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Structural and microstructural characterization of U3Si2 nuclear fuel using X-ray diffraction

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ABSTRACT

In this work, two uranium silicide powdered samples, containing 67% and 42 mol% of Si, were analyzed using X-ray diffraction (named as 67Si and 42Si). For structural characterization, Rietveld refinement was used to estimate cell parameters, volume fraction (weight percent) of crystalline phases and atomic positions. For the main phases, X-ray line profile analysis (XLPA) was used to estimate mean crystallite sizes and microstrains. The 67Si sample presents higher content of USi_2 (tetragonal) and the 42Si sample presents higher content of U_3Si_2 (tetragonal) as identified and calculated from the XRD profiles. Overall there are no appreciable structural changes and the parameters refined are in good accordance with the ones reported in the literature. Mean crystallite sizes determined by XLPA revealed small crystallites of the order of 10^1 nm and low microstrain for all samples.

1. INTRODUCTION

Nuclear fuels based on uranium silicide compounds are used in mostly modern research reactors. Specifically, U_3Si_2 is used on the IPEN IEA-R1 nuclear reactor, with own production since 2004 [1]. U_3Si_2 is particularly interesting since it has properties such as high density, adequate thermal conductivity at room temperature, high melting temperature [2], irradiation performed and accident tolerance [3]. Also, uranium silicide based nuclear fuels will be used in the new Brazilian Multipurpose Research Reactor (Reator Multipropósito Brasileiro - RMB, in Portuguese), an open pool type materials testing reactor (MTR) [4], which aims Brazil's autonomy in the radioisotopes production for nuclear medicine and industrial applications.

In this sense, a detailed structural and microstructural study about these silicide intermetallics is necessary. For instance, the control of crystalline phases when the material is processed is extremely important, since it is very difficult to obtain a precise stoichiometry due to production route restrictions, and each phase has different behavior under irradiation. In this

sense, the correct phase identification and quantification is very important to match the specifications for its use in the nuclear area [5] and its in-reactor behavior [6].

In this work, uranium silicide melts with different stoichiometries were produced and studied using X-ray diffraction techniques, a non-destructive type of analysis. Rietveld refinement was performed to determine the weight percent of chemical elements, cell parameters and atomic positions of each phase present in the material. For the microstructural analysis, Warren-Averbach [7] method was used to estimate mean crystallite size and microstrain for the main phase of each sample.

2. EXPERIMENTAL

The samples were synthesized by melting pure uranium and silicon inside an induction furnace at vacuum (10^{-3} torr). For the sample 67Si, 479.18 g of metallic uranium and 113.03 g of metallic silicon were weighted, aiming 67 mol% of Si. For sample 42Si, 542.67 g of uranium and 47.29 g of silicon were weighted. Both were then heated up to 1769 ºC. After cooling, samples were comminuted using pestle and mortar.

X-ray diffraction data was collected using a Bruker D8 Advance with the following configuration: 2.0 mm antiscatter and divergence slits, 0.2 mm slit for reception, 2.5º soller slits, goniometer radius of 250 mm, scintillation counter, graphite monochromator, 40 kV and 30 mA of Cu-Kα radiation and 25 seconds for each 0.025º step.

3. METHODS

3.1. Rietveld analysis

Rietveld analysis minimizes the difference between the experimental data and the model using a least squares procedure to fit the data. The background was modeled using a Chebychev sixth-order polynomial and the profile with the modified Thompson-Cox-Hastings (TCHz) function. Cell parameters, non-special atomic positions and volume fraction (weight percent) were refined. Also, volume weighted mean crystallite size ($\langle L \rangle_V$) and microstrain was estimated for the main phase. The refinements were performed using the software *TOPAS 4.2* [8].

3.2. X-ray line profile analysis

X-ray line profile analysis (XLPA) was performed using Warren-Averbach method through a software developed by the authors. Warren-Averbach method is the most unbiased method to determine mean crystallite size and microstrains since there is no fit to the experimental data. The Fourier Transform is performed using two peaks that must correspond to parallel reflections, this permits the calculation of the area weighted mean crystallite size ($\langle L \rangle_A$) and the root mean square strain (RMSS) from the Fourier coefficients. A detailed description on how the method can be applied and the definitions used can be found elsewhere [9].

3. RESULTS AND DISCUSSION

First, phase identification was performed using Crystallographica Search-Match. USi_2 (ICSD No. 31643) and $U_{1.07}Si_{2.14}$ (ICSD No. 76751) was identified for the 67Si sample. U_3Si_2 (ICSD No. 31648), USi (ICSD No. 31647) and $USi_{1.0147}$ (ICSD No. 81561) was identified for the 42Si. Information about the crystal structure of each phase can be seen in Table 1. The reflections of each phase can be seen in Figures 1 and 2.

