

# **Progress in Solving the Elusive Ag Transport Mechanism in TRISO Coated Particles: “What is new?”**

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## Progress in Solving the Elusive Ag Transport Mechanism in TRISO Coated Particles: “What is new?”

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**Abstract** – The tristructural isotropic (TRISO) particle for a high temperature reactor (HTR) has been developed to an advanced state where the coating withstands internal gas pressures and retains nearly all fission products during irradiation and under postulated accidents. However, one exception is silver (Ag) that has been found to be released from high quality TRISO coated particles during irradiation and high temperature accident heating tests. Although out-of-pile laboratory tests have yet to elucidate the mechanism of transport of Ag through silicon carbide (SiC), effective diffusion coefficients have been derived to successfully reproduce measured <sup>110m</sup>Ag- releases from irradiated HTR fuel elements, compacts and TRISO particles. It was found that Ag transport through SiC does not proceed via bulk volume diffusion. Presently grain boundary diffusion that may be irradiation enhanced either by neutron bombardment or by the presence of fission products such as palladium (Pd), are the two hypotheses that have been proposed. Recent studies of irradiated AGR-1 TRISO fuel using scanning transmission electron microscopy (STEM), transmission Kikuchi diffraction (TKD) patterns, and high resolution transmission electron microscopy (HRTEM) have been used to further the understanding of Ag transport through TRISO particles. No Ag was observed in SiC grains, but Ag was identified at triple-points and grain boundaries of the SiC layer in the TRISO particle. Cadmium (Cd) was also found in some of the very same triple junctions, but this could be related to silver behavior as <sup>110m</sup>Ag decays to <sup>110</sup>Cd or true Cd release as a fission product. Palladium was identified as the main constituent of micron-sized precipitates present at the SiC grain boundaries. The potential role of Pd in the transport of Ag will be discussed further.

### I. INTRODUCTION

The tristructural isotropic (TRISO) coated particle is a finely-tuned fission product containment system, fully functional in the operating temperature environment of a high temperature reactor (HTR). Each of the billions of coated particles in an HTR core contains a uranium oxide (UO<sub>2</sub>) or oxy-carbide

(UCO) fuel kernel (enrichments < 20w/o <sup>235</sup>U) protected by a series of ceramic coating layers that provide near-complete fission product containment, Fig. 1. The ceramic TRISO coatings consist of a high-strength silicon carbide (SiC) layer sandwiched between two dense pyrolytic carbon (PyC) layers. The SiC layer is the primary fission product barrier of the TRISO particle and serves as the principal

structural layer as well. Research and development efforts continue today worldwide on the TRISO coated particle to improve and extend its fuel performance envelope.

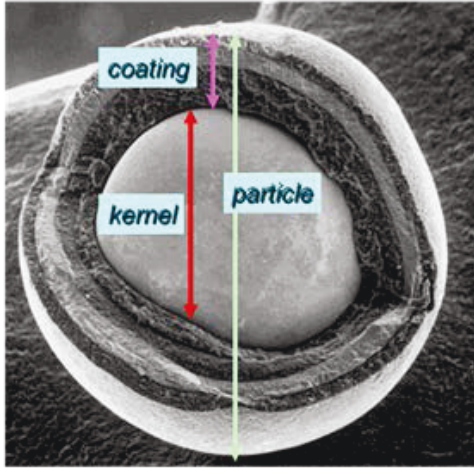


Fig. 1: Scanning electron microscope micrograph of a purposely cracked TRISO particle showing the uranium fuel kernel and the surrounding coating layers. [Source: Forschungszentrum Jülich, Germany]

Low-enriched uranium (LEU) fuel kernels in a modern TRISO coated particle are made up of ~10 to 20 weight %  $^{235}\text{U}$  (fissile isotope) and ~80 to 90 weight %  $^{238}\text{U}$  (fertile isotope). Because of the large inventory of  $^{238}\text{U}$ , a significant quantity of plutonium is bred into the fuel kernel. As a result, approximately 35% to 45% of the burnup accumulated in the LEU fuel kernel comes directly from plutonium fission during normal HTR operation. An important consequence of this large fraction of plutonium fissions is the inventory of several key fission product elements, namely palladium (Pd) and silver (Ag), is increased due to their much higher fission yields from plutonium (Pu) fissile isotopes ( $^{239}\text{Pu}$ ,  $^{241}\text{Pu}$ ) compared to the initial uranium fissile isotope ( $^{235}\text{U}$ ). The mass chains for Pd and Ag are identical in both U and Pu thermal fission. However, the thermal fission yields [1] for all the Pd isotopes are ~9 times higher from  $^{239}\text{Pu}$  and ~13 times higher from  $^{241}\text{Pu}$  than for  $^{235}\text{U}$ . The thermal fission yield for stable  $^{109}\text{Ag}$  is ~32 times higher for  $^{239}\text{Pu}$  and ~53 times higher for  $^{241}\text{Pu}$  than for  $^{235}\text{U}$ . The stable fission product,  $^{109}\text{Ag}$ , is important here because the activation product,  $^{110\text{m}}\text{Ag}$ , (half-life ~250 days) is produced by the  $^{109}\text{Ag}(\text{n},\gamma)^{110\text{m}}\text{Ag}$  reaction.

The fission product element Pd isotopes, ( $^{105}\text{Pd}$ ,  $^{106}\text{Pd}$ ,  $^{107}\text{Pd}$ ,  $^{108}\text{Pd}$  and  $^{109}\text{Pd}$ ), and the activation product,  $^{110\text{m}}\text{Ag}$ , have been identified as key elements when it comes to fission product retention in the TRISO coated particle. The release of  $^{110\text{m}}\text{Ag}$  has been observed in the primary circuit of early experimental HTRs [2],[3],[4] and repeatedly from

intact TRISO coated particles [5],[6],[7],[8] during post-irradiation safety testing at temperatures over the range of 1600°C to 1800°C and durations up to 200 hours and beyond. The fission product element, Pd, has been observed to coalesce at the inner pyrolytic carbon (IPyC)-SiC interface during irradiation of the  $\text{UO}_2$  TRISO coated particles and to chemically interact with the SiC layer [9],[10],[11] thereby reducing its effectiveness as a fission product barrier. Recent post-irradiation examination test results from the USA Advanced Gas Reactor's (AGR) first experiment, AGR-1, also showed Ag and Pd release through intact SiC layers. No significant chemical interaction of Pd with SiC was observed for these UCO TRISO coated particles [12]. The knowledge and understanding of active fission product transport mechanisms are fundamental requirements to improve and extend the performance envelope of modern TRISO coated particle fuel.

