STEM-EDS Analysis of Fission Products in Neutron-Irradiated TRISO Fuel Particles from AGR-1 Experiment

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ABSTRACT

Historic and recent post-irradiation-examination from the German AVR and Advanced Gas Reactor Fuel Development and Qualification Project have shown that 110m Ag is released from intact tristructural isotropic (TRISO) fuel. Although TRISO fuel particle research has been performed over the last few decades, little is known about how metallic fission products are transported through the SiC layer, and it was not until March 2013 that Ag was first identified in the SiC layer of a neutron-irradiated TRISO fuel particle. The existence of Pd- and Ag-rich grain boundary precipitates, triple junction precipitates, and Pd nano-sized intragranular precipitates in neutron-irradiated TRISO particle coatings was investigated using Scanning Transmission Electron Microscopy and Energy Dispersive Spectroscopy analysis to obtain more information on the chemical composition of the fission product precipitates. A U-rich fission product honeycomb shape precipitate network was found near a micron-sized precipitate in a SiC grain about ~5 μm from the SiC-inner pyrolytic carbon interlayer, indicating a possible intragranular transport path for uranium. A single Ag-Pd nano-sized precipitate was found inside a SiC grain, and this is the first research showing such finding in irradiated SiC. This finding may possibly suggest a possible Pd-assisted intragranular transport mechanism for Ag and may be related to void or dislocation networks inside SiC grains. Preliminary semi-quantitative analysis indicated the micron-sized precipitates to be $\text{Pd}_2\text{Si}_2\text{U}$ with carbon existing inside these precipitates. However, the results of such analysis for nano-sized precipitates may be influenced by the SiC matrix. The results reported in this paper confirm the co-existence of Cd with Ag in triple points reported previously.

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1. INTRODUCTION

Tristructural isotropic (TRISO) coated particle fuel is currently used in high temperature gas-cooled reactors and will be the fuel of choice for the Generation IV Very High Temperature Reactor [1]. However, for its successful use in Very High Temperature Reactor, release mechanisms of metallic fission products (FPs), such as Ag and Pd through TRISO particles' coatings, should be clearly understood and eventually quantified [2,3].

Release of Ag from TRISO particles is of most concern from the standpoint of personnel safety issues during maintenance. Many reactor experiments [2,4,5], out-of-pile surrogate experiments [6–9], and modelling studies [10,11] have been performed to understand the possible release mechanism of Ag. Grain boundary (GB) diffusion [7–11] and vapor release through micro-cracks [6] have been proposed,

but none of these mechanisms conclusively explain the release from individual coated particles of up to 100% of the produced Ag observed in in-reactor TRISO particle irradiation tests. However, it should be noted that each compact contained over 4,000 coated particles, and the average fraction of Ag release in each Advanced Gas Reactor (AGR)-1 capsule (four compacts) ranged from 1.2×10^{-2} to 3.8×10^{-1} (a fraction of 2.0×10^{-5} is equivalent to 100% release from a single particle) [3]. Palladium is also a metallic FP of great interest in TRISO fuel. Past studies have shown that Pd can corrode SiC [12,15] and will potentially cause failure of the fuel particle. Furthermore, these experiments also suggest that Pd can potentially assist the transport of other FP such as Ag [16] and U [12] by forming Pd-FP silicides nodules, which can move along grain boundaries.

The examination of FP in neutron-irradiated TRISO coated particles is important and the results can provide insight into FP transport mechanisms proposed and investigated in out-of-pile surrogate experiments. Nano-scale analysis of FP in TRISO particles' coatings has only recently received attention due in large part to the availability of nano-scale analytical tools in facilities where neutron irradiated fuels could be handled, prepared, and analyzed, as well as the availability of neutron irradiated UCO contained fuel particles with known irradiation histories.

Incorporating Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive Spectroscopy (EDS) analysis together is an excellent way for providing new insights into FP transport. A previous study by van Rooyen et al. [4] has demonstrated this by identification of Ag for the first time in neutron irradiated TRISO fuel particles with this technique. This study qualitatively examined FP precipitates in the SiC-inner pyrolytical carbon (IPyC) interlayer and focused specifically on the identification of Ag, Pd, U, and Cd in selected areas. In the present study, the work by van Rooyen et al. [4] has been extended to examine FP precipitates inside the SiC layer (0.5 μ m to 5 μ m from the SiC-IPyC interlayer), along with a quantitative assessment of size, shape, preferential location, and composition of those FP precipitates by STEM-EDS.

