

Quantification of crystalline phases of uranium silicide using the Rietveld method

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Abstract. Uranium silicide is a material widely used as nuclear fuel for MTR (Material Testing Reactor), due to its performance in reactor environment. Some of its characteristics make it also attractive for its use in power reactors. However, each crystalline phase of uranium silicide have different behavior under irradiation. In this sense, it is important to perform crystalline phase characterizations, which are commonly obtained in the fabrication process. For this purpose, in this work U-Si alloys containing 33, 40, 41, 42, 50 and 67 mol% of silicon were molten in an induction furnace. Quantification of formed crystalline phases was carried out by Rietveld refinement of X-ray diffraction data. Calculated densities were compared to measured data from helium pycnometry.

Introduction

Uranium silicide 20% U²³⁵ enriched is an intermetallic compound widely used as nuclear fuel material in MTR's as the meat of fuel elements, due to its thermal conductivity, chemical and physical stability and containment of fission gases under irradiation. Besides that, it has a higher melting point in relation to oxides based fuels. In this way, the interest in the use of this type of fuel in power reactors has been growing in the last years, considering that this fuel could have greater tolerance to failures, representing greater safety in comparison to fuels currently used [1].

Its fabrication in IPEN replaced the previous ceramic powder, U₃O₈, used in the fuel of IEA-R1 Reactor [2]. The U₃Si₂ is a compound with 92.3wt.% U and 7.7wt.% Si and it presents suitable quality under nuclear irradiation due to its high uranium density and failure tolerance in reactor environment. The intermetallic U₃Si₂ requires special operations to be produced. At IPEN, its fabrication is made by melting using metallic uranium, produced by magnesiothermic reaction, and pure silicon. The induction furnace melts U-Si under argon controlled environment around 1700°C, using zirconia crucible. The U-Si phase diagram indicates that, during the melting process of both metals, there is the possibility of formation of other intermediate phases with high melting points [3]. To enhance the performance of the IEA-R1 nuclear fuel, it is important to maximize the amount of U₃Si₂ phase among the other U-Si compounds formed, and avoid the presence of metallic uranium. Therefore, the liquid bath should go up to 1700°C to ensure fusion of all compounds. Pure uranium melts at 1132 °C and pure silicon at 1410°C. U₃Si₂ has a melting point at 1665°C.

During the heating process, uranium melts first, and, as a denser metal than silicon, liquid uranium permeates the silicon, promoting a faster formation of a liquid. If there is not a proper homogenization of the melt, phases with different stoichiometry compositions may crystallize. Furthermore, silicon has higher vapor pressure than uranium, especially at high temperatures. This

enables evaporation of part of the silicon even before the formation of the alloy takes place, de-balancing the stoichiometry. In this sense, after the melting of all components, it must be readily cooled.

U_3Si_2 is one of the most stable uranium phases and its formation is significantly exothermic, helping the melting of the silicon and its incorporation into the liquid bath.

For the routine production of the nuclear fuel powder, the U-Si stoichiometry is calculated with slightly Si-rich composition, in order to guarantee the absence of the metallic uranium phase in the final product, which is unstable under neutron bombardment and very reactive to the aluminum substrate of the fuel element nuclear fuel [4]. The formation of U_3Si phase is also undesirable because it is also deleterious for the nuclear fuel, however, it is formed by peritectoid reaction of U_3Si_2 and metallic uranium at 800°C for 72h, therefore, not expected to be formed during a fast cooling process [5].

Consequently, the product should carry more than one crystalline phase. Considering that the fuel specification imposed by the Nuclear Engineering Center of IPEN limits the minimum concentration of U_3Si_2 , for the nuclear fuel used in reactor IEA-R1 crystalline as 80wt.%, the quantification of the crystalline phases is essential. However, there are very few publications concerning phase quantification of uranium silicides [6]. In this sense, aiming the development of a routine methodology for phase quantification using X-ray diffraction (XRD) and Rietveld refinement method, uranium silicide samples with six different stoichiometry compositions were produced and characterized by XRD and helium pycnometry. Acquired data from XRD were refined using the Rietveld method, and the results compared to powder's real density.

Methods and materials

Six samples of uranium silicide, containing 33, 40, 41, 42, 50 and 67 mol% of silicon were produced from melting metallic uranium with nuclear grade silicon. After the melting, samples was grinded until the granulometry was smaller than 44 μ m (325 mesh). Nomenclature, weighted amounts, molar and weight fractions and maximum furnace temperature of samples are shown at table 1. After cooling, samples were comminuted using pestle and mortar inside an argon atmosphere glovebox.

