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Homogeneity characterisation of sintered $(U,Gd)O_2$ pellets by X-ray diffraction

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Abstract

$(U,Gd)O_2$ sintered pellets are fabricated by different methods. The homogeneity characterisation of the Gd content seems to be necessary for a production control to qualify the process and the final product obtained. In this paper, we propose an analysis of the X-ray diffraction powder patterns through the Rietveld method, in which the differences between the experimental and the calculated data proposed from a crystalline structure model are evaluated. This result allows us to determine the cell parameters, that can be correlated with the Gd concentration, and the existence of other phases with different Gd contents. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Solid solutions of $(U,Gd)O_2$ powders used as nuclear fuel can be obtained through different processes of synthesis. The powders can show different physical and chemical properties, and variations in the behaviour under sintering can appear [1–6,14,15].

Differences of porosity and grain size are observed in the microstructure of sintered pellets, depending on the Gd content and its distribution. It is well known that the grain size diminishes as the Gd concentration increases. The sintered pellets, where a mixture of UO_2 and other $(U,Gd)O_2$ phases with variable Gd concentration appears, show inhomogeneities in the microstructure [6]. The homogeneity characterisation is then necessary for a production control to qualify the process and the final product. A pellet specification [7] establishes that at least 94% of the added gadolinium must form a solid solution with urania, the remaining 6% may exist as unreacted Gd_2O_3 particles larger than 20 μm and not more than 2% of these particles may exist in the range 40–100 μm.

The micrographic technique is the most common method used to qualify the homogeneity of these samples. It is performed to produce an image of the pellet surface. The sample has to be cut, polished and colour etched; in the image the free gadolinia, urania and solid solution grains reflect different colours [7]. This analysis is time consuming and does not quantify the Gd content in the solid solution phase. To measure the Gd content an electron probe microanalysis (WDS) has to be performed using appropriate gadolinia and urania standards. This being an adequate technique is too expensive for routine analysis.

A quicker and less expensive method can be used to study the homogeneity of sintered pellets applying the Rietveld method to the X-ray powder diffraction data. In spite of the X-ray diffraction analysis being unable to detect low quantities of spurious phases, the shape of the peaks change asymmetrically when phases of similar cell parameters coexist. The Rietveld method allows one to evaluate this asymmetry simulating the pattern with a

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model of two phases each with its own cell parameters. The Rietveld method consists of a least-square refinement looking for the best fit of the entire observed powder pattern taken as a whole and the entire calculated pattern based on the simultaneously refined models for the crystal structures, diffraction optics effects, instrumental factors and lattice parameters. This procedure, which minimises the agreement factor (R_{wp}), will provide the best estimated values of the quantities contained in the model.

The crystalline UO_2 structure is of the fluorite type (fcc) with the lattice parameter 547.1 pm [1,6,8,15]. In an urania–gadolinia solid solution, the lattice parameter is diminished as the Gd content increases [1,4,6,9–11,16]. The value of the lattice parameter can be used to quantify the Gd content in the solid solution. A homogeneity study can be done from the profile adjustment data of the diffraction peaks.

2. Experimental procedures

$(U,Gd)O_2$ solid solution powders with 0, 2, 4, 6 and 8 wt% Gd/(Gd + U) were prepared by the inverse co-precipitation method (reverse strike co-precipitation method). NH_3(g) and a $Gd(NO_3)_3$–$UO_2(NO_3)_2$ solution were simultaneously added to an ammonium hydroxide solution. The co-precipitation took place at pH = 9 and the temperature was kept at 60 °C. The precipitates were then dried and the uranium gadolinium oxide was obtained in a tubular furnace at 650 °C in a reducing atmosphere (H_2–N_2, 3 h). On the other hand, in order to compare the samples obtained by this co-precipitation method with those from a mechanical mixing process, a powder with 8 wt% Gd/(Gd + U) (specified value for a new LWR that will be developed in our country) was prepared. The UO_2 was obtained via the ammonium diuranate (ADU) process and the Gd_2O_3, purity 99.99%, was supplied from Sigma Chemical Co.

All the powders were uniaxially compacted. The green pellets were sintered in an H_2 atmosphere at (1700 ± 20) °C for 2 h. When the oxygen vs. uranium ratio (O/U) was around 2.000 it was measured by the polarographic method and for higher values the spectrophotometric method was used, due to the different range of applicability of each technique. Their densities were measured by the Archimedes method.

