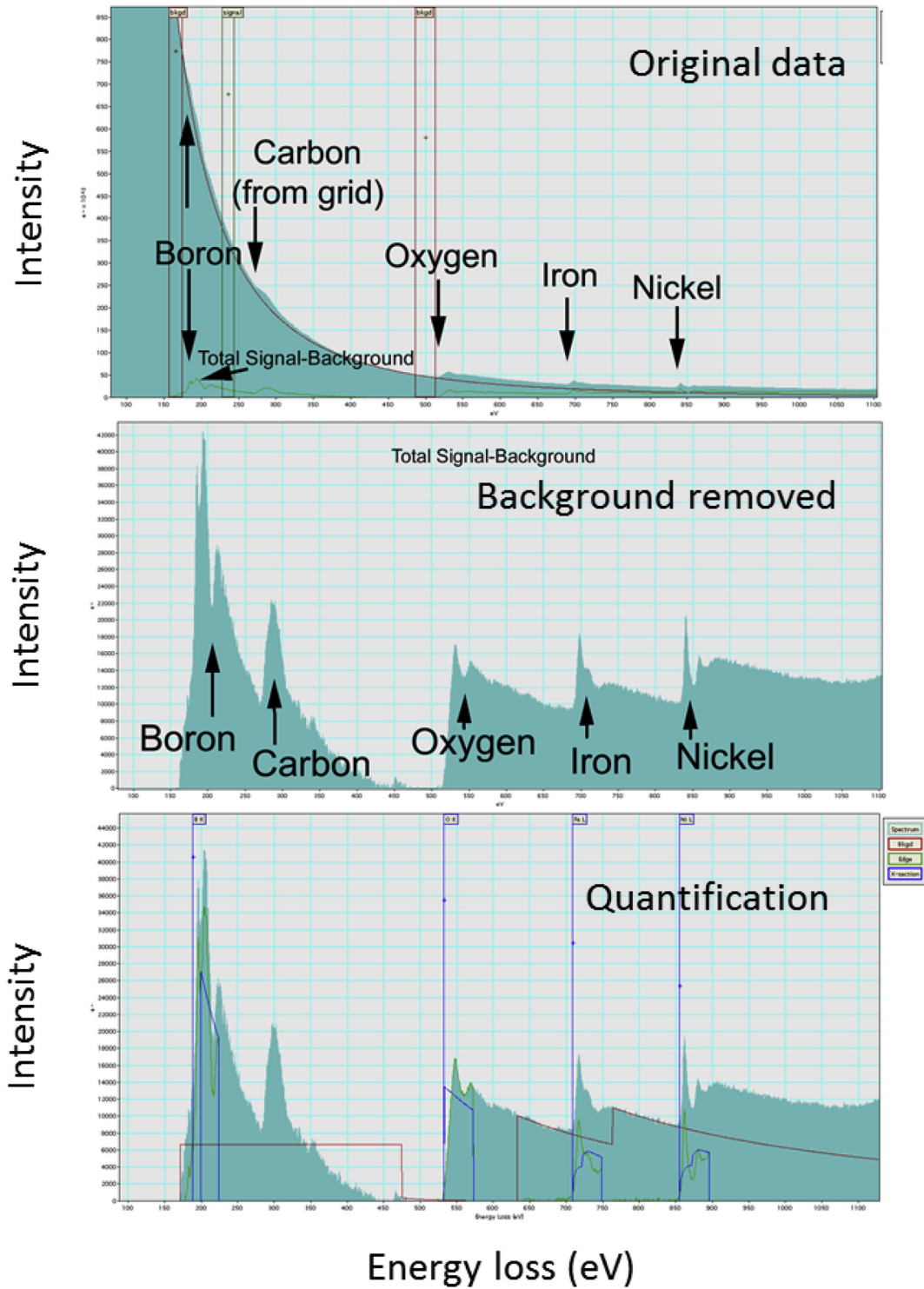


Fig. 4. EEL spectra of a threadlike crystal from the fuel CRUD sample in original and background removed forms. In the bottom diagram the background, edge, X section for quantification are also shown.

exposed to simulated PWR primary water with a dissolved hydrogen level of 5 mL H₂/kg H₂O. As can be seen, the threadlike crystals had a [Ni]/[Fe] atomic ratio of approximately 2:1. The diffraction spots are smeared into broken rings as might be expected for diffraction from an agglomeration of crystals. The corresponding *d* values for the rings are calculated and are in good agreement with the diffraction data for bonaccordite [14].