Table 1: Uranium silicide samples nomenclature, weighted amounts, molar and weight fractions and furnace temperature

Nomenclature	U mass (g)	Si mass (g)	Wt.% U	Wt.% Si	Mol% U	Mol% Si	Furnace maximum temperature (°C)
<i>33Si</i>	627.22	36.46	94.51	5.49	67.00	33.00	1703
<i>40Si</i>	749.37	58.77	92.73	7.27	60.07	39.93	1702
<i>41Si</i>	923.16	75.83	92.41	7.59	58.96	41.04	1700
<i>42Si</i>	542.18	47.18	91.99	8.01	57.55	42.45	1699
<i>50Si</i>	601.30	69.89	89.59	10.41	50.38	49.62	1707
<i>67Si</i>	478.74	112.77	80.94	19.06	33.38	66.62	1769

X-ray diffraction data were collected using a Bruker D8 Advance with the following configuration: 2.0 mm antiscatter and divergence slits, 0.2 mm slit for reception, 2.5° soller slits, goniometer radius of 250 mm, scintillation counter, graphite monochromator, 40 kV and 30 mA of Cu- α radiation and 25 seconds for each 0.025° step. Each sample was analyzed three times, each from a different powder portion. Based on X-ray diffraction data, phase identification was

performed using EVA 4.2 software from Bruker, and the results refined using Topas 5 software, also from Bruker.

Density measurements of the produced samples were performed using Micromeritics Accupyc 1300 densitometer, from roughly 50g of each sample.

Results and discussion

Based on XRD data, it was possible to identify the crystalline phases formed (table 2). From sample 33Si, the excess of uranium results in metallic uranium production. At 40mol%Si, the stoichiometry of U_3Si_2 is attained. With more silicon addition (41 and 42Si), $USi_{1.047}$ phase start to take place, and USi and U_3Si_5 is formed with 50mol% Si. Sample 67Si had two different crystalline phases formed, $USi_{1.84}$ and USi_3 . Except for the 33Si sample, small intensities of UO_2 peaks were noticed in all samples, probably to some superficial oxidation of the lingot or during the milling, even though precautions were taken to avoid this phenomenon.

Table 2: Identified crystalline phases from U-Si produced samples from 33 to 67mol% Si.

<i>XRD identified crystalline phases</i>								
<i>(from higher to lower intensity: +++, ++, +, t)</i>								
<i>Phase</i>	<i>U</i>	<i>U₃Si₂</i>	<i>USi</i>	<i>USi_{1.047}</i>	<i>U₃Si₅</i>	<i>USi_{1.84}</i>	<i>USi₃</i>	<i>UO₂</i>
PDF #	72-0657	80-1374	65-2606	86-0854	13-0108	65-0657	65-0607	41-1422
Sample								
33Si	+	+++						
40Si		+++						t
41Si		+++		++				t
42Si		++		++				t
50Si		+	+	+++	+			t
67Si						+++	++	+

XRD data acquired and calculated plot from Rietveld refinements are shown in figures 1 to 6. In general, calculated plots had fair agreement with experimental data, however, some difference can be noticed in some peaks intensities. This is probably due to the large size of analyzed particles (up to 44 μ m). Also, particularly in the case of high X-ray absorption samples as uranium compounds, the penetration of the X ray is restricted, so the number of diffracted units is reduced. In this sense, a better sample preparation reducing particle size seems important to attain better fit and reduce the standard deviation of phase quantification.

XRD data from samples 50Si and 67Si (figures 5 and 6) and average R_{wp} of these refinements show that these samples had worst adjust than the others. This could be explained due to distortions of the present phases (for instance, at 67Si sample, some peaks appear as doublets), occupation factors of atoms at the crystalline structure, and particles with pronounced aspect ratio, increasing the effect of preferred orientation of particles.

Phase quantification results based on Rietveld refinements are shown at figure 7 (a). The standard deviation was calculated based on the three analysis of each sample. Even though the fit quality of 50Si and 67Si were not optimum, the dispersion of the results remained quite low.

Based on the quantified amount and refined cell parameters of each sample, it was possible to estimate the density of each sample. The results are shown at figure 7 (b), together with density values obtained by helium pycnometry. Most samples had good agreement, except 33Si sample. This composition contains metallic uranium, which has prominent X-ray absorption. In this sense, microabsorption effects can lead to underestimation of U^0 in Rietveld quantification, resulting in lower density values.

