X-Ray Diffraction Structural Analysis of Structural and Fuel Materials for BN-600 Reactors

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Abstract. X-ray diffraction (XRD) analysis is one of physical methods for materials testing and condition monitoring for BN reactor structural and fuel materials operated under hard irradiation and high temperatures. Different XRD techniques help to determine crystal phase composition, form, internal stress, crystal preferred orientation (grain orientation) and other parameters.

At the Institute of Nuclear Materials (INM) D8 ADVANCE remote machine (BRUKER, Germany) placed in the shielded box is used for the examination of samples with activity up to 5.6×10^{11} Bq for ^{60}Co.

At INM there is a lot of information collected on the characteristics of fine structure of austenitic steels used for claddings, irradiated fuel compositions including uranium dioxide and MOX fuel.

Dependence of the effect of the change (within specifications) in main alloying element concentration and low irradiation doses on the lattice parameter of ChS-68 steel solid solution was obtained. Determination of the contribution of the cladding initial state structural factors to the swelling is in process.

The study of possible determination of plutonium concentration in MOX fuel and division of plutonium, oxygen enhancement ratio and fission product contribution to the lattice parameter changes has been carried out.

Key Words: X-ray diffraction analysis, austenitic steel, uranium dioxide, MOX fuel.

1. Introduction

Operation of BN reactor structural and fuel materials at high radiation doses and temperatures causes significant irreversible structural changes, thereby inducing service properties changes. To ensure safe and predictable BN reactor operation service properties are investigated and behaviour of materials under high-temperature irradiation is modeled. This requires ongoing updating of experimental data on changes of structural characteristics of irradiated material.

X-ray diffraction analysis is one of physical methods for materials testing and condition monitoring. Different techniques help to determine crystal phase composition, form, internal stress, crystal preferred orientation (grain orientation) and other parameters. Combined with other techniques of crystalline structure investigation – metallography, electron microscopy etc. – XRD analysis is widely used to investigate structural and phase changes induced by irradiation, fast neutron in particular.

At the Institute of Nuclear Materials (INM) X-ray diffraction analysis of cladding materials and fuel compositions irradiated in BN-600 reactor has been carried out for many years. Experimental examination of fuel assembly elements is primarily complicated by high radiation activity. At the Institute of Nuclear Materials (INM) D8 ADVANCE remote diffractometer (BRUKER, Germany) placed in the shielded box is used for survey of samples with activity up to 5.6×10^{11} Bq for ^{60}Co.

Modern DIFFRAC.EVA, TOPAS software, PDF-2 (2011) and Crystallography Open (2011) databases are used to process XRD data.

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2. Methodical Options for XRD-Analysis of Radioactive Materials

At first, D8 ADVANCE diffractometer was intended to solve different issues of powder XRD.

The device has a function of building modular systems, which facilitates diffractometer configurating. XRD Commander measurement software provides system remote control via local of global network and completely automated measurement and adjustment with scripting commands.

Goniometer vertical position, free automated movements of goniometer arms, and long measuring radius enable designing of a goniometer protected from high external radiation. Goniometer appearance prior to modernization is given in *Fig. 1*.

