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CHARACTERIZATION OF URANIUM SILICIDE POWDER USING XRD

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ABSTRACT

Uranium silicide (U_3Si_2) is an intermetallic used as nuclear fuel in most modern MTR - Materials Test Reactor. Dispersed in aluminum, this fuel allows high uranium densities, up to 4.8 gU/cm^3. At IPEN, the fabrication of fuel elements based on U_3Si_2 for the IEA-R1 reactor is carried out in the Nuclear Fuel Center (CCN), by vacuum induction melting of uranium and silicon, followed by grinding. Before employed in a nuclear reactor, U_3Si_2 must be submitted to a strict quality control, which includes granulometry, density, X-ray radiography for dispersion homogeneity, chemical and crystallographic characterization. Concerning phase composition for a qualified fuel, the fraction of U_3Si_2 should be higher than 80wt.%. Aiming at the development of a routine methodology for quantification of phases via analysis of XRD data using the Rietved method, six samples from two production baths of CCN were submitted to X-ray diffraction. The data were analyzed using software GSAS and line profile analysis methods. The results suggest that fusion product have preferred orientation and grinding step is important for a better refinement.

1. INTRODUCTION

Operating since 1957, the IEA-R1 nuclear reactor, located at IPEN, is a pool type reactor and uses MTR type dispersion fuel element in a 5 X 5 core arrangement. At first, all the fuel elements were imported, and in 1988 IPEN provided the first fuel element fabricated in Brazil. The fissile material used at that time was the U_3O_8 powder, with 20wt.% ^{235}U enrichment. In 1998, pursuing higher neutron flux and less residue generation, the fuel plate fabrication technology of uranium silicide was implanted, with U_3Si_2 powder imported from France. In 2002, IPEN started producing this powder from national enriched UF_6 produced by CTMSP (Navy Technology Center in São Paulo), and in 2004, after several experimental trials, IPEN reached to the production route to fabricate the necessary alloy for nuclear fuel. Ever since, the Nuclear Fuel Center (CCN) of IPEN is responsible for the manufacturing the 20wt.% ^{235}U uranium silicide dispersed in an aluminum matrix fuel for IEA-R1 operation. At CCN, uranium silicide is produced by melting uranium and silicon at an induction furnace, at temperatures around 1750°C at 10^{-3}Torr [1,2].

Uranium silicide (U_3Si_2) is an intermetalic used as nuclear fuel in most modern research reactors. This material is dispersed in aluminum, and allows high densities of uranium in the fuel core, up to 4.8 gU/cm^3, comparing to UAl_x–Al at 2.3gUcm^{-3} and U_3O_8–Al at 3.2gUcm^{-3} [3]. Considering its use in a nuclear reactor, U_3Si_2 must be submitted to a strict quality control, which includes particle size, real density, crystallinity and chemical characterization.

Due to the adopted manufacture route at IPEN, the product usually carries two crystalline phases, U_3Si_2 and USi. These phases have different behavior during irradiation, so the

quantification of them is vital [4]. The fuel specification imposed by the Nuclear Engineering Center of IPEN limits the minimum concentration of U_3Si_2 crystalline as 80wt.%.

To perform this analysis, the Rietveld refinement method seems to be the most suitable route, since X-ray diffraction (XRD) patterns of crystalline substances are virtually unique, and independent of each other [5]. However, the use of this method implies in several precautions, as adequate granulometry of sample, enough counting time during analysis and caution with the refined parameters, as a good fit does not always represent physical likelihood. Additionally, the method itself does not offer a reliable error estimative, and the results can vary depending on the operator.

In this sense, aiming the development of a routine methodology for quantification of phases via analysis of XRD data using the Rietved method, uranum silicide samples produced at CCN were submitted to X-ray diffraction. For Rietveld refinement, the data were analyzed using non-commercial software GSAS [6]. To extract information of crystallite size, single line profile analysis was used, using the method proposed by de Keijser [7]. This method comprises a Voigt function to fit a diffraction peak.