Table 1: Information about the crystalline structure of each phase identified through search-match.

Sample	Phase	ICSD No.	Symmetry	Space group	No.
67Si	**USi_2**	**31643**	tetragonal	$I41/amdS$	141
	$U_{1.07}Si_{2.14}$	**76751**	cubic	$Pm\bar{3}m$	221
42Si	**U_3Si_2**	**31648**	tetragonal	$P4/mbm$	127
	USi	**31647**	orthorrombic	$Pbnm$	62
	$USi_{1.0147}$	**81561**	tetragonal	$I4/mmm$	139

Rietveld analysis was then performed using the CIF files mentioned above as starting models for the refinements. Highly crystalline CeO_2 was used to obtain the instrumental profile function to perform mean crystallite size and microstrain calculations.

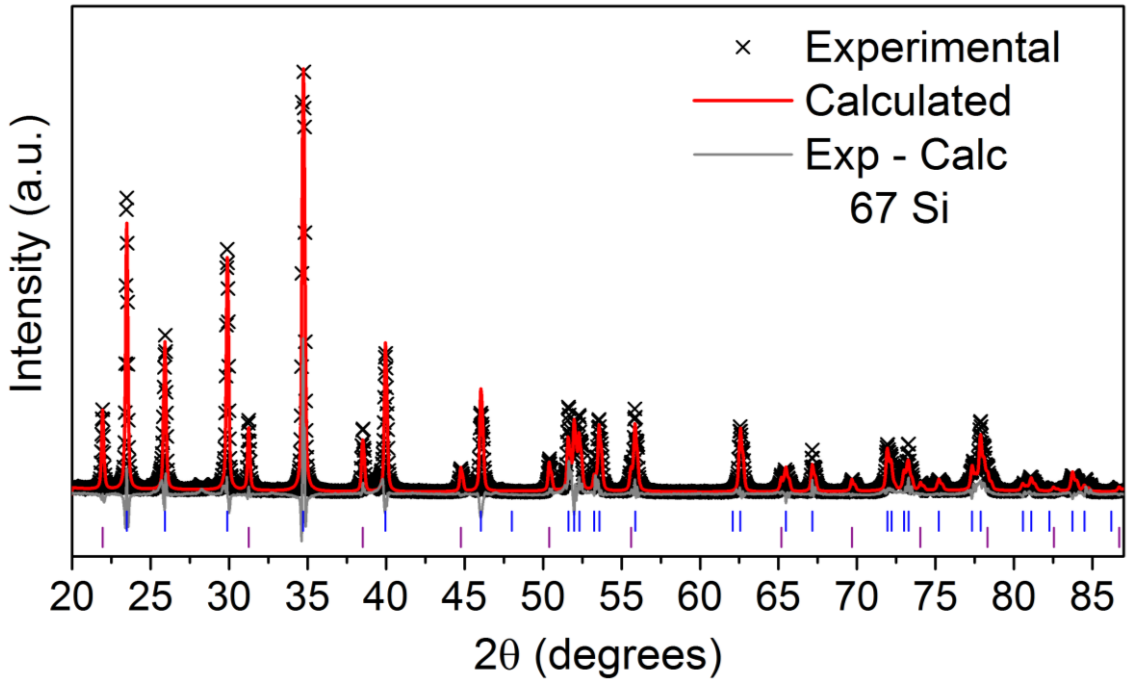

Figure 1: Rietveld refinement for the sample 67Si. The lines below the profiles stands for the reflections of USi_2 (blue) and $U_{1.07}Si_{2.14}$ (purple).