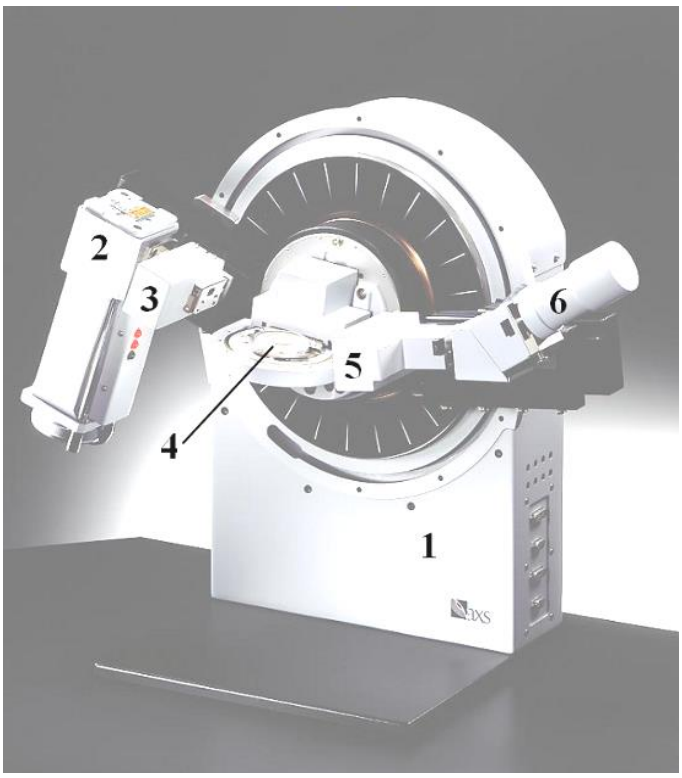

FIG. 1. D8 goniometer: 1 – goniometer, 2 – tube housing, 3 – aperture slit system, 4 – sample holder, 5 – detector slit system, 6 – detector (scintillation counter).

To adjust goniometer to hard conditions in a shielded cabinet the following structural changes have been made. The arm with measuring elements, curved monochromator and scintillation counter has been fixed.

To reduce effect of ionizing irradiation from high active materials on the scintillation counter, the stationary arm has been placed beneath specially designed lead shielding. Lead shielding thickness in a straight line from examined specimen to scintillation counter is not less than 250 mm.

Fixed parts are additionally covered with a stainless steel shroud. X-ray tube with a copper anode is installed on a movable arm. In these conditions 2θ measurement range is between 0 and 150 angular degrees. Appearance of the diffractometer installed inside the shielded box is given in *Fig. 2*.

Control unit with a PC and software, as well as cooling unit for the X-ray tube are located in the permanent staff room, near the shielded box (*see in Fig. 3*). Specimens are prepared for survey and installed into the sample holder with manipulators.

For such studies as high active specimens, single crystal examination, material examination layer by layer and others, a range of sample holders for surveying of specimens from 1 to 25 mm in size has been developed.

D8 remote diffractometer surveys in θ/2θ geometry, with rotation about Phi axis. Survey about θ and Phi enables single crystal examination and misorientation angle determination.

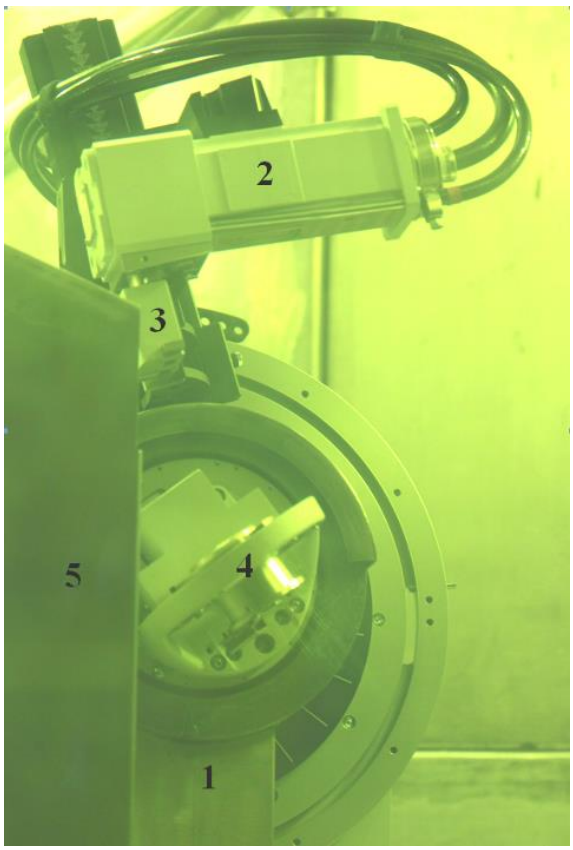

FIG. 2. D8 diffractometer in the shielded box: 1 – goniometer, 2 – tube housing, 3 – aperture slit system, 4 – sample holder, 5 – shielding shroud for monochromator and scintillation counter

FIG. 3. D8 diffractometer near the shielded box.