2. METHODS AND MATERIALS

Six samples of uranium silicide were produced from two baths at CCN, IPEN, from melting metallic uranium (produced from UF_6) with nuclear grade silicon. After the melting, sample is grinded until the desired granulometry, specifically between 150 and 44μm (100 – 325 mesh). To match the nuclear fuel element (NFE) specifications, the particles portion smaller than 44μm should be limited to 20wt%.
For this work, samples were obtained from two production batches. From each batch, three samples were separated: (A) original granulometry of sample used in nuclear fuel (B) portion of particles smaller than 44μm separated during the first grind, (C) original granulometry sample, separately grinded till all portion could pass the 325 mesh sieve. The nomenclature of samples is described in table 1.
Data were acquired with a Rigaku Ultima IV diffractometer, using Cu-Kα radiation of 40kV and 30mA, graphite monochromator, step of 0.02º and 10 seconds per step, two-theta from 10 to 100º and 2/3, 2/3 and 0,6mm slits.
For Rietveld refinement, data were analyzed using the GSAS and EXPGUI software, using ICSD collection code files 73695 (U_3Si_2), 31647 (USi orthorrombic) and 81561 (USi tetragonal).
Single line profile analysis was performed using the (201) plane (at $2\theta = 33.45º$) diffraction peak. The fit was compared to a Y_2O_3 standard previously analyzed. The diffraction peak from samples was chosen considering its high intensity and correspondence with Y_2O_3 (400) diffraction peak.

Table 1: Nomenclature of samples

Sample	Batch	Granulometry	Obs.
1A	33/13	150≥x≥44μm	NFE spec.
1B	33/13	≥44μm	first grinding product
1C	33/13	≥44μm	NFE spec. fully grinded
2A	34/13	150≥x≥44μm	NFE Spec.
2B	34/13	≥44μm	first grinding product
2C	34/13	≥44μm	NFE spec. fully grinded

3. RESULTS AND DISCUSSION

The experimental diffractograms, as well as the simulated from Rietveld refinement ones, are shown in figures 1 to 6. It can be noticed that the calculated patterns of the milled samples (1B, 1C, 2B, 2C) have a better fit, considering the R_{wp} indicator.

From all the samples, it can be seen that the intensities of various diffraction peaks have considerable difference from the ICDD standards. Initially, we thought that these differences were only associated with granulometry, as big particles can be related with big crystallites, and, in this sense, getting a worse statistic results during data acquisition. Even though most samples were passed by a 325 mesh sieve, if the crystallites were as big as the particles, this explanation would be convincing. However, in more than one diffraction pattern, parallel atom planes as 001 and 002 (2theta= 22.7 and 46.5º, respectively) and 110, 220 and 440 (2theta= 17.1 and 34.6 and 73.0º, respectively) have different behavior, what denies this possibility. Another explanation would be the variation of thermal parameters of uranium atoms, but these were very difficult to refine and no considerable improvement was done. Associated with these aspects, fractional occupation of atoms also seems a suitable reason for the intensity variation, however, there were also problematic to refine.

On the other hand, parameters as zero-shift, lorentzian function of peak broadening and cell parameters were refined adequately, and the agreement between calculated and experimental data seems reasonable.

Preferred orientation, using March-Dollase or Spherical Harmonic corrections, generated much better fits, however, its effect on phase quantification is still controversial [8], and, since the primary function of this analysis is to quantify crystalline phases, we decided to avoid the refinement of these parameters.

Bearing in mind the refined parameters, after many refinements of all samples, we decided to restrict the refined parameters to:

- Background polynomial of 10 terms;
- Zero shit (binding this parameter for all phases);
- Scale factor of all evolved phases;
- Cell parameters of U_3Si_2 phase;
- Lorentzian function for peak broadening of U_3Si_2;

Although from all refinement difficulties, the results were consistent from the phase quantification point of view. Rietveld refinement method rarely shows accuracy below some

units of percentage. Moreover, considering the quality of fits, the result seems satisfactory. Additionally, the fraction of U_3Si_2 quantified was higher than 97wt.%, what is far better than the limit of 80wt.% specification for its use in the IEA-R1 nuclear reactor.

Considering the single line profile analysis, the Voigt fits can be seen in figure 7, and the results of crystallite size and microstrain, in tables 2 and 3.

In both lots, the results show that the crystallite size seems to decrease from samples A (particle size between 150 and 44μm) to B and C (particles smaller than 44μm). The bigger crystallites from sample A can be explained from its direct correlation with larger particles. However, for samples B and C, production route should be considered, which comprised fusion and slow cooling. Subsequently, during the milling process, samples B were the first particles to be separated, flowing from the 325 mesh sieve. Samples C were made from a part of sample A, but submitted completely for milling till entirely flow thru 325-mesh sieve. Considering these facts, the results suggest that big crystallites formed during the slow solidification of U_3Si_2 are more fragile and first to be broken and separated from bulk, during milling process. This would explain why samples B show bigger crystallites than samples C, which had equivalent granulometry but were milled for a longer time.