As is evident from the table, the measured *d* values are in good agreement between all four materials. It is apparent that the measured *d* values do not have the required precision that would allow for definite phase identification, although the agreement between the data from Refs. [6,9] would indicate they are likely the same material. Among the two reference materials, only bonaccordite contains boron. Therefore, detection of boron in the

Table 1
Elemental compositions of a threadlike crystal from fuel CRUD as measured with EELS and EDS.

Element	Threadlike crystal (measured with EELS, at.%)	Threadlike crystal (measured with EDS, ^a at.%)	Ni ₂ FeBO ₅ (theoretical, at.%)
B	11	—	11.11
O	52	55	55.56
Fe	14	11	11.11
Ni	23	27	22.22
Cr	—	7	—

EDS, energy-dispersive X-ray spectroscopy; EEL, electron energy loss spectroscopy.

^a Averaged values for 76 threadlike crystals in several CRUD samples.

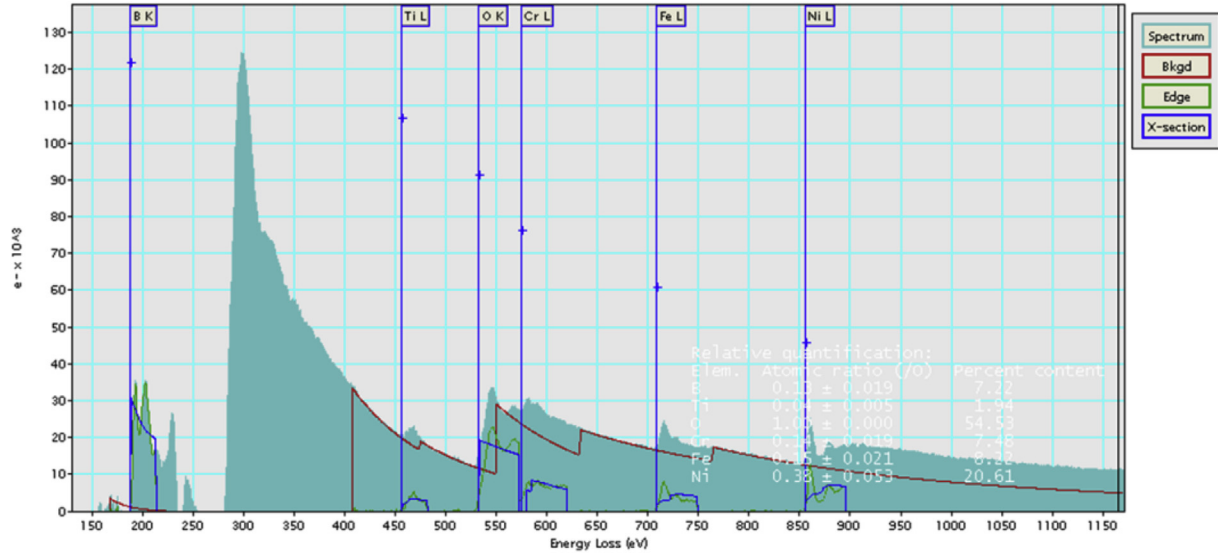


Fig. 5. EEL spectrum of another threadlike crystal from fuel CRUD. In the diagram the background, edge and X section for quantification are also shown.

Table 2
Elemental compositions of another threadlike crystal from fuel CRUD as measured with EELS and EDS.