2. MATERIALS AND METHODS

The TRISO fuel particle examined in this study was CP35 from Compact 6-3-2 from the AGR-1 experiment, which had an estimated Ag retention of 80%. The retention of ^{110m}Ag is estimated by comparing the measured inventory to the predicted inventory normalized by the relative Cs-137 activity to reduce the influence of different kernel sizes on the overall distribution. This particle was therefore chosen for electron microscopy examination, as the particle therefore exhibits good Ag retention characteristics. This study is therefore the continuation in a larger battery of experiments of the AGR program, to identify particle, or more specifically the SiC layer; characteristics that can provide more information on the varying release of Ag within coated particles from the same compact. Details of this fuel particle and the rationale for its selection for this study are further described elsewhere [3, 4]. Two STEM lamellae (identified as 6a and 6b) were prepared by a focused ion beam near the IPyC-SiC interlayer as shown in Fig. 1. The purpose of using two lamellae was to provide larger areas for investigation and no specific microstructural differences were expected in these two lamellae.

The FPs produced during irradiation consist of relatively heavy elements compared with coating material layers used in TRISO fuel particles. Therefore, the High Angle Annular Dark Field detector in STEM, of which contrast in the image is sensitive to atomic number differences (so-called Z-contrast imaging), was chosen to reveal the distribution of FPs. The compositional analysis of these fine FP precipitates was performed by standardless EDS analysis in STEM mode.

The STEM-EDS analyses were conducted with an FEI Tecnai G2 F30 STEM at the Microscopy and Characterization Suite, Center for Advanced Energy Studies, where low-activity irradiated materials can be examined. Pd, U, and Ag were identified using Pd K α 1 peak (21.175 keV), U L γ 1 peak (20.163 keV), and Ag K α 1 peak (22.162 keV), respectively, to avoid uncertainties associated with peak overlaps. An EDS line scan was used for the qualitative identification of FP using an acquisition time of 10–40 secs/point. Transmission Electron Microscopy images and analysis software were used for quantitative

EDS analysis, and longer 480 secs/point area analysis was used for quantitative measurements to increase the signal-to-noise ratio.

The preliminary STEM study [4] focused on the SiC-IPyC interlayer area of Sample 6b with selected areas deeper inside the SiC layer, whereas this study focused on the FP in the SiC layer further from the SiC-IPyC interlayer ($\sim 5\mu\text{m}$) (Position 1 of Fig. 1[b]). Additionally, Sample 6a was also characterized to produce more information.

3. RESULTS AND DISCUSSION

Using High Angle Annular Dark Field imaging and combined EDS measurements, various FP precipitates were identified in the IPyC layer, IPyC-SiC interlayer region, and SiC layer of the TRISO samples (Fig. 1, Fig. 2[a]). These precipitates are categorized based on their size, shape, and location in the microstructure.

3.1 Micron-sized Precipitates ($\geq 100\text{ nm}$)

As shown in Fig. 1, micron-sized precipitates with irregular shape were mainly located at IPyC-SiC interlayer, but some of these precipitates were also observed inside the SiC and IPyC layers. The size of these precipitates varied from approximately 100 nm up to $2\mu\text{m}$, and the precipitates in SiC and IPyC layers were smaller than those in IPyC-SiC interlayer (Fig. 1 and Fig. 3). Additionally, micron precipitates in the SiC layer and the IPyC-SiC interlayer had sharp protrusions connecting them to SiC grain boundaries which indicates that their formation may be associated with GB transport of FP. Fig. 2 shows the EDS spectrum of a micron-sized precipitate located at the SiC layer $\sim 5\mu\text{m}$ away from the interlayer. These precipitates consist of mainly Pd and U, while other minor FPs, such as Cs, Eu, and Ce, were also identified.