Still, about the line profile analysis, the obtained microstrain values (about 10^{-5}) are negligible and show that the disorder of the crystal structure is low.

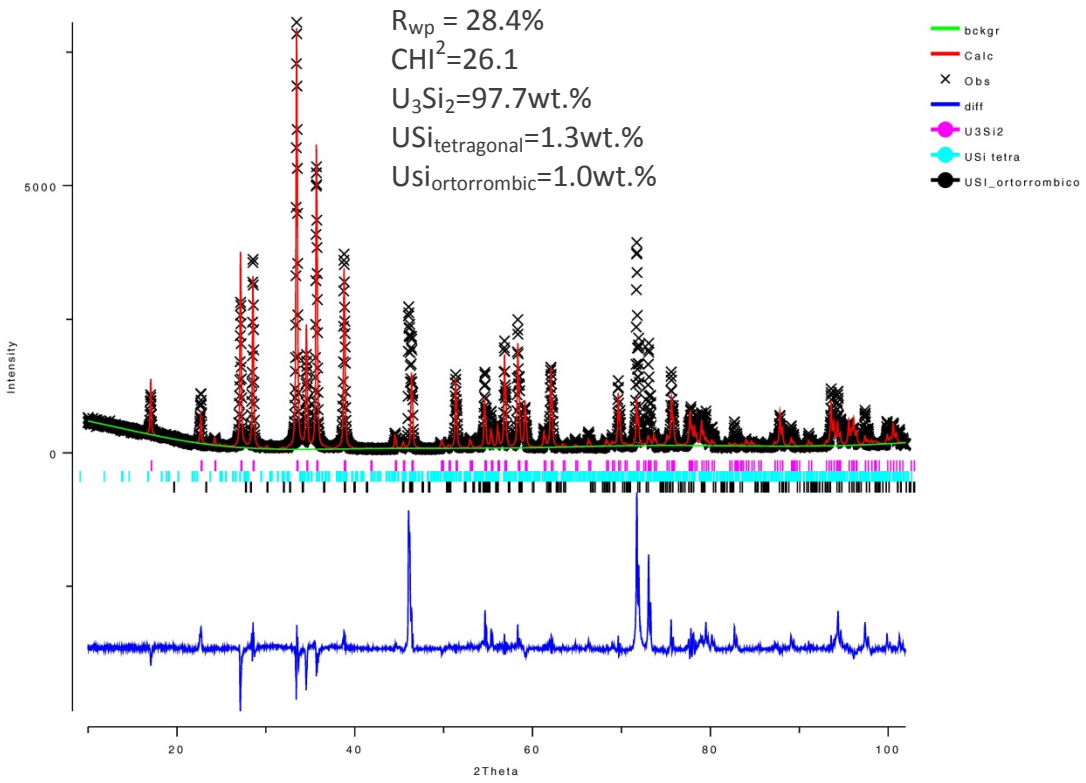

Figure 1: Uranium silicide sample 1A - Observed (black) and simulated (red) diffractograms, including Rietveld refinement parameters and quantification results.