DIFFRAC.EVA software is used to process XRD data. It processes peaks, background and regions, as well as searches crystallographic databases. PDF-2 (2011) и Crystallography Open (2011) databases are used to determine phase composition.

TOPAS software is used to solve the following issues:
1. Determination of crystallite and stress size.
2. Determination of spatial group, determination/adjustment of lattice cell parameters, indexing of X-ray patterns.
3. Determination/adjustment of substance structure: atom coordinates, position population, thermal factors (for particular substances).
4. Quantitative analysis by Rietveld refinement, determination of specimen crystallinity degree.

Therefore D8 diffractometer extends the range of solved at INM issues concerning investigation of structural and phase characteristics of structural and nuclear materials for reactors of different types.

3. Lattice Parameter and Chemical Composition of Austenitic Alloy

Behaviour of structural material under irradiation is mainly defined (except for irradiation conditions) by initial structure state. In many examinations of irradiated material there is not enough data on initial structure characteristics. During investigation of material behaviour at small doses and low temperatures one can model structural characteristics of initial material and use it for further studies.

Generally lattice parameter as an indicator of values for space between planes and atoms in a crystallite is considered to correlate with many material properties: mechanical, corrosion, and physical.

It is well-known [1, 2] that lattice parameter with a certain crystalline structure mostly depends on chemical composition of the material and lattice defects. Dealing with reactor irradiation dose and temperature should be taken into account.

In particular, BN-600 claddings are made of ChS-68 steel (06Cr-16Ni-15Mo-2Mn-2Ti-V-B). During examination of cladding specimens with damage doses from 0.1 to 2 displacements per atom (dpa) and irradiation temperature of 370°C and specimens witnessing initial cladding state, analysis of the variation effect of concentration of the main doping elements within technical specifications (TS) and small irradiation doses on lattice parameter of ChS-68 alloy solid solution has been performed.

Dependence of lattice parameter on external (dose) and internal (alloying element concentration) factors has been modeled. During modeling (1) an assumption is made that dependence of lattice parameter on alloying element concentration within TS is linear:

$$a = a_0 + \sum_k \Delta a_k \frac{\Delta C_i^k}{\Delta C_{TУ}^k} + \Delta a_D D, \quad (1)$$

$$\Delta C_i^k = C_i^k - C_{\min(TУ)}^k, \quad (2)$$

$$\Delta C_{TУ}^k = C_{\max(TУ)}^k - C_{\min(TУ)}^k, \quad (3)$$

where a is lattice parameter, k stands for Cr, Ni, B, Si, Mn, Mo, C_i^k – concentration of k-element in i-experiment, $C_{\max(TУ)}^k$ – maximum k-element concentration according to TS, $C_{\min(TУ)}^k$ – minimum k-element concentration according to TS, D – damage dose.

Ratios of modeling factors are estimated and contribution of each element to lattice parameter changes is evaluated by regression analysis.

$$a = 0{,}36090 - 7{,}3 \cdot 10^{-4} \frac{\Delta C_i^{\mathrm{Cr}}}{\Delta C_{TУ}^{\mathrm{Cr}}} + 1{,}4 \cdot 10^{-4} \frac{\Delta C_i^{\mathrm{B}}}{\Delta C_{TУ}^{\mathrm{B}}} - 4{,}6 \cdot 10^{-4} \frac{\Delta C_i^{Si}}{\Delta C_{TУ}^{Si}} + 0{,}80 \cdot 10^{-3} \frac{\Delta C_i^{\mathrm{Mn}}}{\Delta C_{TУ}^{\mathrm{Mn}}} -$$

$$-1{,}91 \cdot 10^{-3} \frac{\Delta C_i^{\mathrm{Mo}}}{\Delta C_{TУ}^{\mathrm{Mo}}} + 1{,}2 \cdot 10^{-4} D. \quad (4)$$

Estimated values of Student's *t*-test for ratios of modeling factors (1) are given in *Table I*.