## II. TRANSPORT MECHANISMS: AN ABBREVIATED LITERATURE OVERVIEW

Although numerous mechanisms for Ag transport were derived from reactor experimentation release data, out-of-pile experimentation under simulated conditions, and empirical studies over the past 4 decades, no definitive conclusion on the mechanism(s) responsible for Ag transport in an irradiated TRISO particle's SiC layer under very high temperature reactor (VHTR) conditions has been reached. The experimental samples and test conditions have varied significantly and individual results have supported a variety of possible Ag transport mechanisms. Various  $^{110\text{m}}\text{Ag}$  transport mechanisms, such as grain boundary diffusion, surface diffusion or vapor transport through interconnected nano-pores or nano-cracks, Pd-assisted transport alongside grain boundaries, etc., that have been identified in these out-of-pile experiments also must be considered as potentially viable  $^{110\text{m}}\text{Ag}$  transport mechanisms in the SiC layer of TRISO fuel under neutron irradiation. Table 1, though not totally encompassing this research topic, shows previous examples of such investigations with comments on the type of SiC sample studied, its relevance to TRISO fuel, whether the study was performed in- or out-of-pile and the main conclusions derived from the work. In order to evaluate the applicability and significance of these out-of-pile transport mechanisms, as well as transport mechanisms unique to neutron irradiation such as enhanced bulk diffusion due to neutron irradiation-induced defects, characterization of microstructural and composition information, and specifically the identification of Ag in the SiC layer of actual irradiated TRISO coated particles is needed for irradiated TRISO fuel.

Table 1: Examples of different experimental conditions used for studying Ag transport mechanisms focusing on grain boundary characteristics.

Researcher	SiC Configuration	Fabrication Representativeness	Neutron Irradiated	Main Findings
Nabielek [4],[13] (1975, 1977)	Actual coated particle	Yes, spherical chemical vapor deposition (CVD)	Yes	Hypothesis: grain boundary diffusion, small voids based on release, no actual Ag identified in SiC structure
Petti [14] (2003)	Actual coated particle	Yes, spherical CVD	Yes	Grain morphology influences Ag release (equiaxed vs. columnar). No actual Ag identified in SiC structure.
Friedland [15] (2009)	Flat test coupon	Partial, flat CVD but same CVD reactor as coated particles	No	Diffusion coefficient calculation. Fickian grain boundary diffusion
Lopez-Honorato [16],[17] (2010, 2011)	Coated particle with surrogate kernel	Partial, spherical CVD, but deposit process deviation due to Ag deposition and concentration of Ag	No	Not only high angle boundary; mainly tortuosity regardless of manufacturing defects
Xiao et al [18] (2012)	Ab initio calculations: 3C Experimental: 4H	Flat commercial 4H SiC	No	Ab initio total energy calculations and ion beam irradiation: Surface diffusion possible, bulk negligible
Katoh et al [19] (2012)	Calculations	No	No	Ag atoms were shown to segregate strongly on grain boundaries of SiC. Diffusion along Sigma 3 grain boundaries is 11–14 orders of magnitude faster than diffusion through bulk.
Olivier, Neethling O’Connel et al [20], [21], [22], [23], [24] (2012, 2014)	Experimental flat and coated particles	Yes, spherical CVD and flat CVD	Unirradiated and neutron irradiated commercial SiC	Pd assisted transport alongside grain boundaries, Voids aid Pd transport in SiC grains.
Van Rooyen et al [12],[26],[27], [47],[48] (2012, 2014)	Actual coated particle	Yes, spherical CVD	Yes	Ag identified at SiC grain boundaries and triple points. Ag-Pd-Cd co-existing at grain boundaries although Ag-Cd is also found in absence of Pd. Pd found intra- and intergranular. Effect of irradiation damage: alignment of voids at grain boundaries.

López-Honorato et al. [16] developed a method to trap Ag inside the SiC coatings of TRISO coated particles and reported the diffusion of Ag along SiC grain boundaries. However it is important to note that the final SiC layer was deposited at 1300 °C

which is above the melting point of Ag and therefore the possibility of silver vapor transport during the SiC deposition process cannot be ignored. In a second paper by López-Honorato et al. [17], the authors indicated that Ag diffusion along SiC grain

boundaries had been observed. This important finding is contrasted by the results of previous studies (Nabielek et al., [4]; MacLean et al., [25]; Friedland et al., [15]) that failed to find any significant migration of Ag in Ag-implanted SiC annealed at elevated temperatures.

During 2012 and 2014, Neethling, Olivier and O'Connell [20 - 22], did various out-of-reactor annealing experiments with polycrystalline SiC in contact with a Pd-Ag compound. These studies showed that Pd significantly enhanced the transport of Ag along grain boundaries in SiC. It was also reported that Ag or a Ag-Si compound did not penetrate polycrystalline 3C-SiC in the absence of Pd. Enhanced Pd-Ag transport along grain boundaries in neutron irradiated polycrystalline SiC (flat commercial samples) annealed at 1000°C compared to Pd-Ag transport in unirradiated SiC was reported [23]. In addition, Pd was also observed inside (at a distance of about 100 µm from the grain boundary) SiC grains of high fluence ( $9.4 \times 10^{21}$  n/cm<sup>2</sup> at 1460°C) irradiated samples. The neutron irradiation of SiC at high temperatures leads to the introduction of voids in rows along the (111) planes. It was suggested that the presence of these rows of voids enhances the transport of Pd inside the SiC grains [24]. Void formation is aided by the presence of lattice faults such as stacking faults and twins which readily form in SiC on (111) planes.