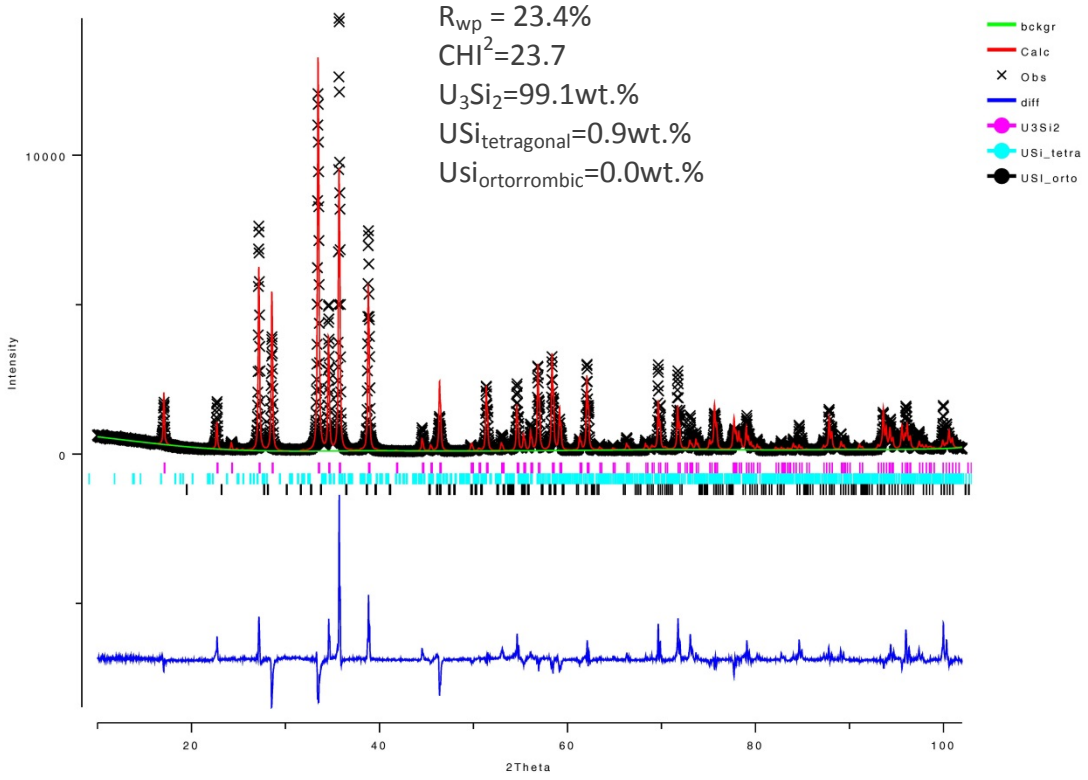

Figure 2: Uranium silicide sample 1B - Observed (black) and simulated (red) diffractograms, including Rietveld refinement parameters and quantification results.

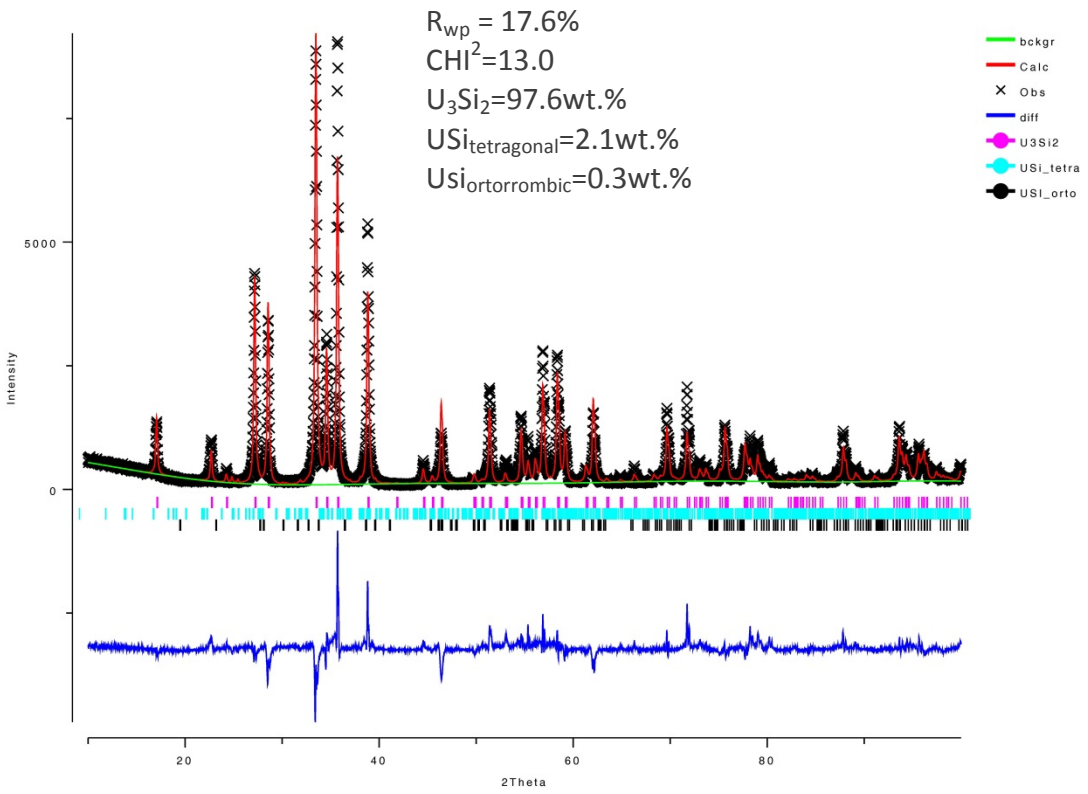

Figure 3: Uranium silicide sample 1C - Observed (black) and simulated (red) diffractograms, including Rietveld refinement parameters and quantification results.