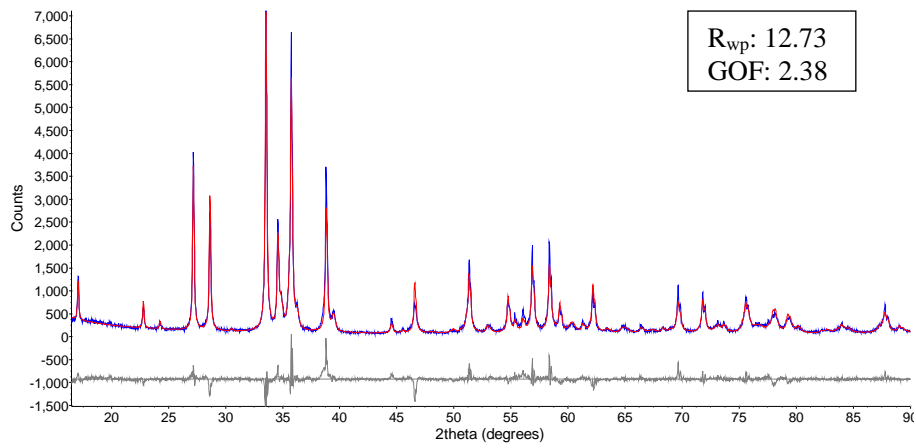


Figure 1: X-ray diffractogram of 33Si sample experimental (blue) calculated (red) and difference (gray). Statistical parameters R_{wp} and GOF are calculated by the average of three analysis.

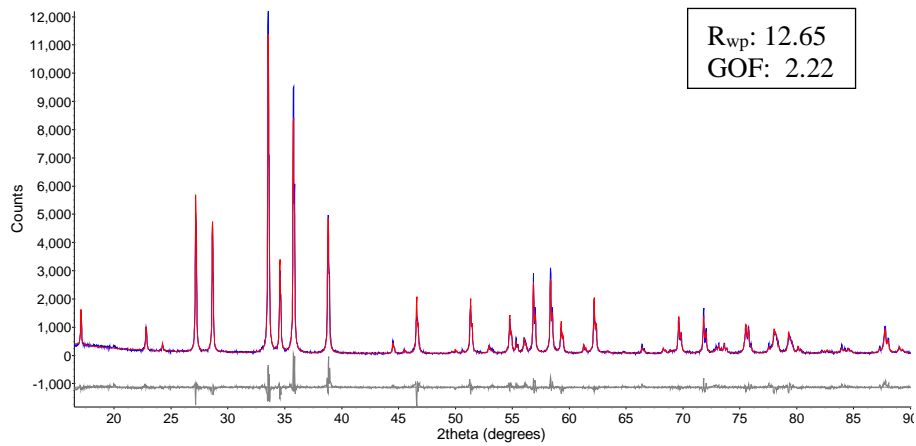


Figure 2: X-ray diffractogram of 40Si sample experimental (blue) calculated (red) and difference (gray). Statistical parameters R_{wp} and GOF are calculated by the average of three analysis.

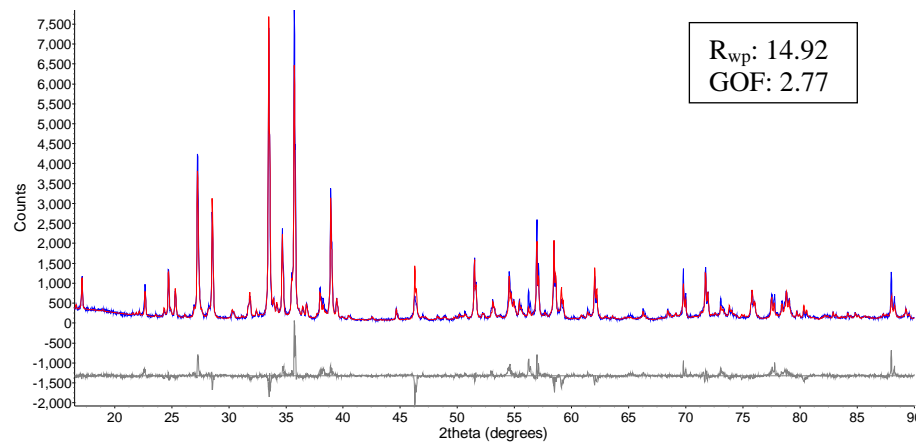


Figure 3: X-ray diffractogram of 41Si sample experimental (blue) calculated (red) and difference (gray). Statistical parameters R_{wp} and GOF are calculated by the average of three analysis.