It needs, however, to be noted that the Pd and Ag concentrations used in these out-of-pile research studies, are orders of magnitude larger than in the actual TRISO coated particles, which could contribute to the different transport and corrosion behavior observed compared to those of the AGR-1 experiment. The electron microscopic work performed on selected AGR-1 coated particles is described in Section III.C [12],[26],[27].

### III. RESULTS

During this study, we focused specifically on the inventory and release of the fission products Pd, Ag, Cd, Eu, and Cs.

#### III.A. Fission Product Inventory results from historic German irradiations

The activation product, <sup>110m</sup>Ag, had not been considered relevant in the early high temperature gas reactor (HTGR) days because of its very low fission yield in highly-enriched uranium. Significant releases were observed in 1972–1976 by DRAGON and Harwell workers from high quality TRISO particles [4], [28]–[32] that retained all other fission products up to 1500°C. At the time, a certain Ag retention was observed in oxide kernels [33], practically no retention at all in high temperature

isotropic (HTI) and low-temperature isotropic (LTI) PyC layers [34] and a temperature dependent retention in SiC which was described by a diffusion coefficient (see Fig. 2) that was later confirmed in many more experiments. Ag transport through SiC presented certain puzzles insofar as

- Releases from individual particles were highly variable (but regular from complete fuel elements); and
- Laboratory experiments with unirradiated silicon carbide did not show any bulk diffusion. In particular, ion implantation of Ag into SiC does not lead to any Ag movement during heat treatment [4].

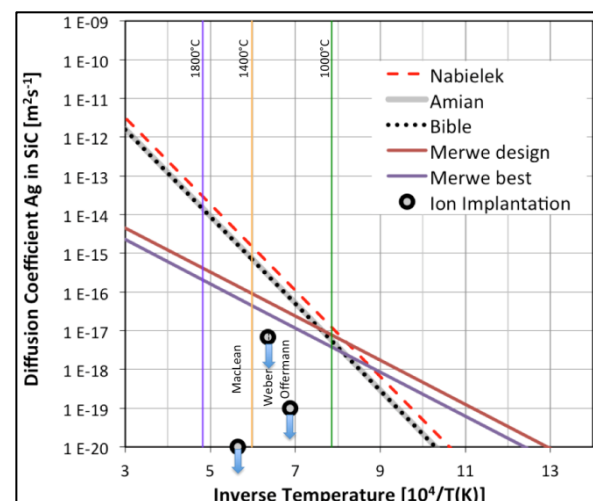


Fig. 2: Diffusion coefficients of Ag in SiC from Nabielek [4], Amian [38],[39], IAEA-TECDOC-974 the “bible” [41], van der Merwe [36] design limits and best estimates. Also shown are diffusion coefficient limits from the mobility of Ag after ion implantation by MacLean [25], Jiang & Weber [37], and Offermann [34].

Early speculation was that a necessary condition for Ag release from high quality TRISO particles was irradiation-induced pathways through grain boundaries, a result of either neutron bombardment or by fission product attack [28].

A systematic study of Ag transport mechanisms [38],[39] by Amian established the basic transport data, Fig. 3 that constituted the Ag transport reference data set for several decades [40],[41] the so-called “Bible”.

An international fission product transport code verification exercise [42] in IAEA-TECDOC-1674, the so-called “Bible II”, showed occasional good agreement between measured and predicted release data from spherical fuel elements and compacts, as shown in Fig. 3. However, quite a number of other experiments have had much lower Ag releases and this is not well understood.



The most representative data on Ag release during irradiation are obtained with spherical fuel elements embedded in graphite cups where all the  $^{110m}\text{Ag}$  in the cups and the interior capsule wall surfaces is measured and related to the total  $^{110m}\text{Ag}$  inventory. A recent re-evaluation of all these

irradiation tests [36] resulted in the development of a new diffusion coefficient with much lower activation energy of 109 kJ/mol (rather than the earlier 215 kJ/mol) and a recommendation for expected values and design limits, Fig. 2.

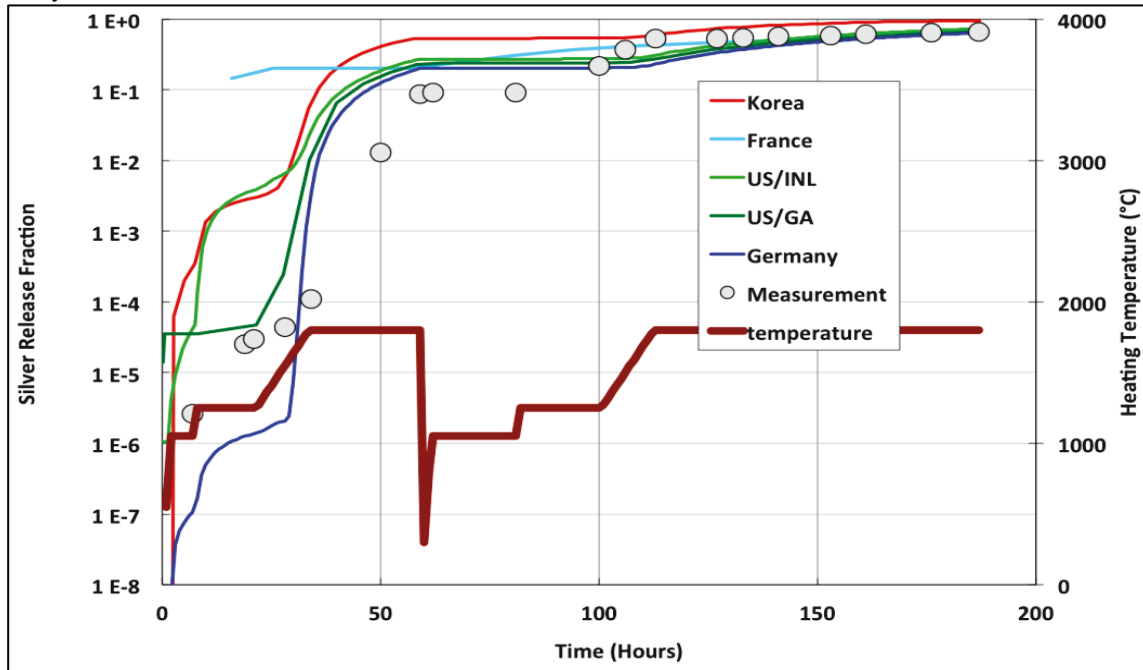


Fig. 3: Measured and predicted  $^{110m}\text{Ag}$  release fractions from 1800°C heating test of irradiated spherical fuel element HFR-K3/3 of 10.2% FIMA. After Figure 10-23 in Bible II [42].