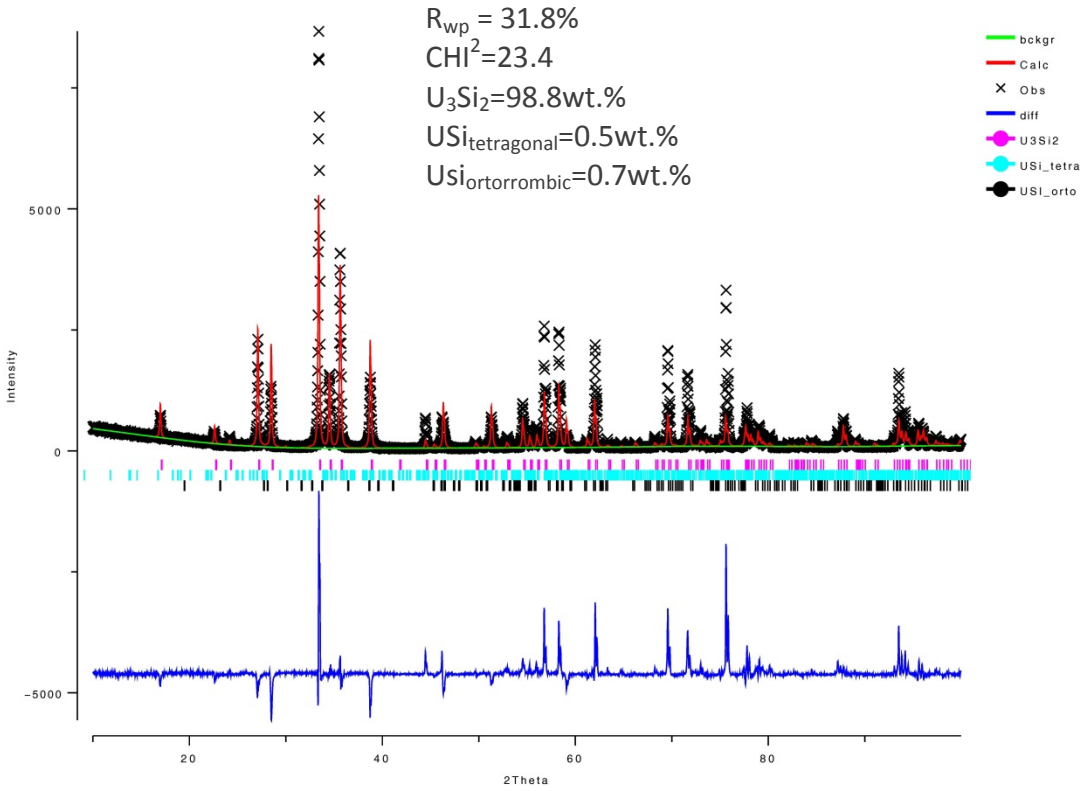

Figure 4: Uranium silicide sample 2A - Observed (black) and simulated (red) diffractograms, including Rietveld refinement parameters and quantification results.

