QUANTITATIVE DETERMINATION OF CRYSTALLINE PHASES IN THE SILICIDE FUEL BY THE RIETVELD METHOD

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ABSTRACT

Uranium silicide has been used as nuclear fuel in modern research reactors. The nuclear fuel is based on a dispersion of uranium silicide and aluminum powder to form a fuel meat fabricated according to powder metallurgy techniques. The U_3Si_2 powder should attend technical specifications referring to the major crystalline constituent, which must be more than 80 wt% of U_3Si_2. IPEN/CNEN-SP currently produces the U_3Si_2-Al fuel to supply the IEA-R1 research reactor, which operates at 3.5 MW in order to produce primary radioisotopes used in nuclear medicine. The uranium concentration in the fuel should be increased from 3.0 gU/cm^3 to 4.8 gU/cm^3 in order to guarantee future fuel supplying for a new research reactor designed for radioisotope production, the Brazilian Multipurpose Research Reactor – RMB, which is planned to be constructed in the country. The new fuel will operate under much more severe conditions than the ones found currently in IEA-R1 reactor. So, the increasing of uranium concentration into the fuel requests urgent development of a new technology to qualify the uranium silicide powder produced by IPEN-CNEN/SP, referring to the characterization of crystalline phases. This paper describes a methodology developed to quantify crystalline phases in the silicide fuel powder, which is based in the Rietveld method for crystalline structures refinement.

1. Introduction

The IEA-R1 Reactor of IPEN/CNEN-SP is a pool type reactor operating since 1957. This reactor uses MTR type dispersion fuel element in a 5 X 5 core arrangement. The Nuclear Fuel Center of IPEN is responsible for the production of the necessary nuclear fuel to keep the continuous operation of the reactor. Development of new fuel technologies is also a permanent concern. The Nuclear Fuel Center had produced 77 fuel elements until now, including 14 control fuel elements.

The program for silicide fuel development at IPEN had great impulse after the approval of the IAEA TC BRA/4/047 "Fuel Improvement for the IPEN Research Reactor" in 1999. The primary purpose of this program was to develop the whole fabrication process of U_3Si_2-Al dispersion fuel plate (including 4.8 gU/cm^3), its irradiation test at the IEA-R1 reactor and post-irradiation analysis. This project proposal would give the necessary background to IPEN to produce and qualify its own U_3Si_2 powder and silicide based on dispersion fuel plates for the IEA-R1 fuel element fabrication. The project steps to achieve the objectives included the following steps:

a) to develop the process for producing UF_4 starting from UF_6;

b) to develop the process for producing metallic uranium starting from UF_4;
c) to develop the process for producing U_3Si_2 powder;
d) to produce miniplates with 20% enrichment for irradiation tests;
e) to irradiate miniplates at the IEA-RI reactor and to perform non-destructive analysis on the irradiated fuel miniplates inside the spent fuel pool.

Figure 1 shows a flow-sheet of the main project activities. More information of the project activities and results are available in the Project Progress Reports [1,2,3].

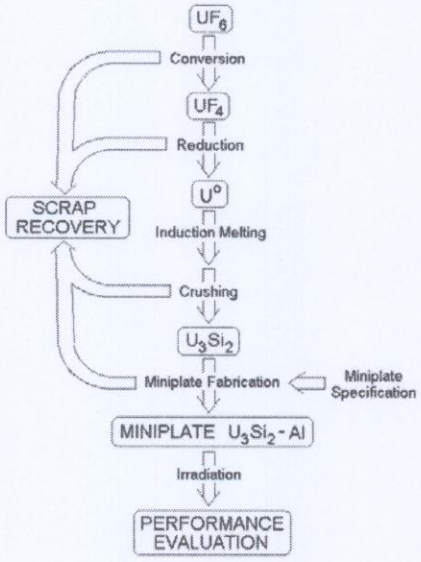

Figure 1: Main BRA/4047 Project activities.

Since 2000, the Nuclear Fuel Center of IPEN has been dedicating great efforts to achieve expertise in production of intermetallic alloy U_3Si_2. After facing some difficulties, as reported previously [4], in 2004 IPEN has arrived to the full experimental route to produce, in production scale, the necessary alloy for nuclear fuel.

From the produced uranium ingot, the metal was melted inside an induction furnace with silicon addition, with an adequate vacuum instrumentation and facilities for handling and melting uranium and uranium alloys. The zirconia crucible was specially designed to reach temperatures higher than 1750°C and to support the aggressive environment created by uranium chemical attack. The load arrangement inside the crucible was studied to help the sequence of melting in the several stages of that molten alloy, before reaching the final intermetallic composition, as shown in figure 1. More than 20 trials were carried out, using natural uranium, before the first LEU U_3Si_2 were successfully made. It was produced 3 enriched U_3Si_2 melting in 2005, which consisted the first own produced load of fuel plate fabrication in IPEN. In general terms, the quality of this intermetallic has fully met the needs postulated by the requirements for a routine nuclear material.