Similar evaluations of in-reactor release fractions are now conducted with the AGR-1 irradiation experiment and are discussed in Section III.B.

### III.B. Fission Product Inventory results from AGR-1

AGR-1 is the first of a series of irradiation tests performed as part of the United States Department of Energy (DOE) AGR Fuel Development and Qualification Program. Irradiation began in the Advanced Test Reactor (ATR) at Idaho National Laboratory (INL) in December of 2006 and ended in November 2009. AGR-1 was intended to serve as a shakedown test of a multi-capsule design to be used in subsequent irradiations, and to test early variants of the fuel produced under the DOE AGR program [43]. A total of 72 compacts were irradiated in the AGR-1 experiment in six different capsules. The experiment completed 620 effective full power days (EFPD) in the reactor and achieved calculated peak burn-up of 19.5% fissions per initial heavy metal atom (FIMA) and fast neutron fluence of  $4.30 \times 10^{25} \text{ n/m}^2$  ( $E_n > 0.18 \text{ MeV}$ ) [43].

At completion of the irradiation, post-irradiation examination and high temperature safety testing were conducted to: (a) assess the overall performance of the test train and components; (b) provide data to verify the test train thermal analyses

and evaluate the particle coating integrity and the fission product retention of the fuel during normal irradiation and high temperature post-irradiation safety tests; and (c) characterize the fuel compacts and individual particles to assess the condition of the matrix material, kernels, and coatings [44].

Specific irradiated compacts were selected for examination. To better understand Ag behavior, the following measurements were made:

- Gamma scanning of 56 irradiated AGR-1 compacts to determine the retained inventory of  $^{110m}\text{Ag}$ . Based on these measurements, a release fraction was calculated
- Deconsolidation-leach-burn-leach (DLBL) to recover particles from the compacts so that irradiated microsphere gamma analysis (IMGA) could be used to gamma count individual particles to quantify their  $^{110m}\text{Ag}$  inventory.
- Advanced microscopy techniques to examine the behavior of Ag and other fission products within the microstructure of the coating layers (see Section III.B.)

The irradiation conditions for compacts from which particles were examined are shown in Table 2.

Table 2: Irradiation conditions for compacts from which particles were extracted for advanced microscopy (Temperature average- volume average (TAVA)).

Compact	Burn-up (%FIMA)	Fast Fluence ( $\times 10^{25}$ n/m <sup>2</sup> )	TAVA (°C)
6-3-2	11.4	2.55	1070
5-3-1	16.7	3.60	1040
4-1-1	19.4	4.13	1072
1-3-1	15.3	3.22	1092

Significant Ag release from TRISO coated particles was observed in the irradiation post irradiation examination. As shown in Fig. 4, based on the gamma scan measurements, releases ranged from zero to 100%. (Values less than zero in Fig. 5 are the result of underestimates in the calculated <sup>110m</sup>Ag inventory in the compact and result in Ag retention greater than 100%.) Attempts to correlate the release to the irradiation conditions were problematic because of the wide range of temperatures experienced within each compact and the associated uncertainties in those temperature predictions. There may be a slight influence of burnup on Ag release. The data suggest that Ag release may decrease as burnup increases; however, the temperature uncertainties in the irradiation make any firm conclusion difficult.

There is relatively good agreement between the Ag release calculated by PARFUME based on the daily volume average temperature and the gamma-scan data in Fig. 4 [45]. PARFUME under-predicts PIE data in the lower burn-up capsules (end capsules) and over-predicts PIE data in the higher burn-up capsules (middle capsules). Assay of the deconsolidation solution indicates significantly more Ag retention in the fuel matrix than that predicted using historical diffusion coefficients for that material. Because PARFUME really calculates release from particles, removing the matrix retention in 17 compacts for which there were data improved the comparison (see Fig. 5)[45].

The effect of the spatial variation in temperatures in a compact was also examined. Typically, the range of temperatures in a compact on a time average basis over the entire irradiation can range from 150 to 250°C and based on daily temperatures at any time in the irradiation, can span 250 to 350°C. Calculations show that the coldest particle in Compact 6-3-2 would release 9% and the hottest particle 67% of their Ag, with a nominal value of 41%. This variation demonstrates the influence that time-at-temperature has on Ag release from TRISO particles [45]. Collectively, the comparison of the calculations against the data suggests that the existing historical diffusion coefficients for Ag in the particles do a reasonably good job of predicting Ag release in the AGR-1 experiment.