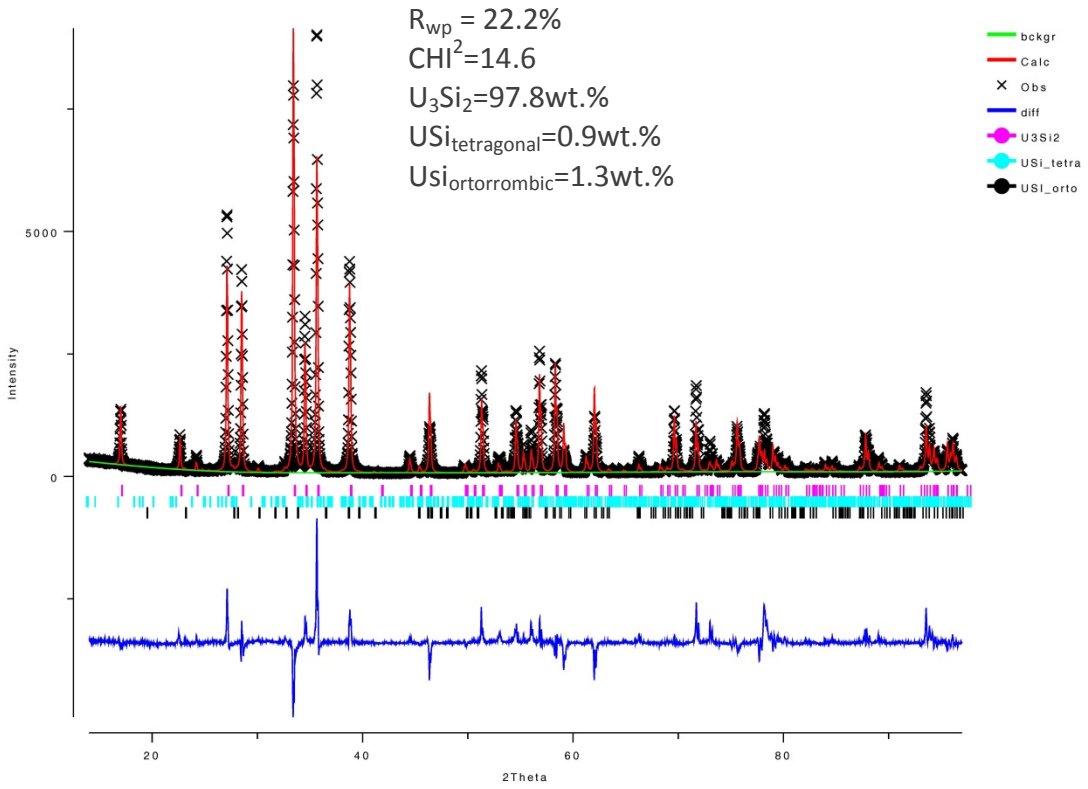

Figure 5: Uranium silicide sample 2B - Observed (black) and simulated (red) diffractograms, including Rietveld refinement parameters and quantification results.