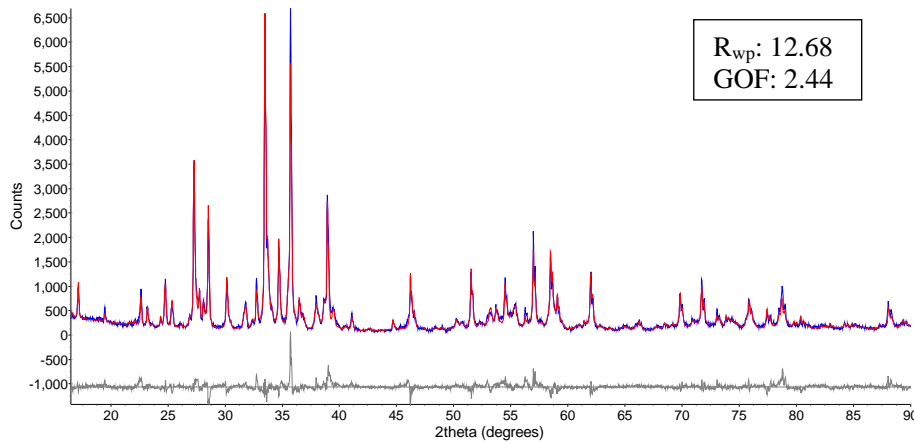


Figure 4: X-ray diffractogram of 42Si sample experimental (blue) calculated (red) and difference (gray). Statistical parameters R_{wp} and GOF are calculated by the average of three analysis.

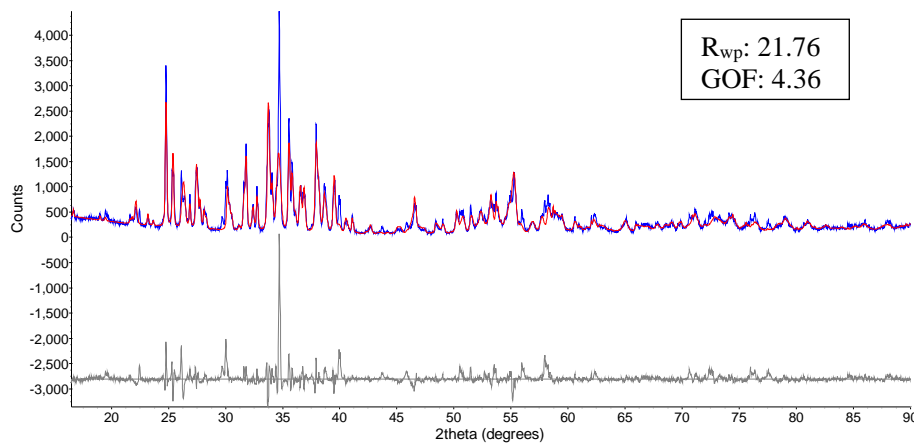


Figure 5: X-ray diffractogram of 50Si sample experimental (blue) calculated (red) and difference (gray). Statistical parameters R_{wp} and GOF are calculated by the average of three analysis.