TABLE I. ESTIMATED VALUES OF STUDENT'S *T*-TEST FOR RATIOS OF MODELING FACTORS.

Factor	**Student's *t*-test**
$\frac{\Delta C_i^{\mathrm{Cr}}}{\Delta C_{\mathrm{TУ}}^{\mathrm{Cr}}}$	4.13
$\frac{\Delta C_i^{\mathrm{B}}}{\Delta C_{\mathrm{TУ}}^{\mathrm{B}}}$	3.18
$\frac{\Delta C_i^{Si}}{\Delta C_{\mathrm{TУ}}^{Si}}$	3.99
$\frac{\Delta C_i^{\mathrm{Mn}}}{\Delta C_{\mathrm{TУ}}^{\mathrm{Mn}}}$	10.00
$\frac{\Delta C_i^{\mathrm{Mo}}}{\Delta C_{\mathrm{TУ}}^{\mathrm{Mo}}}$	9.64
D	7.92

Modeling adequacy and importance of estimated ratios is shown. Regression statistics of modeling is given in *Table II*.

TABLE II. REGRESSION STATISTICS OF MODELING.

Parameter	**Value**
Multiple correlation ratio R	0.97
Determination ratio R^2	0.94
Standard error	$4.5 \cdot 10^{-5}$
Number of experiments	28
Number of freedom degrees	21
F-test	60.1

Contribution of added nickel to lattice parameter of experimental ChS-68 based alloy is calculated by Vegard's law $\Delta a_{\mathrm{Ni}} \frac{\Delta C_i^{\mathrm{Ni}}}{\Delta C_{\mathrm{Ty}}^{\mathrm{Ni}}} = -1.1 \cdot 10^{-4} \frac{\Delta C_i^{\mathrm{Ni}}}{\Delta C_{\mathrm{Ty}}^{\mathrm{Ni}}}$.

The obtained value correlates with contribution of added nickel to ChS-68 steel lattice parameter.

Irradiation at a temperature of 370°C and damage dose to 2 dpa causes lattice parameter increase maximum by 0.00025 nm. As for internal factors, lattice parameter is in direct proportion to boron and manganese concentration, and in inverse proportion to chromium, nickel, silicon and molybdenum concentration.

When concentration of doping elements varies within TS, boron has the smallest effect on lattice parameter (0.00014 nm), while molybdenum effect is the greatest (0.00191 nm).

In terms of quantitative concentration boron has the greatest effect on lattice parameter, and the smallest is that of nickel.

4. XRD Application to Determine Plutonium Concentration in MOX Fuel

MOX fuel is uranium and plutonium oxide mixture in the ratio to use it as a fuel for nuclear reactors originally designed for uranium fuel only.

One of advantages of MOX fuel production is disposal of weapons-grade plutonium. Moreover, MOX fuel can be produced by recycling of irradiated UO_2 reactor fuel, thereby it can be used as unlimited source of raw material in closed fuel cycle.

However, during MOX fuel pellet production from UO_2 and PuO_2 powder mixture they may not interact completely. As a result some solid solutions with different plutonium concentration are detected in pellets. This structure is based on UO_2 — PuO_2 solid solution where separate areas with high uranium concentration are registered.

Moreover, under irradiation quantitative relation of oxygen atoms to metal atoms in solid solution (O/M ratio, where M = U + Pu). O/M ratio, along with plutonium distribution in fuel, specifies physical-chemical, thermophysical, and mechanical fuel properties. Therefore these characteristics should be investigated and taken into account during monitoring of irradiated fuel condition.

X-ray diffraction is one of the ways to evaluate MOX fuel uniformity and Pu concentration. Observed with optical microscope inhomogeneity of the examined material causes asymmetry and apparent separation of diffraction reflexes. Modern techniques enable separation of

asymmetry reflexes, as well as determination of lattice parameters for the main solid solution and uranium-enriched areas by location and intensity of separated reflexes.

Plutonium concentration in MOX fuel can be indirectly estimated by lattice parameter value. According to Vegard's law, lattice parameters of solid solution for materials with similar lattice structures can be estimated by linear interpolation between UO_2 and PuO_2 lattice parameters.