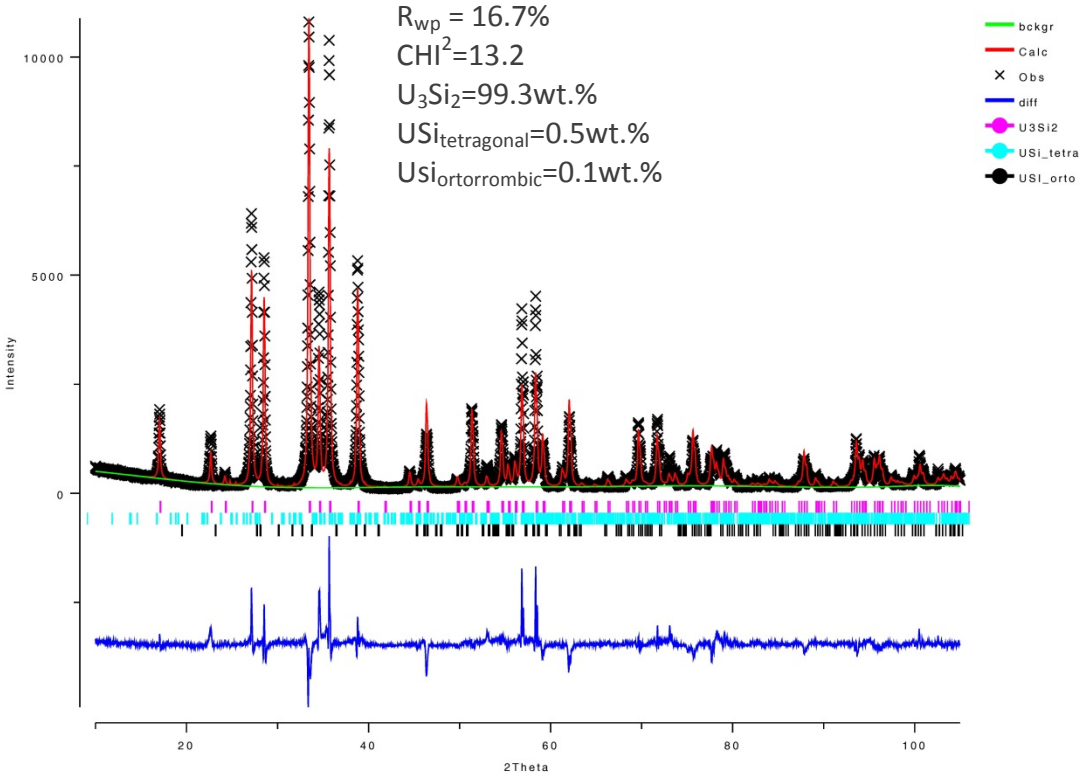

Figure 6: Uranium silicide sample 2C - Observed (black) and simulated (red) diffractograms, including Rietveld refinement parameters and quantification results.

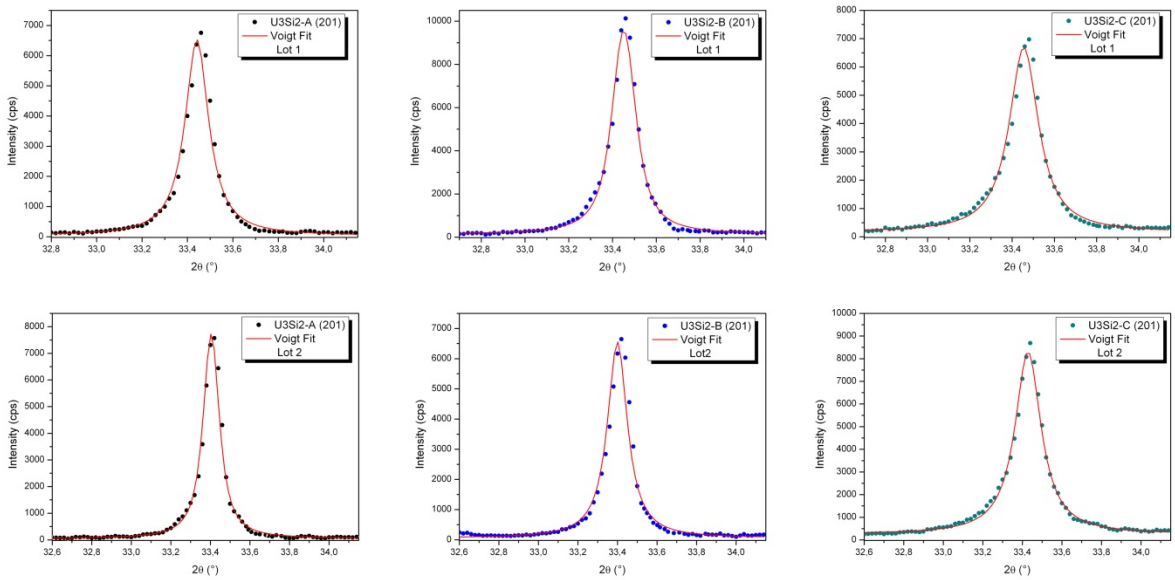

Figure 7: Single-line Voigt fits of X-ray diffraction peak (201) of uranium silicide samples 1A, 1B, 1C, 2A, 2B and 2C.

TABLE 2 – Mean crystallites sizes and microstrain values for the lot 1 of U_3Si_2.

Lot 1	D (nm)	ε
U_3Si_2 A	266	
U_3Si_2 B	127	$\approx 10^{-4}$
U_3Si_2 C	97.9	

TABLE 3 – Mean crystallites sizes and microstrain values for the lot 2 of U_3Si_2.

Lot 2	D (nm)	ε
U_3Si_2 A	205	
U_3Si_2 B	95.2	$\approx 10^{-5}$
U_3Si_2 C	59.2	

4. CONCLUSIONS

Although precautions with sample preparation and analysis were taken, intensity of X-ray diffracted peaks could not be well fit in Rietveld refinement. Probable causes include association of preferential orientation, inadequate granulometry, and differences in thermal factors and fractional occupation of U_3Si_2 atoms. Despite that, the refinements were acceptable and the results for phase quantification seem reliable and in accordance with the specification limit.
The stage from where U_3Si_2 samples were taken from the process plays an important role, considering granulometry and crystallite size for XRD and Rietveld refinement, bearing in mind phase quantification. More studies including additional milling should be done to investigate its influence on crystallite size and intensity of diffracted peaks.

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