The sintered pellets were cut in halves, and from the resulting pairs one was milled to take the X-ray diffraction pattern and the other was prepared to be analysed by energy dispersive X-ray analysis (EDS) in a scanning electron microscopy and by the WDS technique. These samples were included in an acrylic polymer, polished and covered with a graphite layer to promote the electrical conductivity. Graphite was used instead of gold to improve the uranium detection. The U and Gd concentration of the mixed sintered samples were measured by EDS in a scanning electron microscopy (Philips SEM 500), WDS (Cameca SX 50) and X-ray fluorescence (XRF) (excitation source ^{241}Am).

Powder X-ray diffraction patterns were taken using an X'Pert Philips PW3710 diffractometer with graphite monochromatized Cu (Kα) radiation, with 1/2° scattering slit, a 2θ step of 0.02°, and 15 s of counting each step. The Fullproof [12] code was used for the Rietveld analysis of the data. The space group $Fm\bar{3}m$ was proposed for the crystal structure model [13]. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. No regions were excluded in the refinement between 20 and 130 degrees in 2θ. The following parameters were refined: scale factor, background coefficients, zero-point error, unit-cell parameters, pseudo-Voigt asymmetry shape and FWHM parameters, phase fractions, positional co-ordinates, and anisotropic thermal factors. The unit-cell parameters and the coefficients to fit the peak shape for the secondary phase were also refined.

3. Results and discussion

The O/U values of sintered pellets varies from 2.0010 ± 0.0002 to 2.06 ± 0.01 (obtained by polarographic and spectrophotometric method, respectively) as the gadolinium content increases between 0 and 8 wt%. The sintered density of the pellets was, in all cases, higher than 96% of the theoretical density. The data in Table 1 correspond to pellets obtained by the co-precipitation method. The Gd content was determined by XRF analysis. The lattice parameters and the agreement factor R_{wp} were determined through the Rietveld analysis. These results are in agreement with those informed by Fukushima et al. [10] for samples from similar conditions of synthesis and sintered in Ar/H_2 atmosphere, as shown in Fig. 1.

The results obtained from samples of pellets prepared by an inhomogeneous mechanical mixing containing 8 wt% Gd/(Gd + U) are shown in Table 2. In this sample two different phases were characterised. The Gd rich

Table 1
Results obtained from different Gd concentration pellets by X-ray diffraction refinement (Rietveld method) and XRF analyses

Nominal Gd conc. (wt%) (Gd/Gd + U)	Gd conc. (wt%) (XRF analysis)	Lattice parameter (pm)	Agreement factor R_{wp}
0	0	547.07 ± 0.01	10.9
2	2.10 ± 0.03	546.59 ± 0.02	17.1
4	4.03 ± 0.04	545.98 ± 0.04	14.5
6	6.02 ± 0.06	545.52 ± 0.04	15.7
8	7.88 ± 0.07	545.07 ± 0.03	16.0

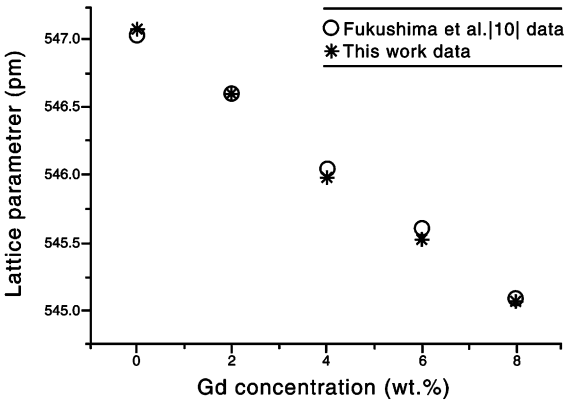

Fig. 1. Comparison between the data obtained in this work and those reported by Fukushima et al. [10] for similar conditions of synthesis.

Table 2
Results from the Rietveld analysis of the pellet obtained by a poor mechanical mixing method