In relation to U_3Si_2 powder to IEA-R1 reactor fuel plate, technical specification requires that the bigger crystalline component of uranium silicide should be U_3Si_2 (>80% in weight). Inside this context, this paper aims to analyze uranium silicide nuclear fuel produced by IPEN/CCN in relation to recommended technical specifications, especially regarding crystalline phases percentage. To develop methodology to quantify uranium silicide fuel crystalline phases, the method developed by Hugo Rietveld will be used [5].

Rietveld developed a method to refine structures, based on the comparison between a calculated diffraction pattern and the observed one, which has been extended after to be

applied in the quantitative phases analysis and micro-deformation studies. The Rietveld Method considers crystallographic theoretical data (crystalline system, spatial group, atomic positions, system parameters, occupation number and isotropic temperature factor) of crystalline phases. The calculated pattern is obtained using the single cell as a basis. This calculated pattern is, so, compared to the observed pattern and the model parameters are adjusted by the minimum square method [6].

2. MATERIALS AND METHODS

U_3Si_2 powder analyzed was produced by Centro de Combustível Nuclear (CCN) of Nuclear and Energy Research Institute - IPEN/CNEN.

X Ray diffraction analysis of the silicide fuel were obtained with a Philips X´Pert equipment, (λ = 1,54 Å) through the powder method. Analyses were done with 0,01°/ 5s and 2θ from 10 to 90° (2 Theta).

Crystalline phases were identified based on JCPDS database [7]. In order to obtain the crystallographic data, necessary to the structural refinement through the Rietveld Method, it was used the ICSD [8].

The used refinement program was the DBWS 98. DMPLOT program made possible the comparison between the theoretical spectrum and the refined one.

3. RESULTS AND DISCUSSION

Figure 2 shows U_3Si_2 powder samples difracction. Identified crystalline phases were: U_3Si_2 (ICSD 31626) and $USi_{1,0147}$ (ICSD 81561). The Input data to the refinement by the Rietveld Method are presented in Table 1.

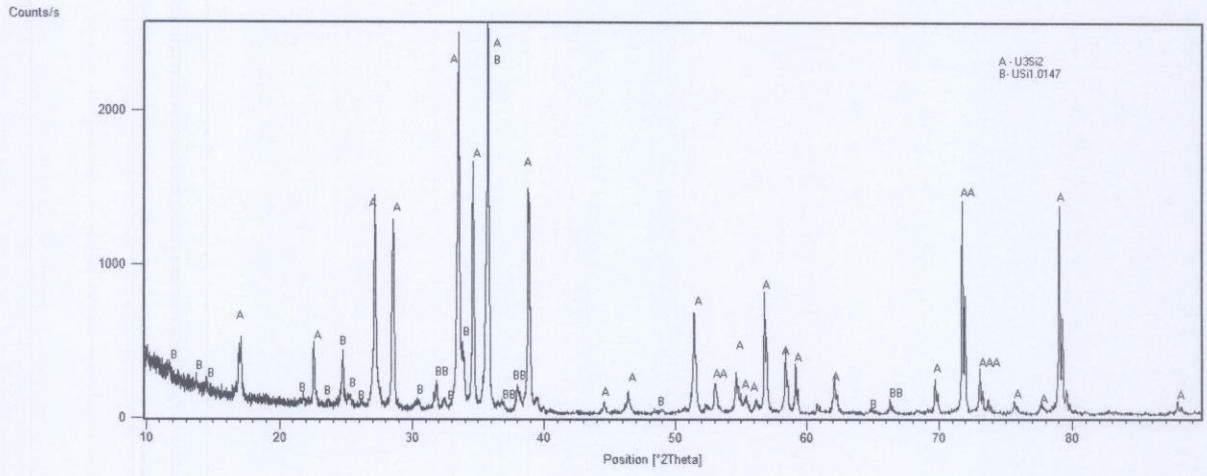

Figure 2: X ray patterns of U_3Si_2 powder.

Table 1: Crystallographic theoretical data of crystalline phase present in silicide fuel.

Crystalline Phases	Lattice parameters (Å)	Atomic Position	Occupation Number	Thermal Isotropic Factors (B_o)
	a = b = 7.3299	U1(2a), x = 0.0 y = 0.0, z = 0.0	U1 (2a) = 1.0	B_o (U1) = 0.5