It is complicated due to the fact that lattice of irradiated MOX fuel depends on oxide nonstoichiometry, and oxygen concentration in lattice varies widely under irradiation. Moreover, uranium and plutonium fission products also change lattice parameter of solid solution.

At INM there is a lot of information collected on uranium dioxide fuel irradiated in BN-600 reactor. Correlation of structural data on UO_2 and MOX fuels shows burnup dependence of lattice parameter marked with almost parallel lines (*see Fig. 4*). As both fuel types have been irradiated in BN-600 reactor in similar conditions, an assumption is made that burnup oxygen ratio for both fuel types is the same with similar uranium and plutonium fission products. In this case lattice parameter variation is caused only by plutonium concentration estimated by Vegard's law.

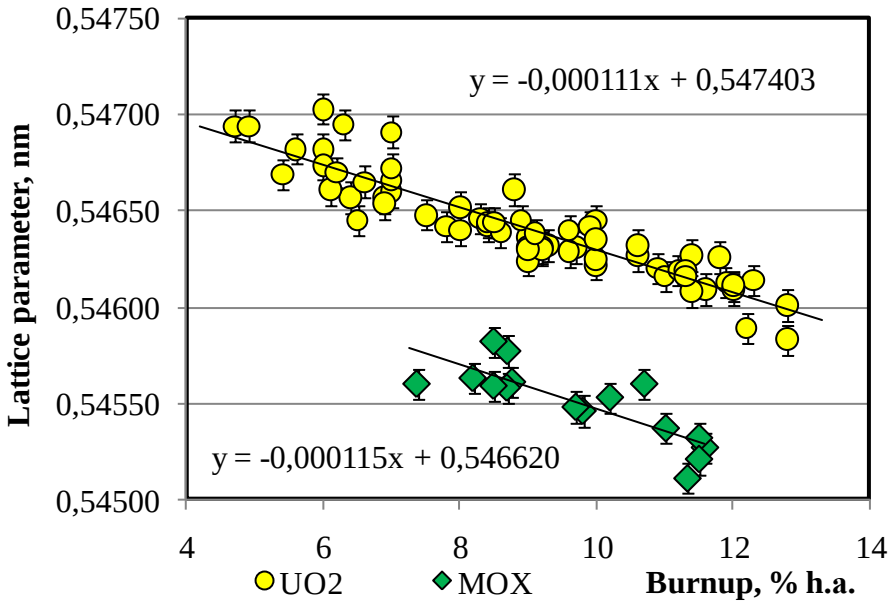

FIG. 4. Burnup dependence of lattice parameter variation.

In *Fig. 5* the estimation results for plutonium concentration in irradiated MOX fuel correlated with literature data [3] for unirradiated material. The data obtained at INM are given with ratio O/M=2.02…2.08, and literature data are with oxygen ratio in the range between 1.96 and 2.00. Marker points indicate experimental data. Straight lines stand for estimated data of lattice parameter variation depending on Pu concentration at different O/M ratios.