Nominal Gd conc. (wt%) (Gd/Gd + U)	Gd conc. (wt%) (XRD analysis)	Lattice parameter (pm)	Agreement factor R_{wp}
8	Phase 1: 0 Phase 2: 25	547.07 ± 0.01 543.08 ± 0.01	13.6

phase has a concentration lower than 40 mol% $GdO_{1.5}$, so both phases can be considered belonging to the same space group and crystalline structure (fcc) [16,17]. The diffraction data refined taking this model into account give good agreement. The cell parameters of each phase are related to a Gd content according to the literature [10]. From these data, the cell parameters of the Gd rich phase correspond to 25 wt% Gd and the other phase is Gd free. The refinement results of this sample are presented in Fig. 2. The difference curve (at the bottom) shows the good agreement between the experimental data and the model theoretically proposed, the Bragg position lines display the peaks corresponding to the two different phases. From the Rietveld analysis the amount of each phase can be determined. In this case the Gd free phase amounts to 65.3 wt% of the whole sample, and the Gd rich phase represents the 34.7 wt%. From stoichiometry calculations the Gd amount in the two phases can be determined. If the total amount of Gd in the sample would concentrate in the phase whose percentile content is 34.7 wt%, then its Gd concentration would be 23 wt%, which is in agreement with the result obtained when the diffraction pattern is refined with the Rietveld method.

The EDS analysis performed on this sample also proved the presence of two phases, one of them free of gadolinium as it is shown in Fig. 3. The result obtained by electron probe microanalysis for the Gd rich phase is:

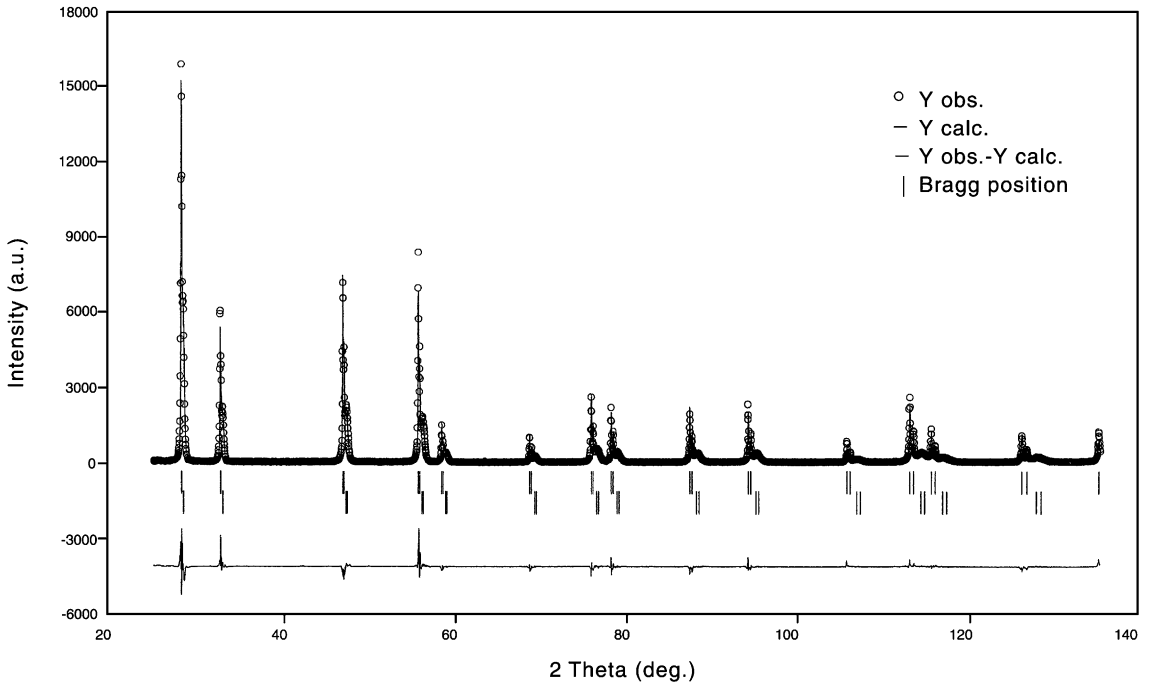

Fig. 2. X-ray refinement of the $(U,Gd)O_2$–8 wt%(Gd/U + Gd) pellet sample obtained by the mechanical mixing method. The small bars at the bottom of the figure correspond to the peaks of the two coexisting phases. The curve at the bottom is the difference between the experimental and the proposed curve by the model data.

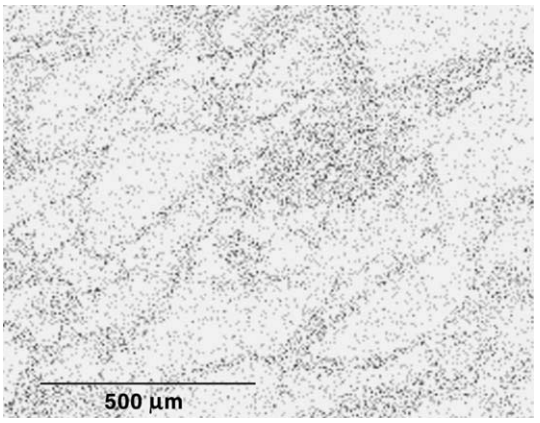

Fig. 3. Area mapping of Gd distribution by EDS of the $(U,Gd)O_2$–8wt%(Gd/U + Gd) pellet sample obtained by the mechanical mixing method. Dark zones show the high gadolinium content.