Semi-quantitative compositional analysis was performed on three micron-sized precipitates from different regions (Fig. 3) and results are shown in Table 1. (The % error displayed in the tables are automatically calculated by the FEI software (100% error indicates that the specific peak was not identified)) The proportion of U, Pd, and Si in the SiC layer and SiC-IPyC interlayer precipitates is close to 1:2:2. This suggests that they may be UPd_2Si_2 ternary silicides, as indicated by selected area diffraction pattern in the previous transmission electron microscopy study of another particle from AGR-1 [5]. The carbon concentration in those silicides is similar compared to those in the SiC matrix whereas the Si concentration is lower. Micron-sized U-Pd-Si silicides are also identified in the originally Si-free IPyC layer, but have slightly different stoichiometry. Considering that the size of precipitates are larger than the STEM lamella thickness ($\sim 100\text{ nm}$), and the probe size of STEM is very small ($\sim 1\text{ nm}$), the influence of the EDS signal from the matrix should be minimal. However, EDS analysis on lighter elements such as C may not be accurate, and should still be confirmed using atom probe tomography as a more accurate measurement.

The above results may indicate that during the transport of U and Pd through the SiC layer, SiC was decomposed at some sites. Part of the Si-formed micron-sized UPd_2Si_2 , and the rest of free the Si could possibly have diffused elsewhere (e.g., IPyC layer) to form other types of silicides. On the other hand, most of the C remained inside the micron-sized silicides, but the chemical state of this carbon is unclear. E.J. Oliver et al. [15] investigated the Pd transport in single crystalline SiC and found that C can form nano-sized precipitates inside Pd silicides. No direct evidence of carbon precipitates was observed in this current study and should be investigated in future studies.

3.2 Nano-sized Precipitates (5 to 20 nm)

Unlike the micron-sized precipitates, which have long been observed by the scanning electron microscopy and transmission electron microscopy studies, [4, 5, 12–14] nano-sized FP precipitates (resulting from a fueled kernel) in neutron irradiated SiC layers for TRISO coated particles were not seen until STEM was introduced as an advanced characterization technique [4]. Ion implanted out-of-pile studies on SiC

showed nano precipitation of metallic products ([21,22]) and although contributed towards understanding of some microstructural effects, could not fully simulate the transport behavior of Ag and Pd behavior in intact TRISO fuel particles. Nearly spherical-shaped nano-precipitates, 5 nm to 20 nm in size, were identified mainly located inside the SiC grains at the SiC-IPyC interlayer and further inside the SiC layer (Fig. 4[a]). Most of these nano-precipitates were identified to be Pd-rich with no detectable Ag and U (Fig. 4[c]), which is consistent with the previous work [4]. Further examination in this study showed that a small amount of Ag was detected in one EDS site (Fig. 4[b]). Fig. 4(b) shows an example of the Pd-Ag nano-sized particle, which is found in the SiC layer $\sim 5 \mu\text{m}$ away from the interlayer. The EDS spectrum clearly showed peaks corresponding to Pd and Ag. Among 10 nano-sized precipitates evaluated in this study, only two contained Ag. These Ag-Pd containing nano-precipitates should be further investigated to determine if they are intergranular or intragranular.

The semi-quantitative analysis results of selected nano-sized precipitates are shown in Table 2. The Si content in precipitates is higher, whereas C content is lower than in the SiC matrix, indicating the precipitates to be FP silicides. The concentration of FP measured in nano-sized precipitates is much smaller than Si or C. This is because the collected EDS signal emanates mainly from SiC matrix ($\sim 100 \text{ nm}$ size, comparable to sample thickness) rather than from small size of precipitates ($< 20 \text{ nm}$). The influence of precipitates size on the EDS results is schematically shown in Fig. 5 as a typical example. For nano-sized precipitates (Fig. 5[a]), Pd enrichment can be observed inside the precipitate, but there is no change in C and Si concentration as shown by the EDS spectra and as indicated in Table 2. On the contrary, the Si counts were clearly lower in the micron precipitate than in the matrix (see EDS line profile in Fig. 5[b]), but the C counts remained the same, consistent with quantitative results shown in Table 1.

3.3 GB precipitates (Width $< 5 \text{ nm}$) and Triple Junction Precipitates (10 to 20 nm)

Nano-sized FP at triple junctions and boundaries of SiC grain was revealed by STEM-High Angle Annular Dark Field imaging (Fig. 6 and Fig. 7). These triple junction precipitates are connected by hair-line-shaped GB precipitates. In the previous study [4], these intergranular precipitates were found to be either Pd-rich (identified up to $4 \mu\text{m}$ from SiC-IPyC interlayer) or Ag-rich (up to $0.5 \mu\text{m}$ from the interlayer). This work confirmed the results of the previous study by analyzing more areas.