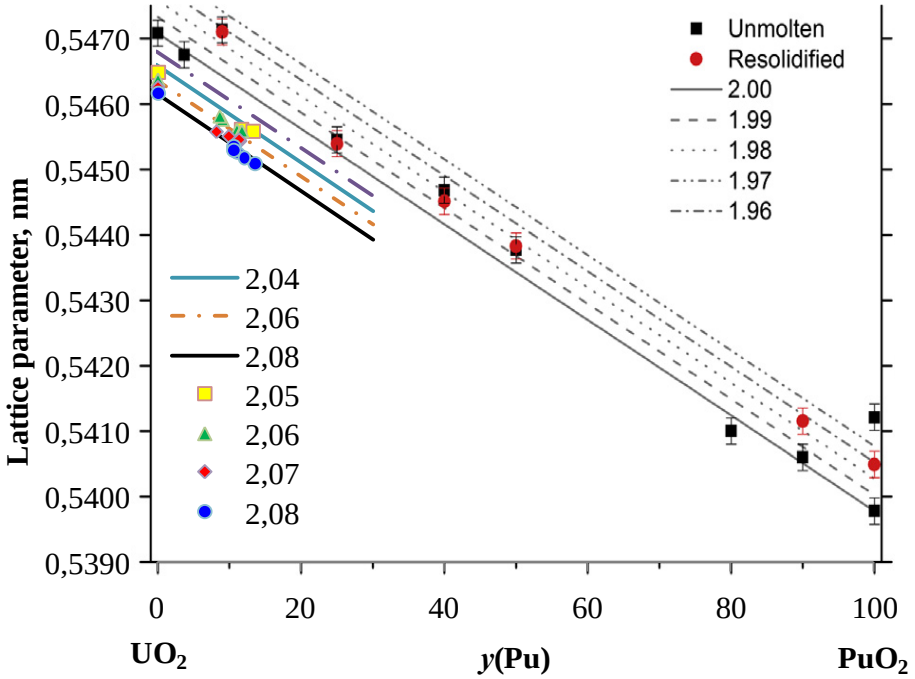

FIG. 5. Pu concentration dependence of lattice parameter variation $(U_{1-y}Pu_y)\ O_{2\pm x}$.

Next figure shows correlation of INM experimental data for irradiated MOX and literature data for unirradiated solid uranium-plutonium solutions with different plutonium concentration (see *Fig. 6*). The obtained data agree satisfactorily with literature data [4, 5, 6] for solid solution with 11 % uranium concentration. According to the above-mentioned assumption lattice parameters of irradiated MOX fuel differ due to fission products.

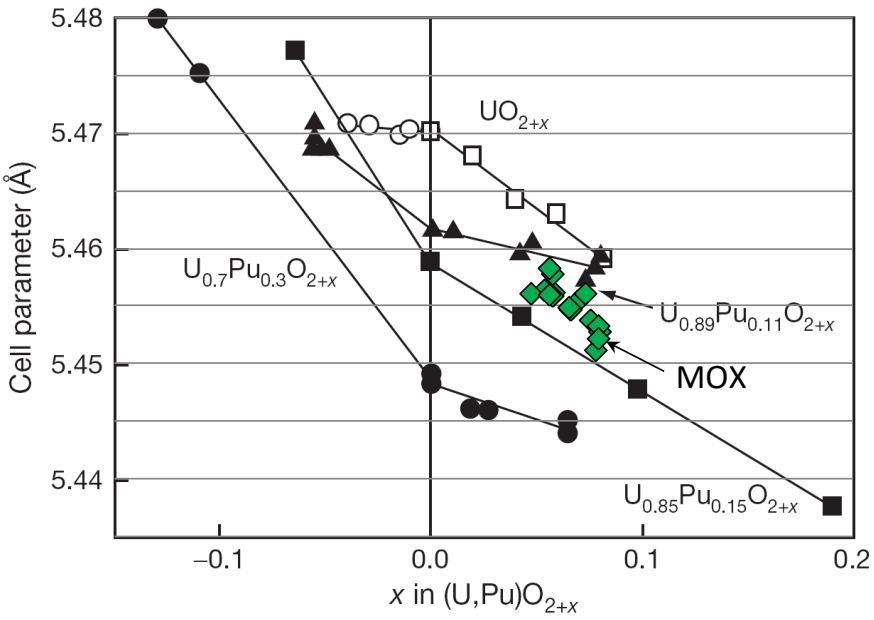

FIG. 6. UO_{2+x} *and* $(U, Pu)O_{2\pm x}$ *lattice parameter variation depending on stoichiometry relation.*

5. Conclusion

Therefore at INM fine structure of irradiated structural and fuel materials for fast reactors is examined with remote D8 ADVANCE diffractometer. Dependence of lattice parameter on chemical composition changes and small damage doses is modeled on the basis of XRD analysis of ChS-68 cladding irradiated in BN-600 reactor. Correlation of data on examination of irradiated uranium dioxide and MOX fuels shows validity of XRD analysis to estimate plutonium concentration in irradiated fuel.

6. References

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