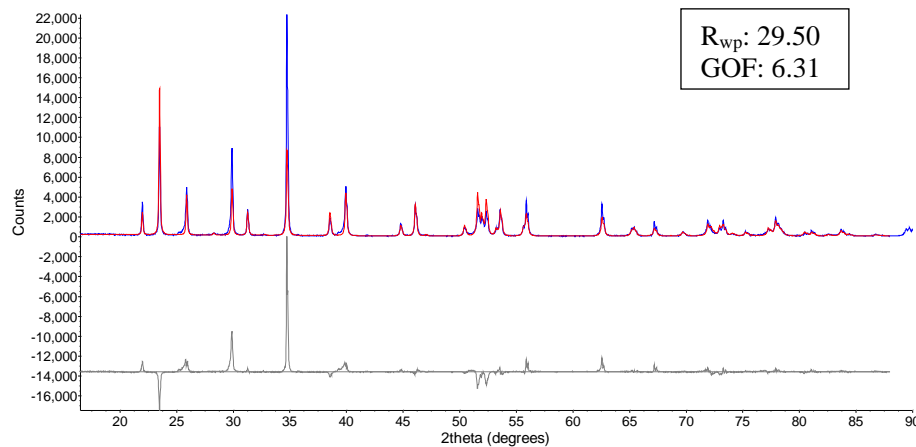
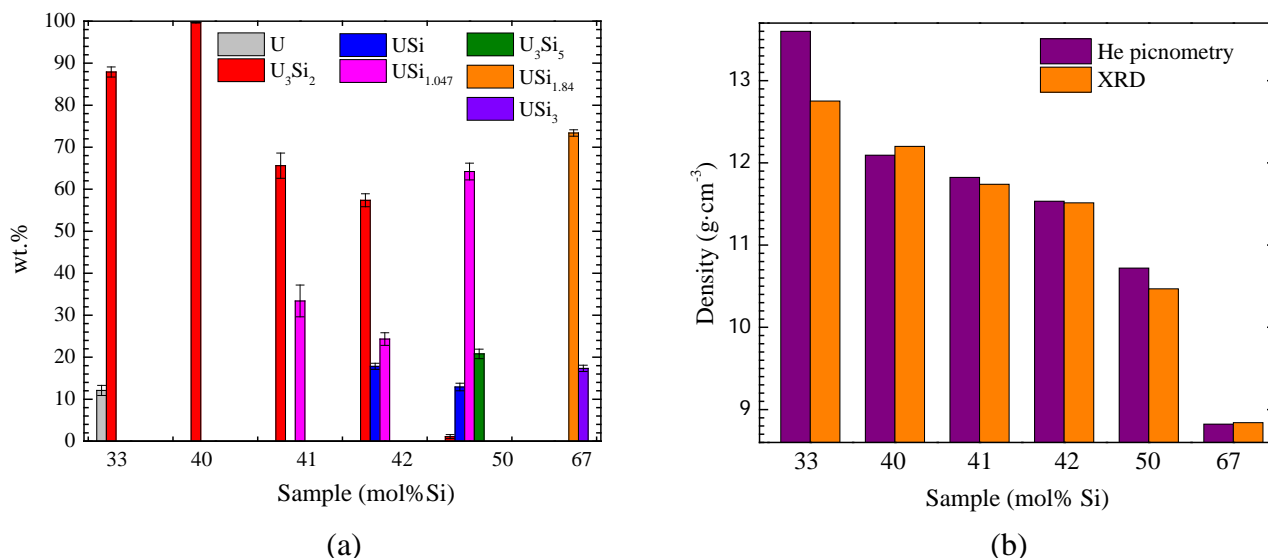


Figure 6: X-ray diffractogram of 67Si sample experimental (blue) calculated (red) and difference (gray). Statistical parameters R_{wp} and GOF are calculated by the average of three analysis.



*UO₂ phase was not plotted in this graph

Figure 7: Quantification results of U-Si samples based of refined results of XRD data (a) and density of compounds calculated from XRD data and measured experimentally (b).

Conclusion

From the six U-Si compositions produced, eight crystalline phases were identified and quantified by the Rietveld refinement from XRD data. A good Rietveld fit was achieved in most of cases, except for the samples containing 50 and 67%Si, possibly due to phase distortions, atoms occupation differences and aspect ratio of the particles, causing higher preferred orientation effect. The standard deviation between quantifications from XRD data remained low and did not show relation to fit quality from Rietveld refinements.

Calculated density of samples, based on Rietveld quantification and refined cell parameters, had good agreement to the measured density results obtained experimentally, except for composition containing 33mol% Si, possibly due to microabsorption effects.

References

- [1] I. Charit. Accident Tolerant Nuclear Fuels and Cladding Materials, JOM, 70-2 (2018) 173–175.
- [2] A. M. Saliba-Silva, M. Durazzo, E. F. Urano Carvalho, H. G. Riella, Fabrication of U₃Si₂ Powder for Fuels Used in IEA-R1 Nuclear Research Reactor, Mater. Sci. Forum. 591–593 (2008) 194–199.
- [3] H. Okamoto. Si-U (Silicon-Uranium). J. Phase Equilib. Diff.. 34-2 (2013) 167–168.
- [4] U. S. N. R. Commission, Safety Evaluation Report Related to the Evaluation of Low-enriched Uranium Silicide-aluminum Dispersion Fuel for Use in Non-power Reactors. U.S. Nuclear Regulatory Commission, 1988.
- [5] R. F. Domagala, T. C. Wiencek, H. R. Thresh. Some properties of U-Si alloys in the composition range U₃Si to U₃Si₂. Argonne National Laboratory (ANL), 1984.
- [6] J. Rosales, I. J. van Rooyen, S. Meher, R. Hoggan, C. Parga, J. Harp. Effect of High Si Content on U₃Si₂ Fuel Microstructure, JOM. 70-2 (2017) 209-213.