Element	Threadlike crystal (measured with EELS, at.%)	Threadlike crystal (measured with EDS, ^a at.%)	Ni ₂ FeBO ₅ (theoretical, at.%)
B	7	—	11.11
O	55	55	55.56
Fe	8	11	11.11
Ni	21	27	22.22
Cr	7	7	0

^a Averaged values for 76 threadlike crystals in several CRUD samples.

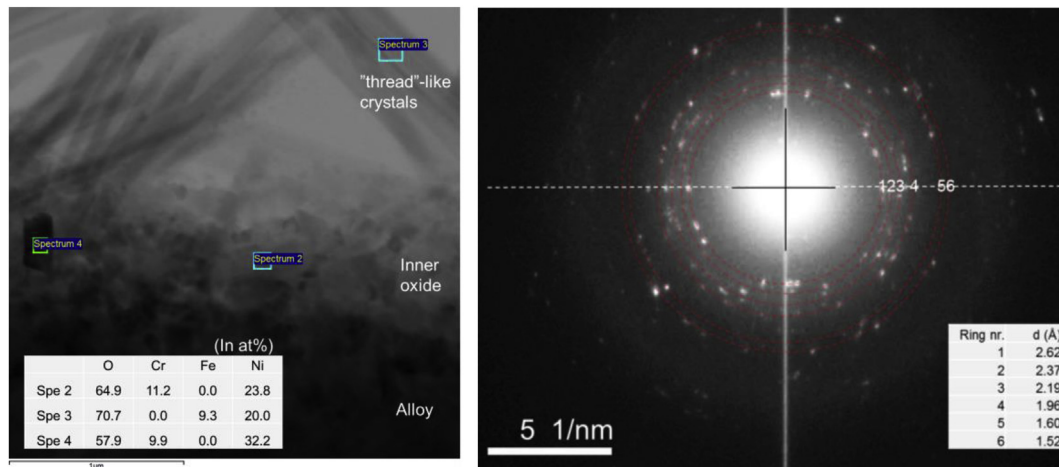


Fig. 6. TEM bright field image (left) showing the threadlike crystals from an Alloy 600 crack tip and their elemental compositions measured with EDS (denoted Spe 3 in the inset) and electron diffraction pattern (right) from multiple threadlike crystals.

crystals distinguishes boron-containing phases from nonboron-containing phases.

In Fig. 7, an EEL spectrum with the background removed is shown for a threadlike crystal shown in Fig. 6. One can see boron peaks that are similar to those found in the fuel CRUD samples shown in Figs. 4 and 5. Because of the presence of the epoxy material around the threadlike crystal, the elemental compositions of the threadlike crystal are not available at present. Therefore, the result of the present EELS measurement is only qualitative to show the presence of boron. The EDS result for this material is shown as inset (left, Spe 3) in Fig. 6.

4. Conclusions

In this work, some threadlike crystals from fuel CRUD and on corroded Alloy 600 material surface have been examined by EDS, electron diffraction, and EELS. The following conclusions may be drawn from the experimental measurements and evaluation:

- (1) In the fuel CRUD sample examined, the presence of boron in a threadlike crystal has been confirmed with EELS measurement. The measured elemental compositions of the crystal are largely in agreement with that of bonaccordite.
- (2) On the corroded Alloy 600 material surface, some threadlike crystals that look similar to the ones in the fuel CRUD sample have been measured with electron diffraction and EELS. The presence of boron in these crystals has been confirmed, whereas the ratio of [Ni] to [Fe] as determined with EDS is similar to that of bonaccordite.

4.1. Future work

Verification of boron-containing solid phases in fuel CRUD is important from the viewpoint of understanding the root causes of

CIPS. If bonaccordite is regularly formed in operating cores, a significant quantity in fuel CRUD would contribute to CIPS. If bonaccordite is a common phase that appears in the PWR system but constitutes only a small fraction of the total boron trapped in fuel CRUD in a CIPS-troubled core, one needs to continue refining information about the major boron-containing phases in fuel CRUD. As PWR fuel CRUD is exposed to oxidizing conditions through the addition of hydrogen peroxide during shutdown, it is likely to remain in the fuel pool for a relatively long time where it could be collected and analyzed. Any more soluble boron-containing solids such as lithium borates would not be identified in CRUD that has been exposed to shutdown chemistry or fuel pool conditions for any length of time, although a laboratory test loop equipped with an instant draining system [15] could aid in capturing such soluble solids.