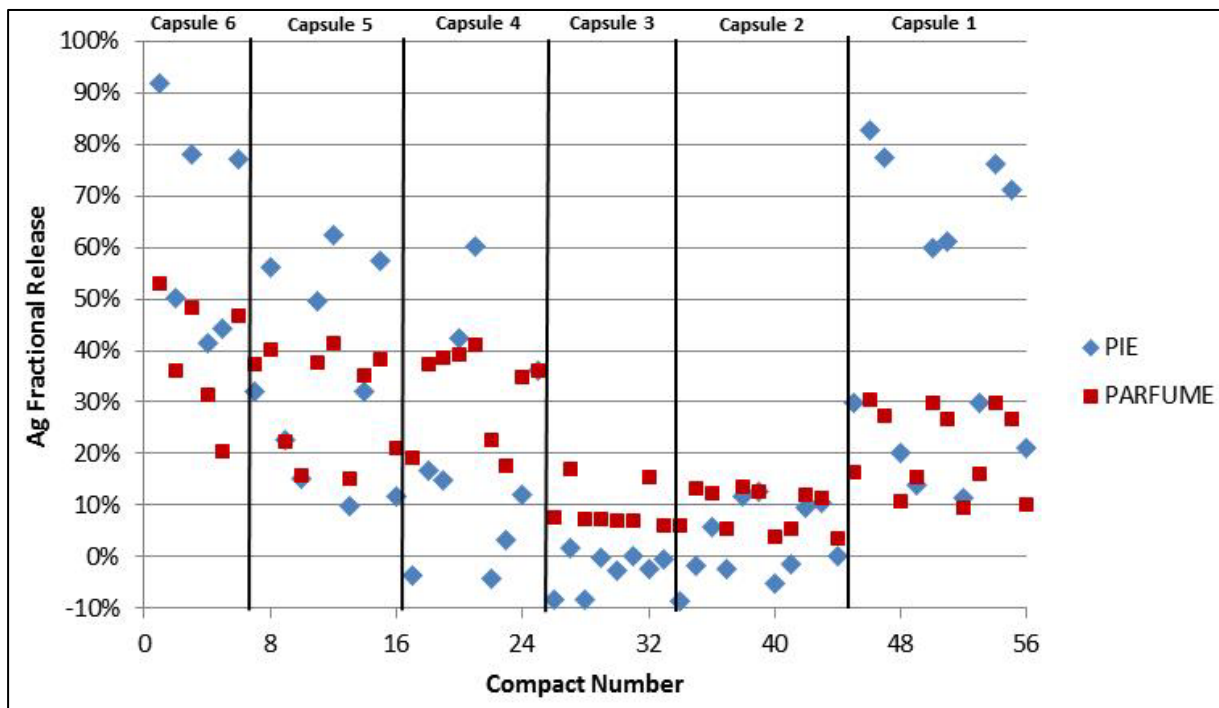


Fig. 4: Comparison of measured <sup>110m</sup>Ag releases from compact gamma-spectrometry to calculations made by PARFUME.



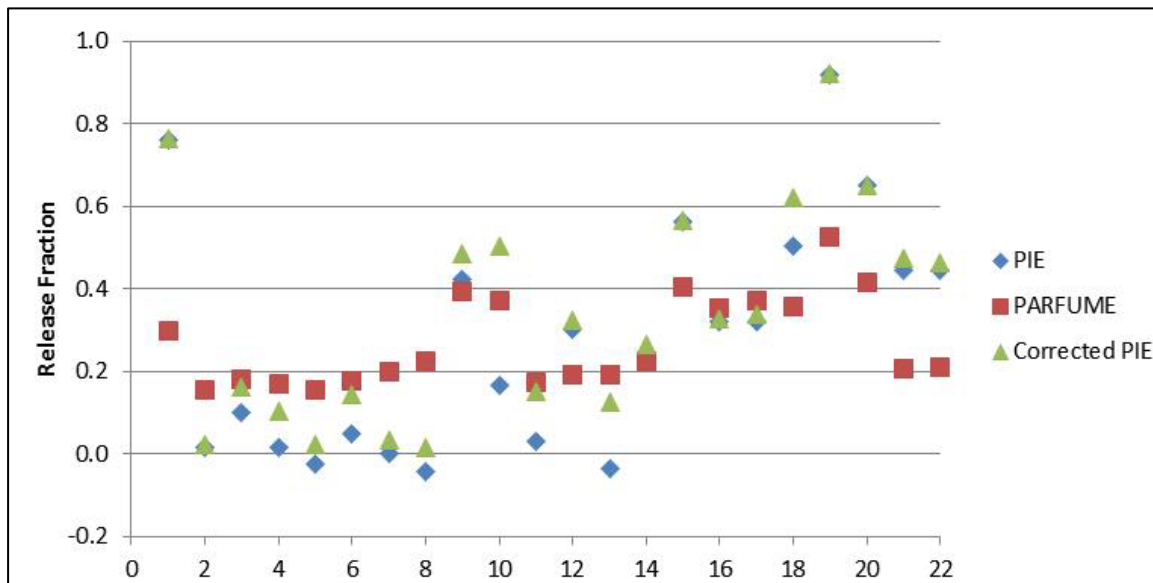


Fig. 5: Comparison of  $^{110m}\text{Ag}$  release are accounting for matrix retention with calculations made by PARFUME.

### III.C. Nano- and microstructural analysis from AGR-1

As advanced electron microscopy examination of selected particles from AGR-1 compacts are in progress, only results from Compact 6-3-2 and Compact 4-1-1 are discussed in this section.

#### Compact 6-3-2

The initial electron microscopy examination of the AGR-1 coated particles from compact 6-3-2 using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), wavelength dispersive spectroscopy (WDS), and transmission electron microscopy (TEM) attempted to identify Ag in fission product precipitates. Although evidence of fission product precipitates was found on SiC grain boundaries (Fig. 6) and in the IPyC layers, no Ag was conclusively identified using those techniques [12],[47]. At this stage of the examination only the micron-sized precipitates could be identified. The selected area diffraction patterns showed similarity with a  $\text{UPd}_2\text{Si}_2$  structure, but the chemical composition varied [12]. In this earlier work, it was speculated that Ag would be able to substitute for Pd in a  $\text{U}(\text{Ag},\text{Pd})_2\text{Si}_2$  solid solution rather than forming a separate phase since they have identical atomic radii (both 0.144 nm for the pure elements [46]).

Nano-sized voids aligned at the grain boundaries have been found in the vicinity of a fission product precipitate [48] as shown in Fig. 7. The potential correlation between these nano-sized voids and fission product transport was investigated as part of AGR-1 PIE [47],[48], [49].