Pd-rich intergranular precipitates were identified up to $5 \mu\text{m}$ from SiC-IPyC interlayer as shown in Fig. 5(a) and Fig. 6. Quantitative results in Table 3 suggest the Pd-rich triple junction precipitates to be Pd silicides with no detectable U or Ag. Variation in Pd concentration may be influenced by the matrix signals, the extent of which depends on different precipitates' sizes.

Ag-rich intergranular precipitates were identified up to $1.5 \mu\text{m}$ from SiC-IPyC interlayer (Fig. 7) providing evidence of Ag can transport along SiC grain boundaries. EDS spectrum shows that no U and Pd exist inside the Ag-rich precipitates, but a small amount of Cd was identified.

3.4 Network of Ultra Fine Precipitates ($< 5 \text{ nm}$)

A network of ultra-fine precipitates (size $< 5 \text{ nm}$) was observed for the first time inside the SiC grains adjacent to a micron-sized precipitate in the SiC layer (Fig. 2 and Fig. 8). The EDS results indicate these precipitates to be U-rich along with other minor FP such as Ba, and Ru. Mechanism(s) of formation for this honeycomb-shaped precipitate network is unclear; however, one assumption is that they may be related to a void or dislocation network inside SiC grains.

Table 1. Quantitative EDS results showing the composition of different micron-sized precipitates shown on Fig. 3.

Elements	SiC Matrix		M1		M2		M3	
	Concentration (at.%)	Error (%)	Concentration (at.%)	Error (%)	Concentration (at.%)	Error (%)	Concentration (at.%)	Error (%)
C(K)	47.14	1.10	46.93	0.12	48.39	0.20	58.33	0.25
Si(K)	52.79	0.89	21.69	0.05	20.36	0.08	12.21	0.08
Pd(K)	0.00	100.00	21.08	0.20	20.86	0.32	17.85	0.31
U(L)	0.07	0.11	10.30	0.24	10.39	0.37	11.61	0.39

Table 2. Quantitative EDS results showing the composition of Pd-Ag (Fig. 4[b]) and Pd-rich (Fig. 4[c]) nano-sized spherical precipitates.

Elements	SiC Matrix		S1		S2		S3	
	Concentration (at.%)	Error (%)	Concentration (at.%)	Error (%)	Concentration (at.%)	Error (%)	Error (at.%)	Error (%)
C(K)	47.14	1.10	31.30	0.41	26.21	0.34	32.37	0.38
Si(K)	52.79	0.89	66.36	0.41	66.51	0.37	62.38	0.36
Pd(K)	0.00	100.00	1.88	0.26	7.04	0.50	5.25	0.98
Ag(K)	0.00	100.00	0.46	0.17	0.06	0.11	0.00	100.00
U(L)	0.07	0.11	0.00	100.00	0.18	0.13	0.00	100.00

Table 3. Quantitative EDS results showing the composition of three Pd-rich triple junction precipitates shown on Fig. 6.

Elements	SiC Matrix		T1		T2		T3	
	Concentration (at.%)	Error (%)	Concentration (at.%)	Error (%)	Concentration (at.%)	Error (%)	Concentration (at.%)	Error (%)
C(K)	47.14	1.10	41.13	0.35	36.0	0.36	33.43	0.26
Si(K)	52.79	0.89	51.40	0.27	58.98	0.33	55.75	0.92
Pd(K)	0.00	100.00	7.47	0.34	4.83	0.35	10.77	0.98
U(L)	0.07	0.11	0.00	100.00	0.19	0.13	0.05	0.09

3.5 Transport Mechanism of Different Fission Products (FPs)

The FP precipitates observed in this work are within the inner part of TRISO fuel particle (up to 5 μ m from the SiC-IPyC interlayer); therefore, it is hard to conclude if these precipitates account for the release of certain FPs. However, the identification of these precipitates indicates possible active transport mechanisms for different FPs.