U_3Si_2 ICSD 31626 P 4/m b m (127) Tetragonal	c = 3.9004 $\alpha = \beta = \gamma = 90$	U2(4h), x = 0.181 y = 0.681, z = 0.5 Si1(4g), x = 0.611, y = 0.111, z = 0.0	U2(4h) = 1.0 Si1(4g) = 1.0	B_o(U2) = 0.5 B_o(Si1) = 0.5
$USi_{1,0147}$ ICSD 81561 I 4/m m m (139) Tetragonal	a = b = 10.587 c = 24.310 $\alpha = \beta = \gamma = 90$	U1 (4e), x =0.0, y = 0.0, z = 0.2579 U2 (8f), x = 0.25, y = 0.25, z = 0.25 U3 (8j), x = 0.2652, y = 0.5, z = 0.0 U4 (16n), x = 0.0 y = 0.2594, z = 0.0617 U5(16n), x = 0.0, y = 0.3567, z = 01924 U6(16m), x = 0.3132, y = 0.3132, z = 0.1156 Si1 (2a) x = 0.0, y = 0.0, z = 0.10 Si2 (4c) x = 0.0, y = 0.5, z = 0,.0 Si3 (4e) x = 0.0, y = 0.0, z = 0.098 Si4 (4e) x = 0.0, y = 0.0, z = 0.43 Si5(8h) x = 0.234, y = 0.234 z = 0.0 Si6 (16n) x = 0.0 y = 0.259, z = 0.3037 Si7(16n) x = 0.0, y = 0.385, z = 0.399 Si8(16m) x = 0.125, y = 0.125, z = 0.1552	U1 (4e)= 1.0 U2 (8f)=1.0 U3 (8j)=1.0 U4 (16n)=1.0 U5(16n)= 1.0 U6(16m)=1.0 Si1 (2a) =0.5 Si2 (4c)=1.0 Si3 (4e)=1.0 Si4 (4e)=1.0 Si5(8h) =1.0 Si6 (16n)=1.0 Si7(16n)=1.0 Si8(16m)=1.0	U1 (4e)=0.0 U2 (8f) =0.0 U3 (8j)= 0.0 U4 (16n)= 0.0 U5(16n)= 0.0 U6(16m)= 0.0 Si1 (2a)=1.0 Si2 (4c)=2.0 Si3 (4e)=2.1 Si4 (4e)=1.3 Si5(8h)=0.5 Si6 (16n)=0.7 Si7(16n)=1.1 Si8(16m)=0.9

Figure 3 shows the comparison between U_3Si_2 powder experimental and simulate diffractions through Rietveld Method. It is possible to observe a good concordance between diffractions, with good definition to peaks intensities and positions. Refinement quality is verified through two statistical numeric indicators R_p and R_{wp}, comparative parameters between theoretical and experimental diffractions, which can be used to the model convergence following. R_{wp} waste considers the fault associated to each intensity value, related to counting numbers, using w (2θ) pondering factor. According to MCCUSKER, L. D. et al. [9], R_{wp} value to good results is 2-10%, while typical values obtained vary 10-20%. R_{wp} value found was 8.55%, in the best values range.

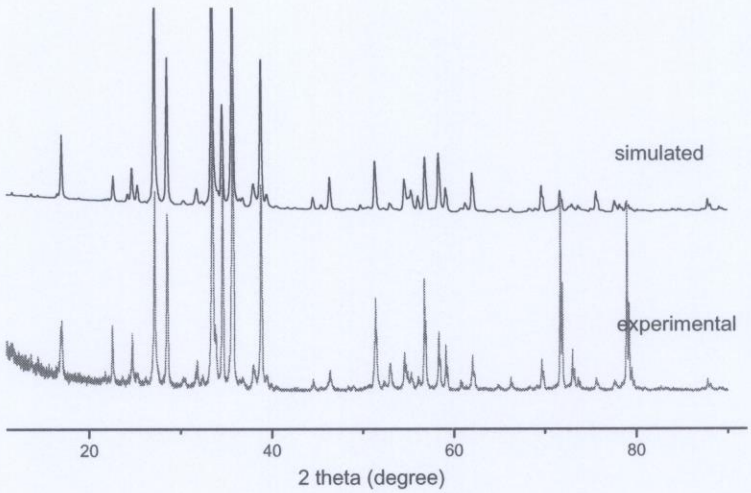

Figure 3: X ray patterns of U_3Si_2 powder: experimental and simulated by the Rietveld Method.

Table 2 shows quantitative percentage of each U_3Si_2 powder crystalline phase and the single cell parameters after refinement. It is possible to observe that U_3Si_2 powder have 90.31% of the U_3Si_2 phase and 9.69% of $USi_{1,0147}$, matching, so, established technical specifications (U_3Si_2 > 80%).

Table 2: Refined Lattice parameters and percentage of the crystalline phases calculated by Rietveld Method.

Crystalline Phases	Refined Lattice Parameters (Å)	Percentage of the Crystalline Phases
U_3Si_2	a = b = 7.3186 c = 3.9073	90.31
$USi_{1,0147}$	a = b = 10.630 c = 24.324	9.69

4. Conclusions

Methodology to silicide fuel crystalline phases quantification through Rietveld showed itself very apropriated. Rietveld Method, due to the fact of using all X ray diffraction profile in calculations, overcomes several compounds peaks superposition problem and turns possible to obtain results from all crystalline phases simultaneously, without the need of pattern samples and calibrations curves. It means an expressive gain in relation to other techniques to multiphase systems crystalline phases quantification through X ray diffraction.

Obtained results showed that U_3Si_2 powder produced by IPEN/CNEN matches technical specifications according to U_3Si_2 (90.31%) crystalline phase percentage.

5. References

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