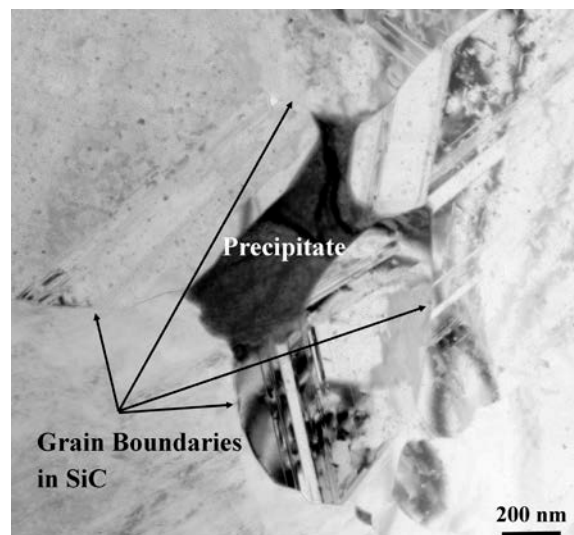


Fig. 6: TEM micrograph showing a representative image of a micron-sized precipitate in the SiC layer of CP34 from coated particle AGR1-632-34, TEM Position 2a.

INL researchers using more advanced characterization techniques (scanning transmission electron microscopy(STEM), electron energy loss spectroscopy (EELS)) directly identified for the first time the presence of Ag in neutron-irradiated AGR-1 TRISO coated particles, as shown in Fig. 8 [26], [50]. During this study Pd was identified in both intra- and intergranular locations throughout the entire thickness of the SiC layer, as shown in (Fig 9) [26], [51].

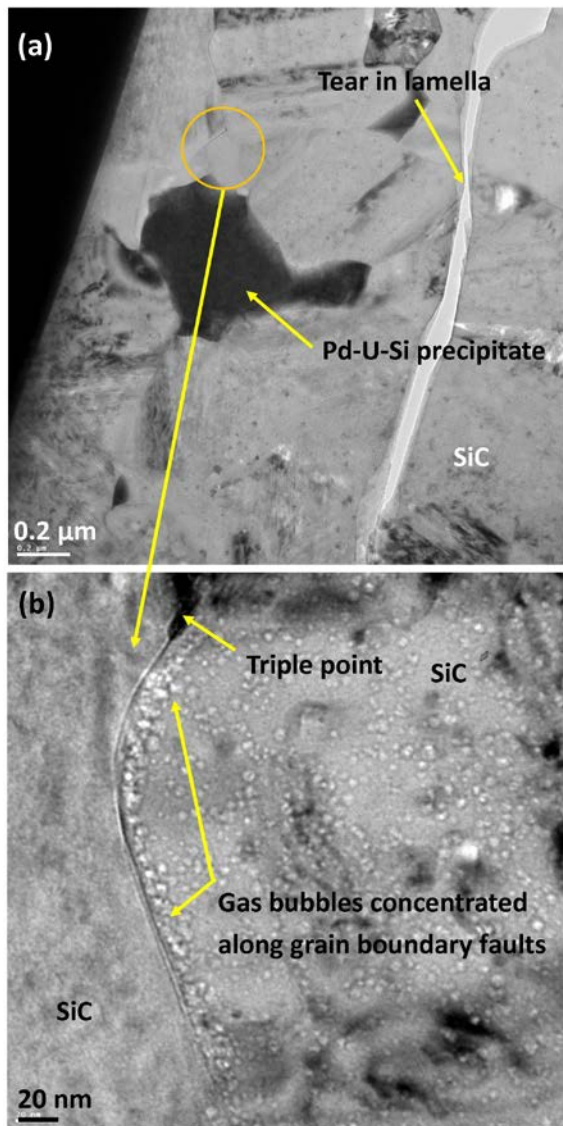


Fig. 7: TEM micrographs of particle AGR1-632-034 TEM sample 2a show in (a) a micron sized Pd-U-Si precipitate in the SiC layer, with (b) a higher magnification image of the grain boundary marked with an orange circle in image (a). The spherical shaped cavities concentrated alongside grain boundaries near the Pd-rich precipitate (image (b) is adapted from [12], [47]).

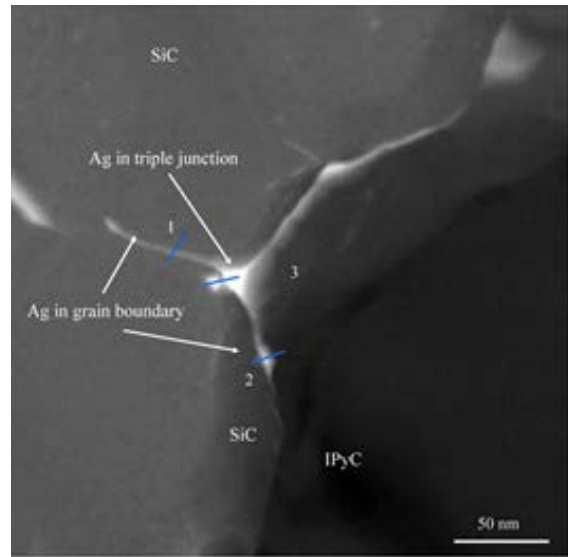


Fig. 8: Image showing the HAADF STEM image of the first direct identification of silver- containing grain boundaries and triple junction at the outmost edge of the SiC adjacent to the IPyC on lamella AGR1-632-35-6b [26].

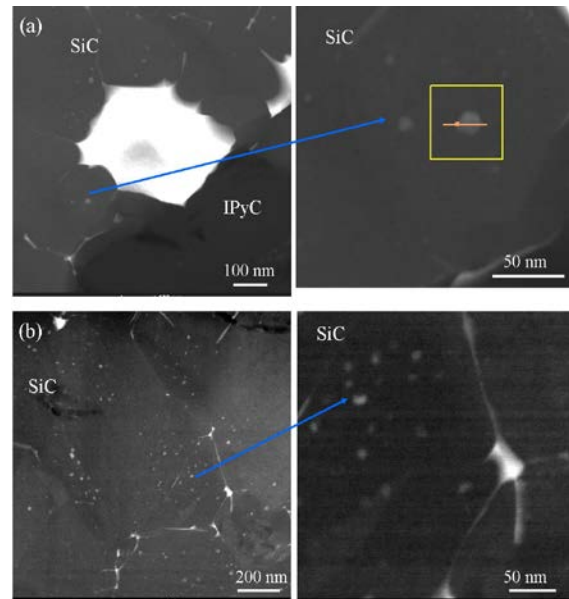


Fig. 9: STEM high angle annular dark field (HAADF) images showing nanometer-size Pd precipitates (~10 – 20 nm) inside SiC grains (a) at the SiC-IPyC interface and (b) approximately 4 μm inside the SiC layer (adapted from [26]).