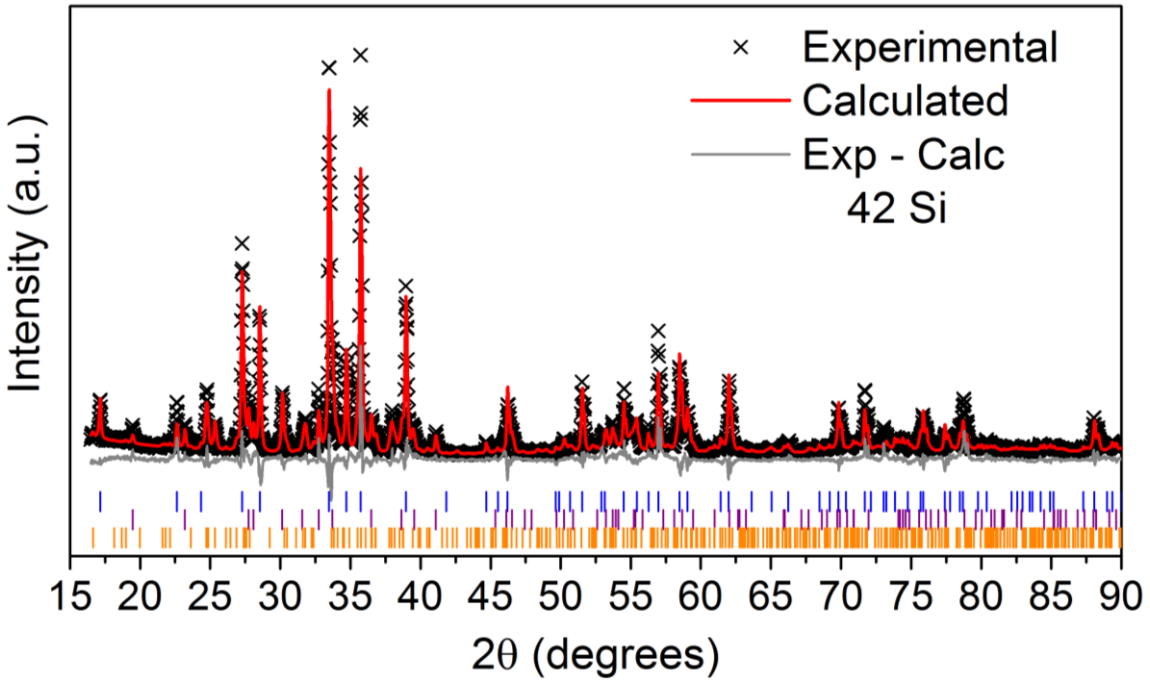

Figure 2: Rietveld refinement for the sample 42Si. The lines below the profiles stands for the reflections of U_3Si_2 (blue), USi (purple) and $USi_{1.0147}$ (orange).

An agreement factor (R_{wp}) of 18.9% and 15.7% was achieved for 67Si and 42Si, respectively. Scale factor, 6 background coefficients for the Chebyshev polynomial, cell parameters and atomic positions (for the main phase of each sample) were refined. Atomic displacement factors were kept fixed during the refinements.

The results were summarized in Table 2.

Table 2: Results for the Rietveld refinement for samples 67Si and 42 Si.

Sample	**67Si**		**42Si**		
Phase	**USi_2 (# 31643)**	**$U_{1.07}Si_{2.14}$ (# 76751)**	**U_3Si_2 (# 31648)**	**USi (# 31647)**	**$USi_{1.0147}$ (# 81561)**
a (Å)	3.9398(1)	4.0460(1)	7.3065(2)	5.6636(80)	10.6455(12)
b (Å)	3.9398(1)	4.0460(1)	7.3065(2)	7.6616(10)	10.6455(12)
c (Å)	13.7499(41)	4.0460(1)	3.9260(17)	3.9008(53)	24.4145(44)
x_{U2}	-	-	0.1802(3)	-	-
x_{Si}	-	-	0.3771(19)	-	-
z_{Si}	0.4217(14)	-	-	-	-
$\langle L \rangle_V$ (nm)	64(2)	67(6)	73(5)	56(7)	40(4)
e (10^{-5})	30(2)	25(7)	0*	0*	59(17)
weight %	86.3(5)	13.7(5)	57.6(4)	15.3(4)	27.1(4)

* Negligible microstrain

Even though powder was toughly comminuted, it seemed that the particle size could not be reduced to an optimum size (particles >10 μm lead to graininess issues), it can explain the slightly high R_{wp} (> 15%).

According to the weighted inputs, the phases expected for the sample 67Si were 100wt.% USi_2, in accordance with the results obtained, since the both phases identified have this stoichiometry. Considering the 42Si sample, the phases expected were 75wt.% U_3Si_2 and 25wt.% of USi (tetragonal + orthorrombic). This mismatch could be because of oxidation of uranium during the fusion (which normally segregates at ingot), and/or the error associated with the intensities of X-ray diffraction peaks due to the coarse-grained sample. To overcome this, for future works, the sample will be grained using a mill to achieve a finer powder.

The mean crystallite size for all phases is similar, ranging from 40 to 73 nm, where U_3Si_2 from 42Si has the higher mean crystallite size of all. The microstrain is negligible for the U_3Si_2 and USi (orthorrombic) phases within the 42Si sample; however, the USi (tetragonal) presents the higher microstrain among all phases. The microstrain values for the 67Si sample are similar within the error. All the structural parameters refined are close to the ones reported in the literature. Therefore, there is no significant deviation from the ideal values.