In a CIPS core, the total amount of trapped boron under sub-cooled nucleate boiling condition must be small, on the order of 0.11 kg (0.25 lb) ^{10}B as H_3BO_3 relative to the total mass of solids on a CIPS core ranging from 18 to 23 kg (40–50 lb). In other words, the concentration of boron-containing species in fuel CRUD must be very low, which adds to the difficulty in collecting and analyzing them experimentally with, e.g., X-ray powder diffraction or EDS. When a super surface sensitive analytical technique is applied, one may face a different and equally difficult question that the detected boron might come from some boron species that are adsorbed or precipitated from drying of a wet fuel CRUD sample collected from pool. Taken together with previous bonaccordite observations though, the data presented here continue to support bonaccordite being a contributor to boron mass in the core. Future identification of the major boron-containing species may be done directly on fuel CRUD layer using, e.g., FIB for sample preparation and high-resolution TEM capable of low-boron detection or other more advanced analytical techniques for analysis of boron species and their boron contents as well as distribution across a fuel CRUD layer.

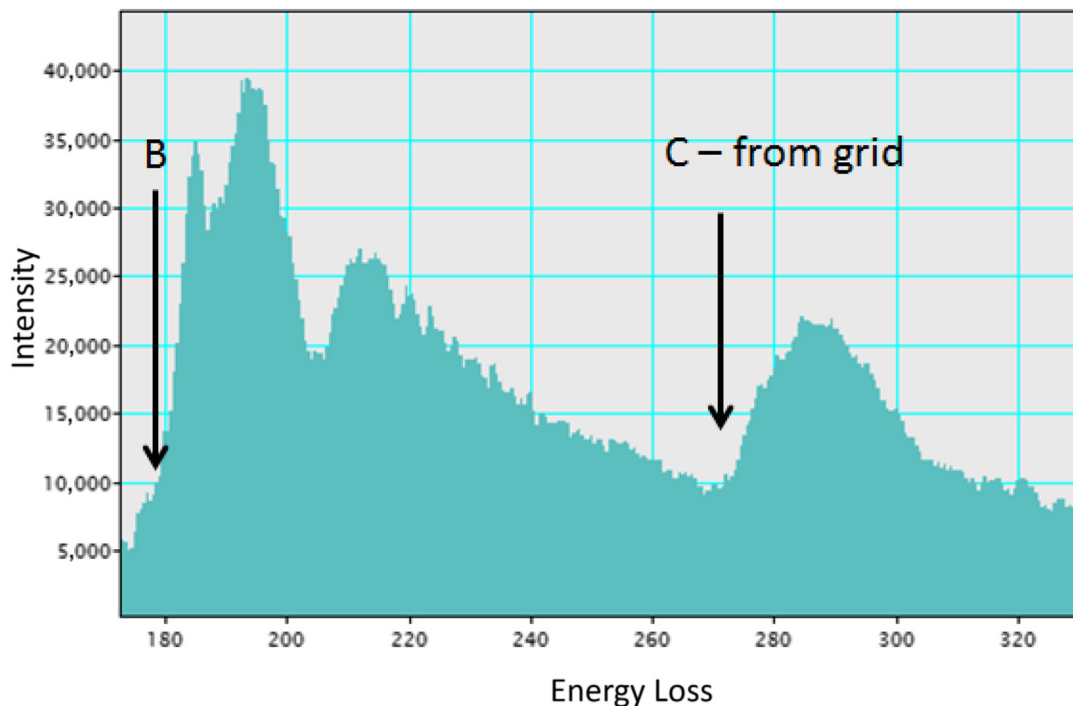


Fig. 7. EELS spectrum (with background removed) the threadlike crystals from an Alloy 600 crack tip showing boron peaks for boron in the energy loss range from 180 to 200 eV.