STEM examination of additional lamella from AGR1-632-35 revealed that only Pd was found in all 16 triple points analysed on the outermost region of SiC. Ag was located mostly with Pd in the inner and centre sections of the SiC layers. U was never found with Ag, but often found with Pd [51]. The depth of fission product nano- networks extended to the outer edge of the SiC layer as shown in Fig. 10.

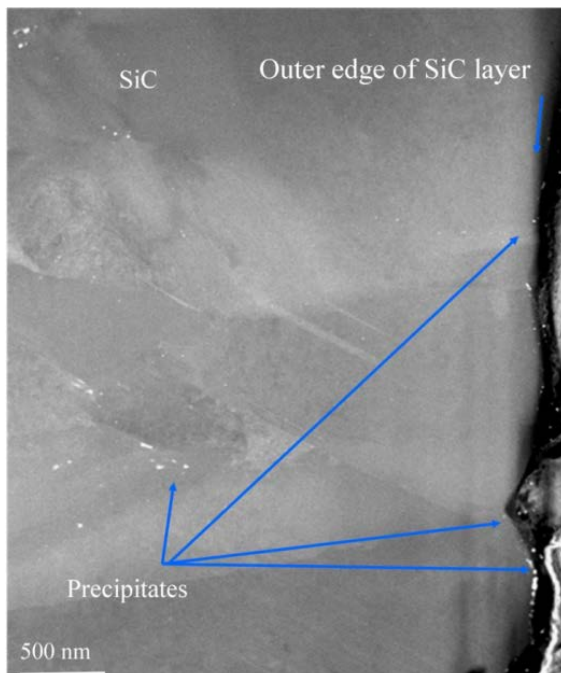


Fig. 10: Image showing the HAADF STEM image of the fission product nano-networks extending to the outermost edge of the SiC layer.

#### *Compact 4-1-1*

HRTEM and HRSTEM investigations were performed on 3 lamellas from AGR1-411-030 and reported in paper HTR-31255 [52]. The main findings are that Pd nano precipitates were identified at stacking faults as shown in Figs. 11 and 12. Additionally, Ag was found in various triple points and grain boundaries and was always in co-existence with Pd and Cd. Pd and U were found separately or co-existing in some cases (Ag was not present in concentrations above the detection limit of EDS system used).

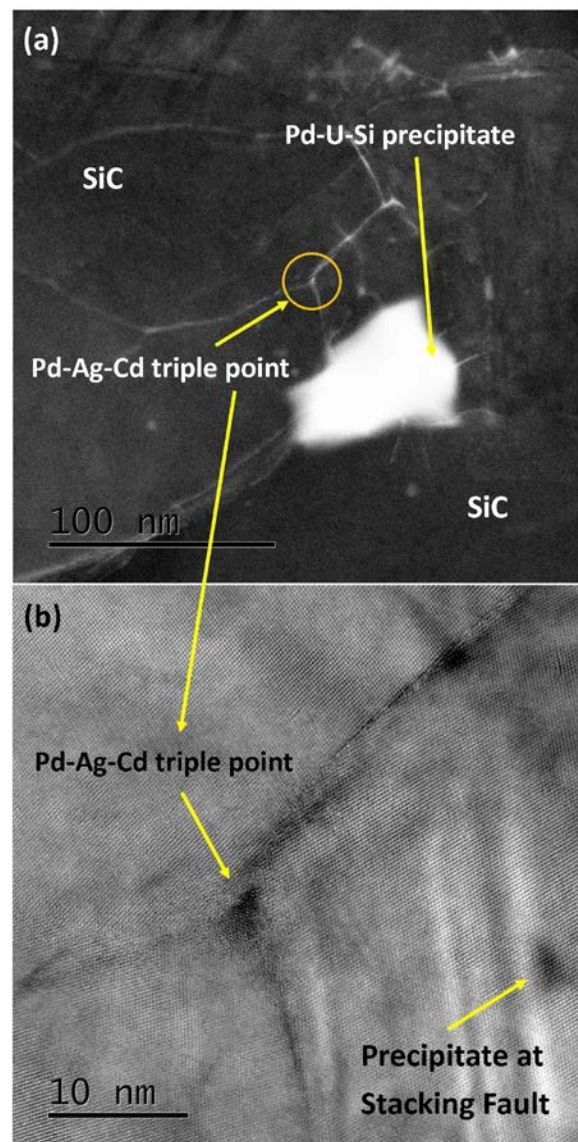


Fig. 11: The HAADF STEM image of specimen AGR-411-030 position 1b, shows in (a) the fission product networks on the grain boundaries and triple points as well as the micron-sized Pd-U-Si precipitate. The bright field (BF) STEM image in (b) shows the Pd-Ag-Cd triple point at higher magnification (exhibiting dark contrast which is complimentary to the HAADF STEM image) and a precipitate at a stacking fault.