Pd containing precipitates were historically found to aggregate at the SiC-IPyC interlayer and can corrode SiC layer [13,14]. No significant Pd corrosion was observed in as-irradiated AGR-1 particles, but scanning electron microscopy-WDS examination [5,9] showed numerous Pd precipitates at the SiC-IPyC interlayer as well as a distribution of Pd precipitates inside SiC layer. The better resolution of STEM reveals that these precipitates have sharp protrusions that are connected by SiC grain boundaries, as shown in Section 3.1, which indicate that they are likely formed by a GB transport mechanism.

Simulated TRISO particle experiment by Pearson et al. [12] and Pd-polycrystalline SiC diffusion experiment by Olivier et al. [15] suggest that Pd can react with SiC to form Pd-silicide nodules at SiC grain boundaries, and those nodules can then migrate along grain boundaries by dissolving SiC at the leading edge and forming SiC at the tailing edge. Other metallic products, such as U [12] and Ag [16],

can then dissolve in those Pd-silicide nodules and transport the products together along the grain boundaries. However, it should be noted that localized Pd corrosion has been found in neutron irradiated particles with breached buffer and pyrolytic carbon [17] but no significant Pd corrosion was found in a large majority of coated particles of the AGR1 experiment which exhibit Ag and Pd releases. Clarification is needed to differentiate between the potential mechanistic differences. The micron-sized Pd precipitates at grain boundaries of SiC layer in this study are likely to form and migrate by the same mechanism.

While the micron-sized precipitate has stoichiometry close to $\text{Pd}_2\text{Si}_2\text{U}$ (Table 1), no U was identified in the nano-sized hair-line GB precipitates or triple junction precipitates. Those nano-sized GB and triple junction Pd precipitates have also been observed in Pd-SiC surrogate diffusion experiment, and their formation may be associated with a more rapid liquid state reaction [15]. The melting point of $\text{Pd}_2\text{Si}_2\text{U}$ ($\sim 1500^\circ\text{C}$) [18] is higher than the melting point of Pd-silicides (from 960 to 1330°C depending on stoichiometry) [19] and the average fuel particle temperature during the Compact 6-3-2 irradiation (1070°C) [5]. Therefore, U transports along GB only by “mobile nodule” formation without forming nano-sized intergranular precipitates.

Besides the intergranular precipitates, nano-sized spherical Pd precipitates and ultra-fine U precipitates observed within the SiC grains also suggest possible intragranular transport mechanisms for Pd and U. The U precipitates distribute in a honeycomb-like network (Fig. 2[a] and Fig. 8) inside SiC grain, which may be related with voids or dislocation network produced by neutron radiation [22]. The Pd spherical precipitates were not observed in the surrogate experiment [15], which may also associate with radiation effects. However, the nature of how radiation facilitates the formation and migration of those intergranular precipitates still requires understanding.

Micro-crack vapor release [6] and GB diffusion [7–11] has been proposed as two competing hypotheses. Another study suggests Ag alone cannot transport through SiC, but the existing Pd can greatly assist Ag transport by forming Pd-Ag-Si nodules along SiC grain boundaries [16]. In this study, Ag was found in SiC grain boundaries and triple junctions up to $1.5\ \mu\text{m}$ from the SiC-IPyC interlayer, providing direct evidence of Ag GB diffusion. Compared with Pd rich grain boundaries and triple junctions, which were identified up to $5\ \mu\text{m}$ in SiC layer from SiC-IPyC interlayer, the intergranular Ag was identified within a shorter range. This may imply that Ag GB transport is slower than Pd; however, more GB precipitates need to be examined to confirm this. It is worth noting that in these areas of studying, no Pd was identified in Ag-rich grain boundaries and triple junctions and no Ag was identified inside the micron-sized Pd-U-Si precipitates. This may suggest that the Pd assisted Ag transport through “mobile Pd-silicide nodules” as proposed in [12] and [16] is not likely to be the main mechanism for Ag GB transport. However, it should be noted that atomic migration along the grain boundaries, below the STEM and EDS detection limits, is possible and likely. From this study, it seems that Pd is not required for Ag intergranular transport. The single instance where an Ag-Pd nano-sized precipitate was found inside the SiC grains suggests a possible Pd-assisted intragranular transport mechanism for Ag. Similar to the intragranular Pd precipitates, Ag-Pd intragranular precipitates were not observed in the surrogate experiment [16], indicating a possible relation with radiation effects. Recent work by Coward et al., [22] on ion-irradiated work, also reported a potential correlation of Ag transport in β -SiC grains with void formation. This needs to be explored in further neutron irradiated TRISO coated particle high resolution transmission electron microscopy. Small amounts of Cd were also seen in the Ag-rich GB precipitates and triple junction precipitates, which suggest that it can transport with Ag by intergranular mechanism.