Conflict of Interest

All authors have no conflicts of interest to declare.

Acknowledgments

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References

- [1] J.A. Sawicki, Callaway Cycle 9 as they relate to the severe AOA observed for this core, *J. Nucl. Mater.* 374 (1988) 249–269.
- [2] J.A. Sawicki, Analyzes of crud deposits on fuel rods in PWRs using Mössbauer spectroscopy, *J. Nucl. Mater.* 402 (2010) 24–129.
- [3] J.A. Sawicki, O.T. Woo, Electron diffraction on bonaccordite Ni_2FeBO_5 particles formed on fuel pins in PWRs, *J. Nucl. Mater.* 424 (2012) 277–278.
- [4] J. Chen, C. Marks, B. Bengtsson, J. Dingee, D. Wells, J. Eskhult, Characterization of fuel deposits from Ringhals unit 4, Presented at International Conference on Water Chemistry of Nuclear Reactor Systems, NPC2014, October 26–31, 2014, Sapporo, Japan.
- [5] B. Bengtsson, J. Chen, P. Andersson, Precipitation of iron species on the cold side of PWR steam generator and its possible correlation to dose rate elevation, Presented at International Conference on Water Chemistry of Nuclear Reactor Systems, NPC2014, October 26–31, 2014, Sapporo, Japan.
- [6] J. Stjärnsäter, J. Chen, F. Lindberg, P. Ekstroem, P. Efsing, The effect of hydrogen on the oxide formation and crack growth rate in CT specimens of Alloy 600 exposed in simulated PWR environments, in: Proceedings of International Symposium Fontevraud 8 on “Contribution of Materials Investigations and Operating Experience to LWRs’ Safety, Performance and Reliability, September 15–18, 2014, Avignon, France.
- [7] J.M. Zuo, J.C. Mabon, Web-based electron microscopy application software: Web-EMAPS, *Microsc. Microanal.* 10 (2004) 1000–1001.
- [8] J. Chen, B. Bengtsson, H. Bergqvist, D. Jaedernaes, On the phase compositions of fuel CRUD formed in PWRs using steam generator tubing materials of Alloy 600 and 690, in: Proceedings of International Conference on Water Chemistry in Nuclear Reactor Systems, NPC 2012, September 23–27, 2012, Paris, France.
- [9] J. Chen, H. Bergqvist, D. Jaedernaes, B. Bengtsson, Characterization of PWR fuel CRUD by high resolution transmission electron microscopy, in: Proceedings of International Conference on Water Chemistry of Nuclear Reactor Systems NPC2010, October 4–7, 2010, Quebec, Canada.
- [10] H. Bergqvist, J. Chen, D. Jädnäs, B. Bengtsson, Characterization of PWR CRUD phases and their variation under plant operation by transmission electron microscopy, in: Proceedings of 14th International Conference on Environmental Degradation of Materials in Nuclear Power Systems, August 23–27, 2009, Virginia Beach, USA.
- [11] D.A. Perkins, J.P. Attfield, Resonant powder X-ray determination of the cation distribution in FeNi_2BO_5 , *J. Chem. Soc. Chem. Commun.* 4 (1991) 229–231.
- [12] K. Dozaki, D. Akutagawa, N. Nagata, H. Takiguchi, K. Norring, Effects of dissolved hydrogen content in PWR primary water on PWSCC initiation property, *E-J. Adv. Maint.* 2 (2010) 65–76.
- [14] S.A. De Waal, E.A. Viljoen, L.C. Calk, Nickel minerals from Barberton, South Africa: VII Bonaccordite, the nickel analogue of ludwigite, *Trans. Geol. Soc. of South Africa* 77 (2) (1974) 375.
- [15] N. Doncel, J. Chen, H. Bergqvist, Confirmation of $\text{Li}_2\text{B}_4\text{O}_7$ presence in fuel CRUD formed under simulated PWR water chemistry conditions, in: Proceedings of International Conference on Water Chemistry of Nuclear Reactor Systems, NPC2006, October 23–26, 2006, Jeju Island, Korea.