Finally, Warren-Averbach method was used for the two samples. Figure 3 shows the Fourier coefficients from the Warren-Averbach method for the mean crystallite size determination and in the inset the linear regressions used for the microstrain estimation. So, the area-weighted mean crystallite size and root mean square strain (RMSS) for all the phases identified were estimated, apart from the USi in the 42Si sample.

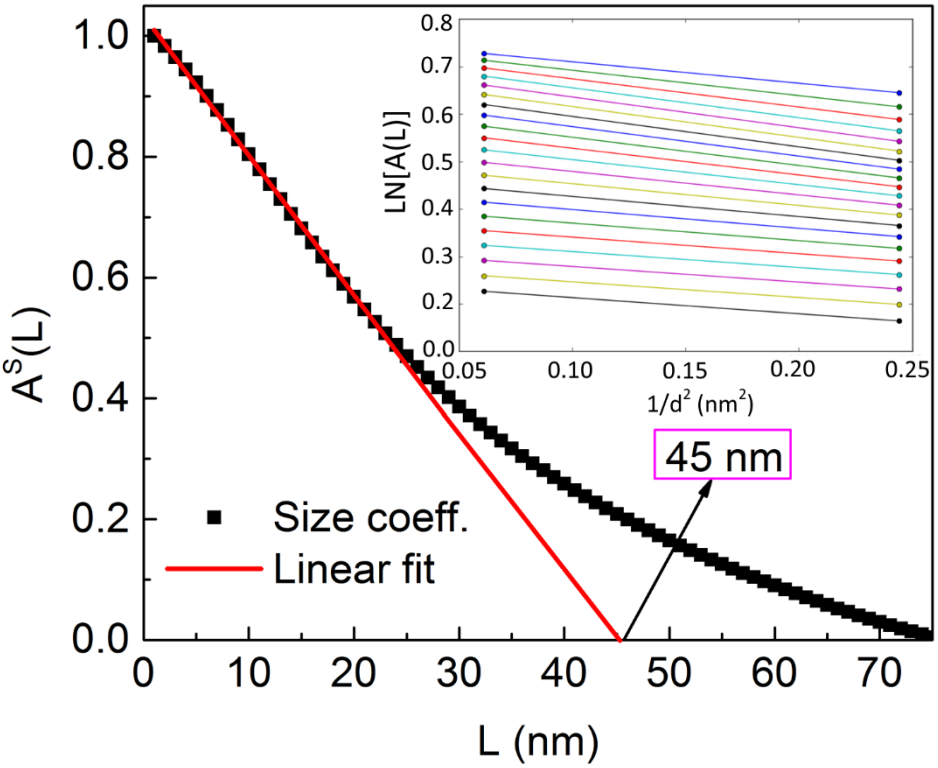

Figure 3: Warren-Averbach plots for U_3Si_2 (# 31648) for the 42Si sample. Fourier coefficients for mean crystallite size determination. In the inset the plots for the RMSS calculation.

Table 3: Results for the Warren-Averbach method for samples 67Si and 42 Si.

Sample	67Si		42Si		
Phase	USi_2 (# 31643)	$U_{1.07}Si_{2.14}$ (# 76751)	U_3Si_2 (# 31648)	USi (# 31647)	$USi_{1.0147}$ (# 81561)
$\langle L \rangle_A$ (nm)	40 (2)	-	45 (2)	34 (2)	-
RMSS (10^{-4})	1.9	-	0.3	2.4	-

The W-A method was not satisfactory applied in $U_{1.07}Si_{2.14}$ and $USi_{1.0147}$ phases since they present many overlapping peaks. The results were summarized in Table 3. As can be seen the results fully agree with ones calculated using Rietveld refinement. From Tables 2 and 3 it is possible to conclude that U_3Si_2 phase for the 42Si sample has the larger crystallite size as showed from Rietveld and W-A analyses. Also, the estimated RMSS (10^4 order) can be considered low for all phases, which also agree with Rietveld calculations.

CONCLUSIONS

In this work, two uranium silicide samples with 67 mol% and 42 mol% of Si (termed as 67Si and 42Si respectively) were analyzed using X-ray diffraction techniques. Two phases were identified for the 67Si sample: USi_2 (tetragonal) and $U_{1.07}Si_{2.14}$ (cubic) with higher content of the first one. For the 42Si sample, three phases were identified: U_3Si_2 (tetragonal), USi (orthorrombic) and $USi_{1.0147}$ (tetragonal), with higher content of the first one. Rietveld analysis revealed that no appreciable structural changes are present and all parameters refined are in accordance with the ones reported in the literature. X-ray line profile analysis was applied to determined mean crystallite size and microstrain, which indicated very low microstrain for all samples although mean crystallite size of the order of 10^1 nm were found.

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