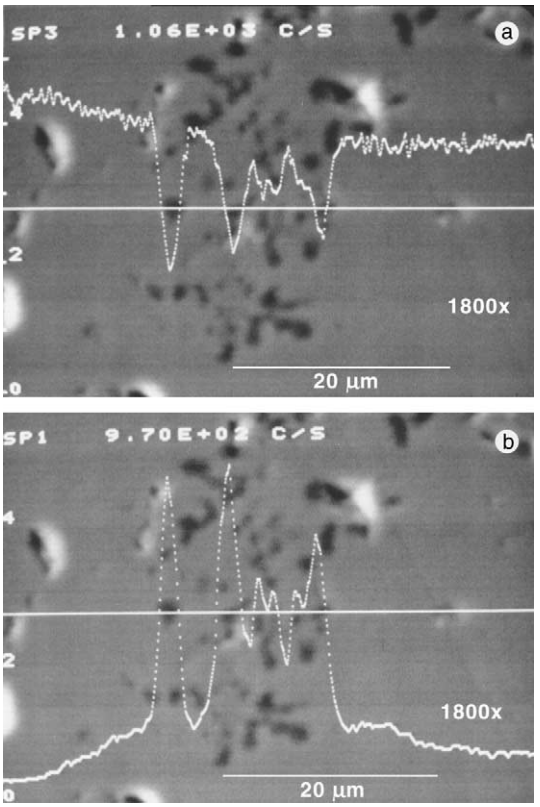

Fig. 4. Line scans of U (a) and Gd (b) signals within 20 μm of the sample shown in Fig. 2. The maximum of the Gd signal corresponds to the minimum of the U signal. Dark zones are the highest in Gd concentration.

uranium 64 wt% and gadolinium 24 wt%. The Gd concentration varies in these rich zones from 21% to 26%. The images of the uranium and gadolinium profiles are shown in Fig. 4, where the depletion of uranium in the gadolinium rich zones can be observed.

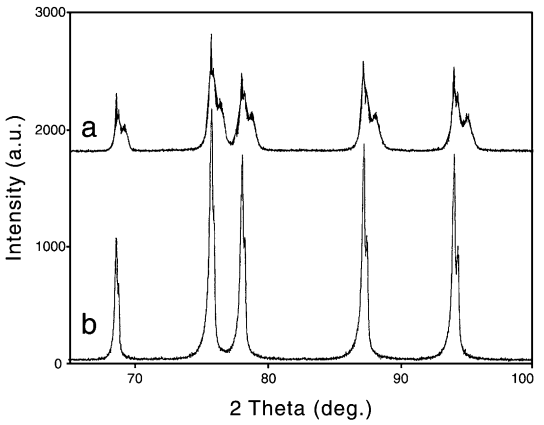

Fig. 5. Diffractograms of the heterogeneous sample shown in Figs. 1–3 (a) and the pure UO_2 pellet (b). The peak positions of the Gd depleted phase and the pure UO_2 are coincident.

The comparison of the diffractograms from inhomogeneous $(U,Gd)O_2$ pellets containing 8 wt% Gd/(Gd + U) and the pure UO_2 sample (Fig. 5) shows the duplication of the diffraction peaks corresponding to the two coexistent phases observed in the heterogeneous sample. One of these duplicate peaks corresponds exactly to the peak of the pure UO_2 phase, as confirmed by the EDS and WDS analysis.

4. Conclusions

The homogeneity of the samples can be determined by the analysis of the diffraction data. The analysis performed with the Rietveld method allows one to determine the presence of phases with different lattice parameters corresponding to different gadolinium concentrations in heterogeneous samples. The lattice parameter data obtained from the diffractogram analysis allows one to establish the real concentration of gadolinium, as the lattice parameter is related to the gadolinium content when the sintering process has been performed in the same conditions. The method used in this study proves to be effective, less time consuming, and less expensive to determine the homogeneity of mixed oxides pellets than the methods used at present.

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