4. CONCLUSIONS

Previous studies [4,20] have illustrated the potential of STEM-EDS method to identify Ag at the SiC-IPyC interlayer in a neutron irradiated TRISO fuel particle during postirradiation examination. In the present study, we further examined FP precipitates inside SiC layer ($0.5\ \mu\text{m}$ to $5\ \mu\text{m}$ from the interlayer), along with a quantitative assessment of size, shape, preferential location, and composition of those FP precipitates

Ag was found in SiC grain boundaries and triple junctions up to 1.5 μm from the SiC-IPyC interlayer, providing direct evidence of Ag GB diffusion. No Pd was found in those nano-sized Ag GB and triple junction precipitates, which suggests that Pd may not be required for Ag GB transport. The co-existence of Cd with Ag in triple points reported previously [4] was confirmed by the present study.

The presence of Pd rich nano-sized intragranular precipitates previously reported by van Rooyen et al. [4] was further investigated. In a single instance an Ag-Pd nano-sized precipitate was found inside the SiC grains, which suggests a possible Pd-assisted intragranular transport mechanism for Ag. Further high-resolution STEM work is needed to explore the intragranular Ag-Pd precipitate formation and potential correlation with void formation. Those nano-sized precipitates were not observed in the surrogate Pd/Ag-SiC diffusion experiments [15,16], thus the precipitates may be associated with neutron radiation effects. More precipitates need to be examined to understand the nature of their formation and migration.

Honeycomb shape U-rich FP networks inside SiC grain were found near a micron precipitate in SiC about $\sim 5\ \mu\text{m}$ from the SiC-IPyC interlayer, indicating a possible intragranular transport path for uranium. This is the first work showing such a finding in irradiated SiC, which may be related to void or dislocation network inside SiC grains.

Preliminary quantitative analysis indicated the micron-sized precipitates to be $\text{Pd}_2\text{Si}_2\text{U}$ with carbon existing inside these precipitates. The nano-sized precipitates are also likely to be FP-silicides considering their high Si content compared to the SiC matrix. However, the quantitative results for nano-sized precipitates are greatly influenced by the background SiC matrix, which makes it impossible to obtain the accurate chemical compositions.

5. ACKNOWLEDGEMENT

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Fig. 1. Images showing (a) positions in a post irradiated TRISO fuel particle from where STEM lamellae were fabricated, (b) positions investigated in lamella 6b (Position 1: SiC layer, Position 2: SiC-IPyC interlayer and Position 3: IPyC layer) and (c) positions investigated in lamella 6a (Positions 1 and 2: SiC layer).

Fig. 2 (a) Distribution of various FP precipitates in the SiC layer $\sim 5\mu\text{m}$ from SiC-IPyC interlayer of sample 6b (position1 in Fig. 1[b]), numbers are used for marking different regions which will be shown in higher magnification in other figures, and (b) EDS area scanning spectrum inside the micron-sized precipitate (within the green box) (Cu is an artifact from transmission electron microscopy grid).

Fig. 3. Micron-sized ($\geq 100\text{nm}$) precipitates identified at (a) SiC layer (b) SiC-IPyC interlayer and (c) IPyC layer, green boxes are regions of EDS quantitative analysis.

Fig. 4. (a) Different types of nano-precipitates identified inside a SiC grain (position1 in Fig. 2[a]), (b) EDS spectrum indicates S1 is a Pd-Ag precipitate and (c) EDS spectrum indicates S2 is a Pd-rich precipitate.

Fig. 5. Typical EDS line scan profiles of Si and C across (a) a nano-sized precipitate and (b) a micron-sized precipitate.

Fig. 6. High magnification image of position.2 in Fig. 2(a), showing Pd-rich GB precipitates and triple junction precipitates.

Fig. 7. Ag-rich GB and triple junction precipitates in SiC layer of sample 6a, ~1.5 μm from SiC-IPyC interlayer (position 1 in Fig. 1[c]).

Fig. 8. U-rich precipitates networks at (a) position.1, (b) position.3 and (c) position.4 in Fig. 2(a).