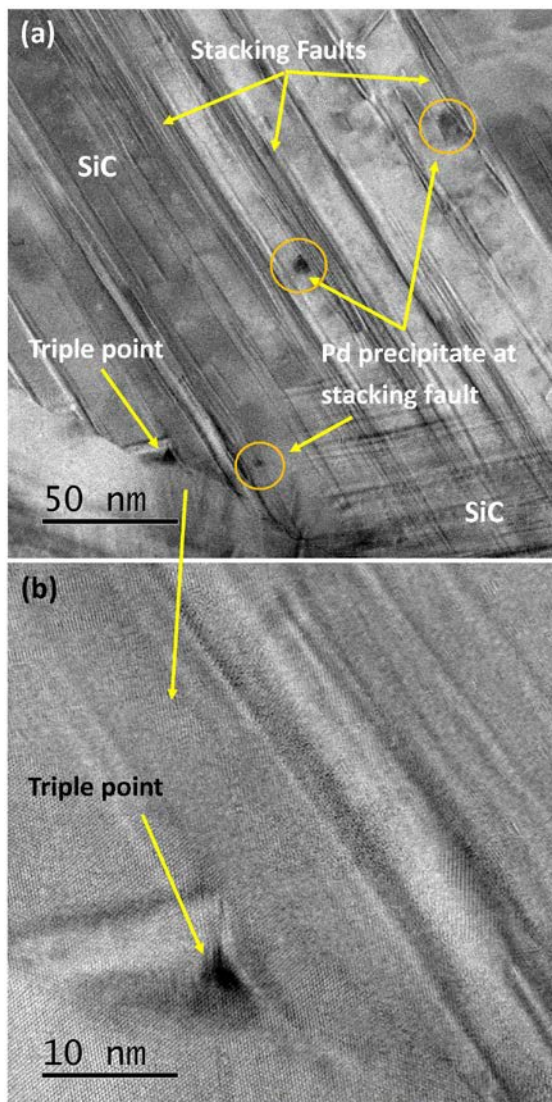


Fig. 12: High resolution BF STEM images of (a) Pd precipitates (Pd precipitates visible as dark nano regions) which accumulated at stacking faults in a SiC grain, and (b) the triple point imaged at higher magnification.

#### III.D. Discussion of AGR-1 microscopy results

The preliminary conclusions inferred from the results of STEM, HRTEM and HRSTEM examinations of coated particles from Compacts 6-3-2 and 4-1-1 revealed some common observations:

- No significant Pd corrosion of the SiC layer at the IPyC-SiC interface was observed.
- Ag was found at grain boundaries and triple points.
- No Ag above the EDS detection limit was found in SiC grains.
- Pd was found at intra- and intergranular sites in the SiC layer.

- U was either observed separately at grain boundaries or in co-existence with Pd, but was never found with Ag.
- Movement of U and Ag into the SiC layer (from the IPyC-SiC interface) was not as deep as for Pd.

The difference in results obtained from STEM, HRTEM and HRSTEM examinations of the two compacts are the following:

- Compact 4-1-1:
  - Ag was not found separately, but always found in co-existence with Cd and Pd at grain boundaries and triple points.
  - Pd precipitates were found at stacking faults.
- Compact 6-3-2
  - Ag found separately, as Ag-Cd precipitates and as Ag-Pd precipitates
  - Ag-Pd at triple points and grain boundaries were only found in the inner region of SiC close to the IPyC-SiC interface.
  - Alignment of voids along grain boundaries were observed in the vicinity of fission product precipitates at triple points.

#### IV. IMPLICATION OF RESULTS ON TRANSPORT MECHANISMS

Although interpretation of all the advanced micro-analytical data and images are still in progress and no final conclusion can be made, it seems possible that Ag, Cd and Pd cluster and transport together at grain boundaries and triple points because of their common chemical properties (all are noble metals). However, several questions remain:

- Do these findings point to a Pd-assisted transport mechanism and/or to grain boundary transport?
- If the hypothesis about Pd-assisted transport is correct, then why does Pd exist both intra- and intergranular and Ag only intragranularly in SiC?

As an alternative, the vapor pressure of Cd is higher than Ag and Pd. Does it mean that the presence of Cd with Ag is an indication of potentially a vapor transport mechanism at least to the surface of the SiC where it then moves along grain boundaries and triple points?

There are numerous results that suggest neutron damage may also have an impact on the transport mechanism:

- Most out-of reactor testing does not provide representative diffusion coefficients for Ag transport in TRISO particles under irradiation.

- O'Connell and Neethling [23],[24] recently reported that the transport of a Pd-Ag mixture along grain boundaries in neutron-irradiated commercial polycrystalline SiC annealed at a 1000°C in contact with the Pd-Ag mixture, was significantly enhanced compared to Pd-Ag transport in unirradiated SiC. In this out-of-reactor study the penetration of Pd in neutron-irradiated commercial SiC was investigated by annealing the irradiated ( $9.6 \times 10^{21}$  n/cm<sup>2</sup> at 1439°C) 3C-SiC in contact with a vapor-deposited Pd layer for 24 hours at 1000°C. A TEM investigation of the neutron-irradiated SiC revealed the presence of a high concentration of voids aligned in rows along the (111) planes of SiC together with Pd inclusions. The rows of neutron irradiation-induced voids in SiC were found to enhance the penetration of Pd in the SiC grains. The clustering of voids in bands parallel to the (111) planes is consistent with the suggestion that void nucleation is aided by impurities segregated at lattice faults such as stacking faults, which readily form on (111) planes in 3C-SiC due to its very low stacking fault energy [53].
- Van Rooyen et al.[12],[48] also reported in 2012 the presence of voids aligned along grain boundaries in the vicinity of Pd-containing precipitates inside SiC grains in irradiated AGR-1 TRISO coated particles (see Fig 7).

Finally, the observation, that fission products occupy different locations within the SiC, may provide some new thinking about underlying mechanisms.

The fact that no Ag was detected inside the SiC grains of AGR-1 TRISO coated particles is consistent with computational estimates of bulk Ag diffusion in SiC which show that such diffusion is energetically unfavorable [18], [19]. This is also consistent with the findings of earlier German research [28]. Thus, Ag transport appears to be dominated by the more energetically favorable grain boundary route, possible in association with Pd and Cd (similar noble metals). Additional evidence for this transport mechanism is also provided by the number of Pd silicides present in the Pd-Si phase diagram which indicates that Pd silicide formation is thermodynamically favorable and provides a driving force for the penetration of SiC by Pd [52].

## V. CONCLUSIONS

A definitive mechanism for Ag transport in SiC still requires further study. However, the recent out-

of-reactor testing on irradiated and unirradiated SiC and the advanced microscopic examination of irradiated AGR-1 TRISO particles have provided valuable information that is focusing future research directions.

The recent advanced electron microscopic results on irradiated AGR-1 coated particles further suggest that the Ag transport mechanism is likely more complex and may be a combination of mechanisms as previously proposed [49].

From this study, neutron damage, grain boundary characteristics, chemical interaction with Pd, and vapor transport are highlighted as potential interactive mechanisms in Ag transport.

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